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Bis(pentamethylcyclopentadienyl)ytterbium: Reactions with Organic Compounds and Related Molecules

D.J. Berg
(Ph.D. Thesis)

October 1987

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Bis(pentamethylcyclopentadienyl)ytterbium:
Reactions with Organic Compounds and Related Molecules

David Jay Berg
Ph.D. Thesis

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

October 1987

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Bis(pentamethylcyclopentadienyl)ytterbium:

Reactions with Organic Compounds and Related Molecules.

David Jay Berg

Abstract

The complex $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ acts as a reducing agent towards nitrogenous bases with reduction potentials of ca. -2.0 V or less, forming paramagnetic coordination compounds. Magnetic susceptibility measurements have been used to identify four different electronic structural types. In 1:1 complexes, chelate formation allows isolation of radical anion complexes which exhibit magnetic coupling between the unpaired spin on Yb(III) and the radical anion (Type A). In other 1:1 complexes, radical anion disproportionation occurs to give complexes composed of $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})]^+$ cations and $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L}^{2-})]^-$ anions (Type C). Paramagnetic complexes of 2:1 stoichiometry are formed which consist of two Yb(III) ions and one organic dianion. Magnetic coupling was observed for some 2:1 complexes (Type D) but not for others (Type E).

The reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})_n$ ($\text{L} = \text{Et}_2\text{O}$, $n = 1$; $\text{L} = \text{NH}_3$, $n = 2$) with organic dichalcogenides (REER , where $\text{R} = \text{alkyl or aryl}$ and $\text{E} = \text{O, S, Se, Te}$) allows preparation of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ complexes. The X-ray crystal structure of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{TeC}_6\text{H}_5)(\text{NH}_3)$ has been obtained. Reactions with $\text{R}_3\text{P}=\text{E}$ ($\text{R} = \text{C}_6\text{H}_5$ or $n\text{-Bu}$, $\text{E} = \text{S, Se, Te}$) produce the bridging chalcogenide complexes, $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2[\mu\text{-E}]$. The crystal

structure of the bridging selenide has been obtained. In addition, the crystal of a novel bridging ditelluride complex, $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2[\mu\text{-Te}_2]$ is reported.

The reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ with Me_3Al produces $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)]_2$ for $\text{ER} = \text{OSiMe}_3$ or TeC_6H_5 , and $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)(\text{ER})]_2$ when $\text{ER} = \text{OCMe}_3$, SC_6H_5 , $\text{S-p-C}_7\text{H}_7$, or SeC_6H_5 . The crystal structure of the p-tolythiolate derivative shows an unusual 12-membered ring structure. The reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ with alkyl lithium reagents leads to anion formation and loss of LiC_5Me_5 , rather than formation of neutral alkyl derivatives. The reaction of MeCu with $\text{Yb}(\text{C}_5\text{Me}_5)_2$ affords the base-free methyl complex, $[\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Me}]_2$.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ reacts with REH_2 ($\text{E} = \text{N}, \text{P}$) to form coordination compounds, $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{REH}_2)$ when REH_2 is less acidic than $\text{C}_5\text{Me}_5\text{H}$ ($\text{pK}_a = 26.5$). More acidic amines and phosphines protonate C_5Me_5^- with formation of insoluble one-ring products. The structure of one of these products, $[\text{Yb}(\text{C}_5\text{Me}_5)(\text{C}_6\text{H}_5\text{PH})(\text{thf})_2]_2$ has been obtained. Thermolysis of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{REH}_2)$ generally results in both ring loss and oxidation.

Acknowledgements

Now that my graduate career is drawing to a close, I would like to thank all the people who made the last four years so memorable. First I am indebted to Dick Andersen for providing an exciting research environment and many hours of interesting discussions on subjects ranging from chemistry to baseball. Special thanks are also due Carol Burns for many helpful discussions and more than a few laughs. Joanne Stewart, Nicki Rutherford, Phil Matsunaga, Steve Stults, Rob Rosen, John Brennan, Jim Boncella, Mike Fabiano, Tony Stuart and Sharon Beshouri (in no particular order) also contributed a lot of wit and wisdom and made life a lot more fun. I am grateful to Norm Edelstein and George Shalimoff for all their help with the SQUID. Jerry Bucher was a great help in a number of areas, all of which escape me at present. I am also indebted to Alan Zalkin for doing all of the crystal structures in this thesis.

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To my parents for all their support over the years.

Introduction

The organometallic chemistry of the lanthanides is substantially different from that of the transition metals. The bonding in lanthanide complexes is essentially ionic in nature ¹. This has been attributed to the fact that the 4f orbitals are buried within the filled 5s and 5p shells and therefore cannot overlap with filled ligand orbitals ². The small crystal field splittings ($< 1000 \text{ cm}^{-1}$) observed for lanthanide ions provides good evidence for the isolation of the 4f valence orbitals from the ligand environment ³.

Lanthanide ions are extremely electrophilic by virtue of their high charge to size ratio and as such, tend to form strong bonds with "hard" Lewis bases (O, N donors). Since there are no orbital symmetry restrictions, these ions strive to achieve the maximum coordination number allowed by ligand-ligand non-bonding repulsions. Very often coordinative saturation is achieved by formation of a polymeric structure in the solid state. In this regard, the lanthanides are quite similar to the alkaline earths, as might be expected on the basis of their comparable size and tendency to form ionic bonds. In fact, $\text{Yb}(\text{C}_5\text{H}_5)_2$ has been shown to be isostructural with $\text{Ca}(\text{C}_5\text{H}_5)_2$ ⁵. Clearly, in order to isolate soluble, monomeric lanthanide complexes, it is necessary to sterically saturate the metal center. This can often be achieved by using bulky organic anions or strongly coordinating neutral donors such as pyridine, ammonia, or tetrahydrofuran.

Since the 4f electrons are shielded from the ligand environment, little variation in chemical properties is expected as a function of

the f^n electron configuration. This is true as a first approximation; differences in chemical behaviour between the 3+ ions are primarily due to the decrease in ionic radius across the series ⁶. However, when the redox properties of the metals are also considered, the chemical behaviour of the lanthanide elements vary dramatically from element to element. Samarium, ytterbium and europium all possess divalent oxidation states of sufficient stability to form organometallic compounds (Table 1). Thus unlike most of the lanthanides, which only possess a 3+ state, these metals are capable of forming compounds with redox behaviour. Divalent halides of samarium and ytterbium have been used as one electron reducing agents in organic synthesis ⁷. It has also been shown that $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ reduces transition metal carbonyls to form complexes that contain $(\text{C}_5\text{Me}_5)_2\text{Yb}^+$ and transition metal carbonyl anions as contact ion pairs ^{8 9}. Cerium possesses a 4+ oxidation state that has long been used as a one electron oxidizing agent in organic synthesis ⁶.

The stability of the divalent oxidation state was originally attributed to the special stability of the half filled (f^7) and filled (f^{14}) 4f shells for Eu^{2+} and Yb^{2+} , respectively. More recently, Johnson ¹⁰ has proposed a comprehensive explanation based on the strong correlation between the stability of the divalent state and the third ionization potential of the metal, which better explains the stability of Sm^{2+} and the less stable divalent lanthanides (Nd^{2+} , Dy^{2+} and Tm^{2+}).

Table 1: Oxidation Potentials of Divalent Lanthanide Ions^(a)

<u>Ion</u>	<u>4fⁿ Electron Configuration</u>	<u>ξ° (V)</u> <u>M²⁺ → M³⁺ + e⁻</u>
Nd ²⁺	f ⁴	(b)
Sm ²⁺	f ⁶	1.5
Eu ²⁺	f ⁷	0.35
Dy ²⁺	f ¹⁰	(b)
Tm ²⁺	f ¹³	2.3
Yb ²⁺	f ¹⁴	1.1

(a) Reference 10 (b) MX₂ (X = Cl, Br, I) compounds are known but ξ° has not been measured.

The organometallic chemistry of the divalent lanthanides has developed much more slowly than that of the trivalent state¹¹. The major difficulty which hampered early synthetic efforts was the insolubility of most divalent compounds in hydrocarbon solvents. This was due to insufficient steric saturation when only two organic anions were coordinated to the metal center. Thus ligands such as C₅H₅⁻, which worked well in preparing soluble, monomeric compounds of trivalent lanthanides (eg. Yb(C₅H₅)₃¹²), were of insufficient size to prevent polymerization in the divalent state (eg. Yb(C₅H₅)₂⁵). This difficulty has been overcome by the use of bulky organic anions¹¹.

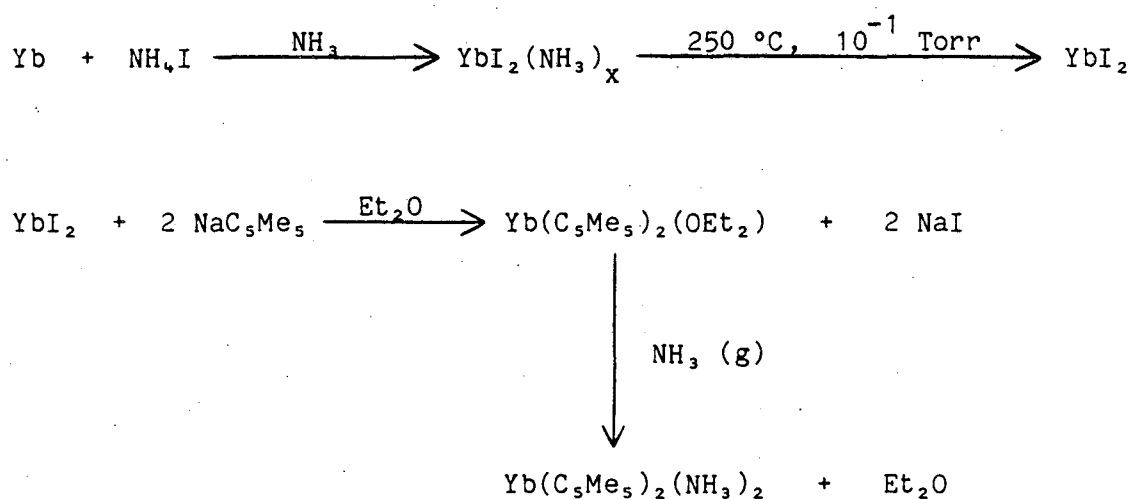
Pentamethylcyclopentadienide, $C_5Me_5^-$, has had the greatest impact on divalent lanthanide chemistry^{8 9 11}. To demonstrate the effectiveness of this ligand, consider that $Yb(C_5Me_5)_2$ dissolves readily in pentane while the C_5H_5 analogue is an insoluble polymer. The bulky bis(trimethylsilyl)amido ligand has also been used with some success in preparing divalent lanthanide compounds.

A second advantage of the $C_5Me_5^-$ anion is that it tends to form compounds which crystallize well and are therefore suitable for single crystal X-ray diffraction studies. This can be extremely important because the broad line widths and lack of coupling information severely limit the utility of paramagnetic NMR as a tool for structural characterization. The usefulness of NMR is further diminished because many lanthanide complexes have different solid state and solution structures. This is because the ionic bonding in these complexes presents no orbital barrier to fluxional or ligand redistribution processes. Thus, although the complex isolated from solution represents the most thermodynamically stable form in the solid state, a bewildering array of species may exist in equilibrium in solution.

This work focuses on the reactions of $Yb(C_5Me_5)_2(L)_n$ ($L = Et_2O$, $n = 1$; $L = NH_3$, $n = 2$) complexes with reducible organic substrates. The chemistry of Yb(II) was investigated for three reasons. First, synthesis of the divalent compounds (Scheme 1) is well established and the starting materials can be prepared on a gram scale or more. Second, the oxidation potential of $Yb(C_5Me_5)_2(CH_3CN)_2$ (1.3 V versus S.C.E. in CH_3CN ¹³) is similar to a wide variety of organic substrates (Table 2). Eu(II) is too weak of a reducing agent to reduce most organic

compounds. Third, and perhaps most importantly, Yb(II) is diamagnetic ($4f^{14}$) while Yb(III) is paramagnetic ($4f^{13}$). This is extremely useful because the oxidation state of the metal is readily apparent from proton NMR and magnetic susceptibility measurements. This is a decided advantage over samarium, where both the divalent and trivalent oxidation states are paramagnetic.

Scheme 1



The reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with 2,2'-bipyridine and 2,2'-bipyrimidine have been shown to produce paramagnetic complexes which exhibit unusual magnetic behaviour⁸. This was attributed to magnetic coupling between the paramagnetic Yb(III) ion and the organic radical anion. Thus reduction of heterocyclic systems with $\text{Yb}(\text{C}_5\text{Me}_5)_2$ provides a unique opportunity to isolate and study the electronic and magnetic properties of an organic radical anion. In this work, the

Table 2: Reduction Potentials of Selected Organic Substrates

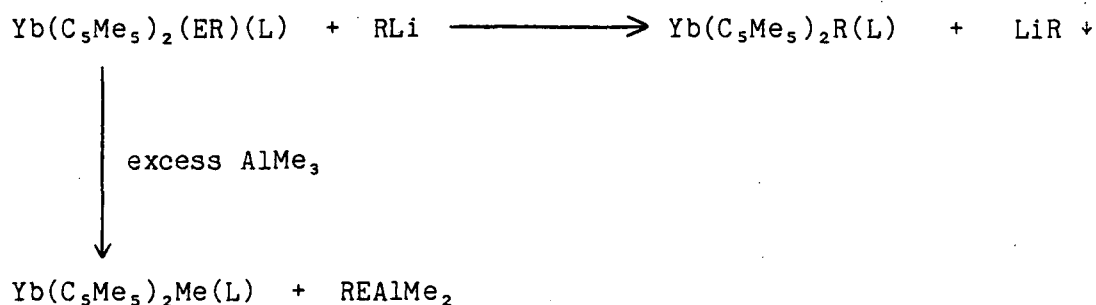
<u>Substrate</u>	<u>ξ (V)^(a)</u>	<u>Reference</u>
2,2'-Bipyridine	- 2.1	14
Azobenzene	- 1.4	14
Diphenyl disulphide	- 1.7	15
Diphenyl diselenide	- 1.2	15
Diphenyl ditelluride	- 1.1	16
Benzoyl peroxide	+ 0.15	17
Tetraethylthiuramdisulphide	- 0.5	18
Triphenylphosphinesulphide	- 2.4	19

(a) Relative to the saturated calomel electrode (S.C.E.)

reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with a wide range of nitrogenous bases will be investigated in order to develop a better understand of the magnetic and electronic properties of these complexes. In addition, an attempt will be made to bracket the oxidation potential of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ with respect to coordinating substrates.

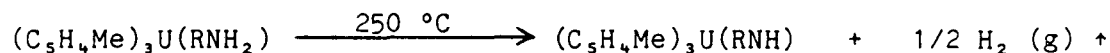
The reduction potentials of the organic dichalcogenides given in Table 2, suggests that it should be possible to cleave these compounds and form $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) complexes. No synthetic routes have been devised for this class of compound. The organic chalcogenide complexes might themselves prove to be useful starting materials for the preparation of alkyl complexes. With this goal in mind, the reactions of these complexes with potential alkylating agents such as AlMe_3 , RLi and Me_2Mg will be investigated (Scheme 2).

Scheme 2



The thermal oxidation of uranium(III) amine complexes to the corresponding uranium(IV) amides has been reported ²⁰ (Equation 1). Since the U(III)-U(IV) oxidation potential (1.5 V in $(\text{C}_5\text{H}_4\text{Me})_3\text{U}(\text{thf})$) is similar to that of the Yb(II)-Yb(III) couple, it seems reasonable to expect similar reactivity in the Yb(II) system. In order to compare the reactivity of the two systems, a number of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$ ($\text{L} = \text{RNH}_2$, RPH_2 , etc.) complexes will be synthesized and then pyrolyzed. The formation of the trivalent lanthanide amide and phosphide complexes is interesting because very few of these complexes have been synthesized ²².

Equation 1



It is the ultimate goal of this research to explore the unique chemistry of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$ as a hydrocarbon soluble, one electron reducing agent. Particular emphasis will be placed on reactions which yield trivalent products not readily obtainable from trivalent precursors.

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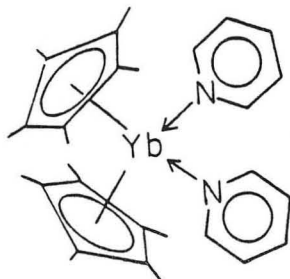
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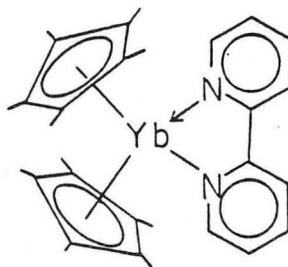
Chapter 1: Reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with Nitrogenous Bases

Early work by Tilley ¹ indicated that the coordinated diethyl ether of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ was readily displaced by heterocyclic nitrogenous bases such as pyridine and 2,2'-bipyridine yielding the diamagnetic bis pyridine adduct I and the paramagnetic mono chelate complex II.

Boncella ² later showed that II could be oxidized to the salt III with silver iodide. This observation, along with the paramagnetism of II as observed in NMR experiments, suggested that this compound contained a radical anion coordinated to a ytterbium(III) center. The unusual temperature dependence of the magnetic susceptibility of II (Figure 1a) compared with a typical ytterbium(III) compound such as III (Figure 1b) also supported this conclusion. Finally, the visible spectrum of II contained three broad absorptions between 800 and 900 nm characteristic of the 2,2'-bipyridine radical anion. No such absorptions were evident in the visible spectrum of III.



I



II

Figure 1 Plots of χ_M^{-1} vs. T for Complexes II and III.

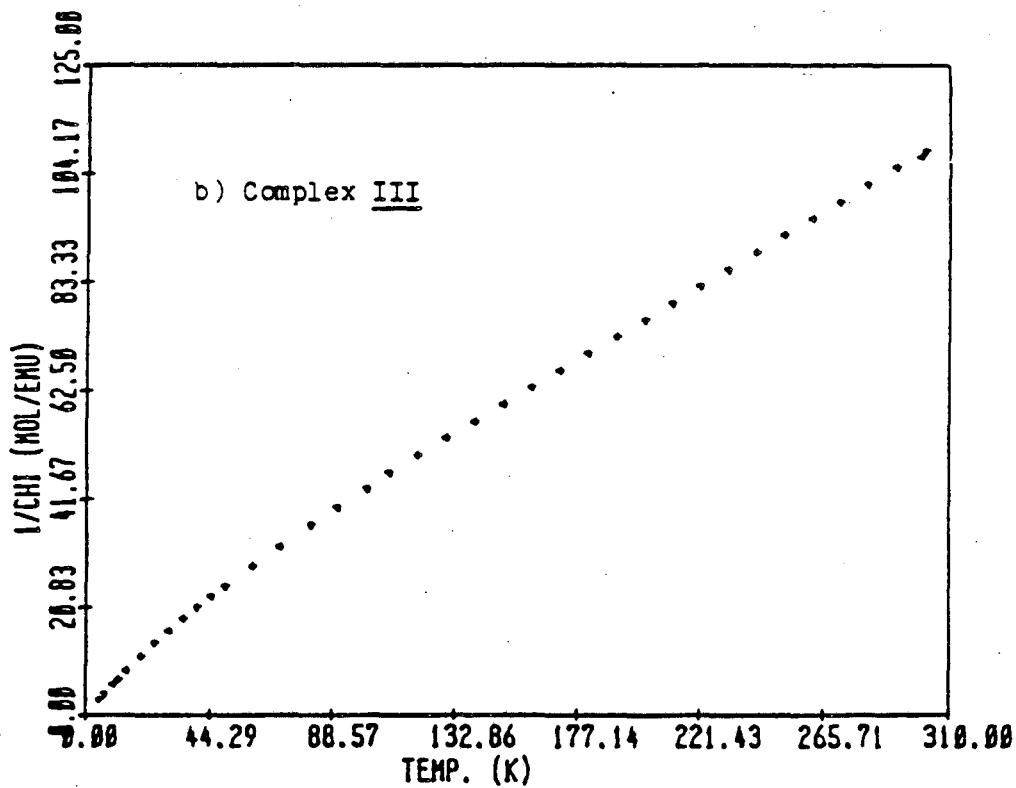
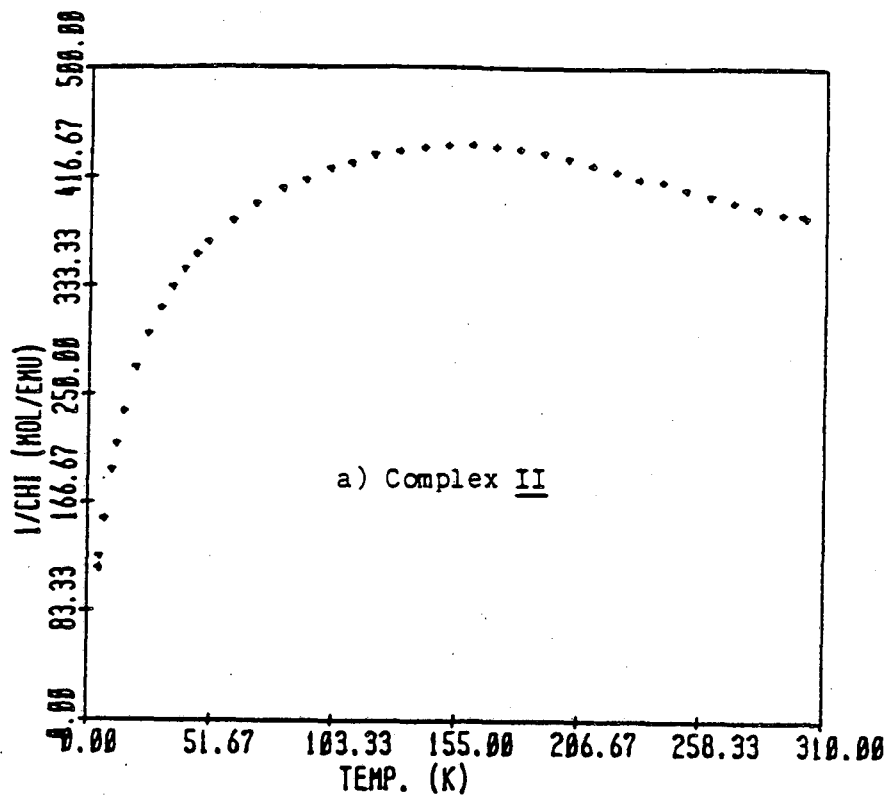
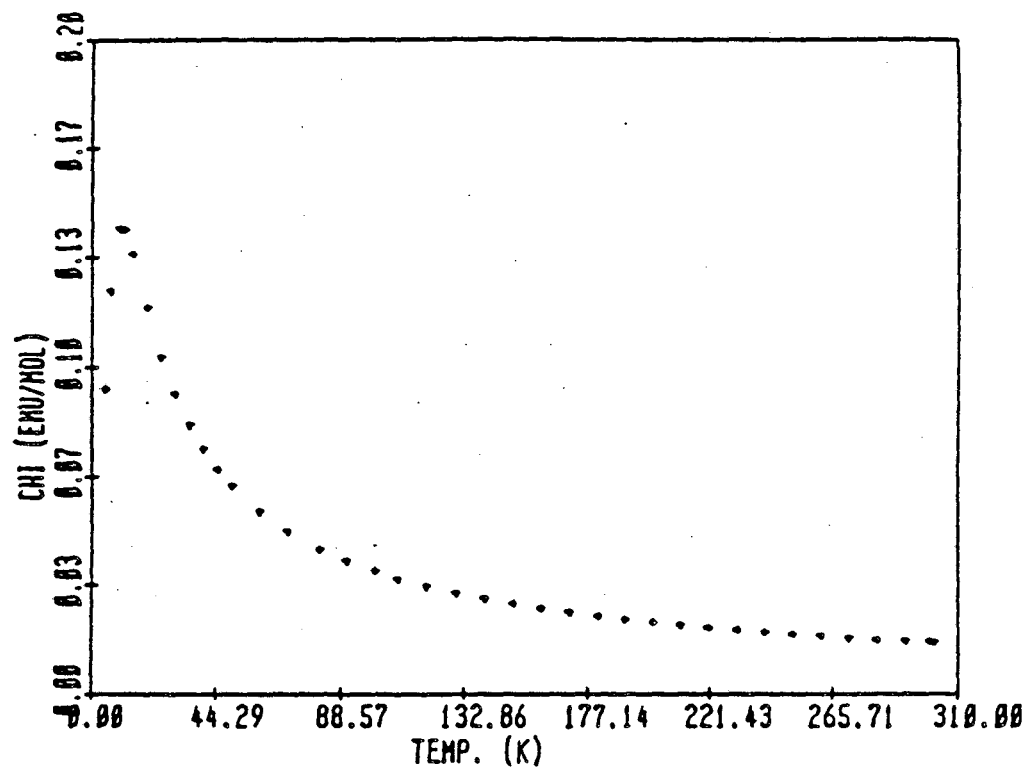
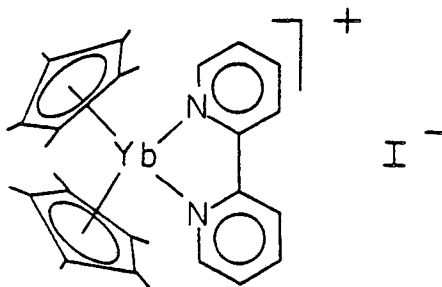


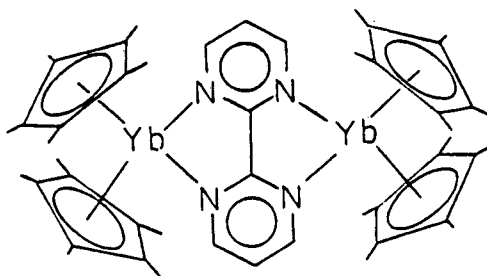
Figure 2 Plot of x_M vs. T for Complex IV.





III

Boncella also investigated the reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with 2,2'-bipyrimidine since this ligand is capable of binding two $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units. Complex IV was the only product of this reaction regardless of stoichiometry.



IV

The magnetic susceptibility of IV (Figure 2) showed a different temperature dependence from either the radical anion II or a typical ytterbium(III) compound as represented by III. An X-ray crystallographic study was carried out on IV and on 2,2'-bipyrimidine which showed a significant shortening of the 2,2' carbon-carbon bond

of the complexed ligand relative to the free organic molecule.

Reduction populates the π^* LUMO of 2,2'-bipyrimidine which has the symmetry 2 shown in Figure 3. Since the 2,2' carbon-carbon π -interaction is bonding for this orbital, the 2,2' carbon carbon distance was predicted to decrease, exactly as observed in the crystal structure determination. This remarkably successful result does not however indicate whether a one or two electron reduction has occurred; that is whether the complex is a mixed valence-radical anion (Figure 4a) or an ytterbium (III) - dianion species (Figure 4b).

Figure 3 Symmetry of the π^* LUMO of 2,2'-bipyrimidine

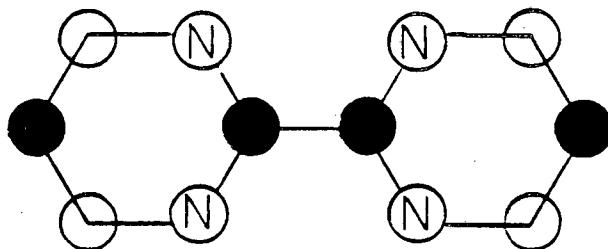
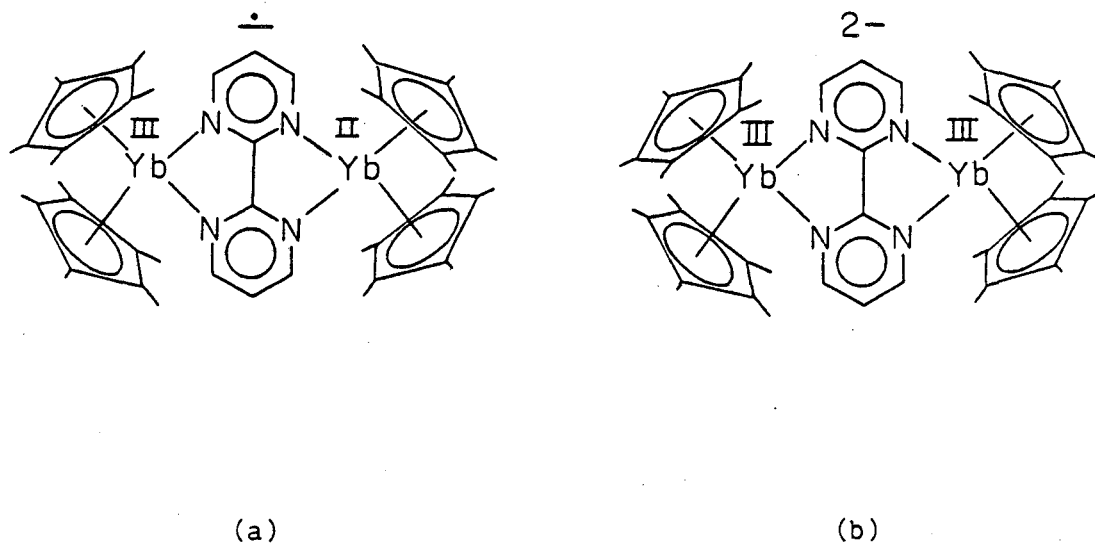


Figure 4 Possible Electronic Structures for
 $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2$ (2,2'-bipyrimidine)

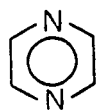


In view of these results, the reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with a wide variety of nitrogenous bases have been carried out. Magnetic susceptibility measurements are used extensively to classify the complexes according to their electronic structural type. This is possible because species containing non-interacting radical anions or dianions and ytterbium(III) ions are distinguishable by the magnitude of the observed magnetic moment. Of course in the case of interacting spins, the temperature dependence of the magnetic susceptibility is in itself very informative (Figure 1a). The ability of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ to act as a reducing agent towards nitrogenous bases as a function of free ligand reduction potential is also examined.

Synthesis and Characterization

The reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with the nitrogenous bases depicted in Figure 5 proceeds rapidly on mixing in ethereal or hydrocarbon solvents. Physical properties of the resulting complexes are given in Table 1. In most cases the complexes may be recrystallized from diethyl ether or toluene but the reaction with pyrazine, quinoxaline, 1,5-naphthyridine and 4,4'-bipyridine produces insoluble powders of 1:1 stoichiometry (2, 6, 7, and 10) which do not melt to 330 °C. This may be because these ligands possess two basic nitrogen atoms incapable of coordinating to the same ytterbium. Secondary interactions with another $\text{Yb}(\text{C}_5\text{Me}_5)_2$ unit then result in a polymeric structure like that shown in Figure 6. Since 4,4'-bipyridine and pyrazine are no more bulky than pyridine, which forms a 1:2 adduct ¹, there is clearly enough room in the coordination sphere of the ytterbium ion to accommodate such an interaction. Steric repulsion between methyl groups of pentamethylcyclopentadienyl rings on different ytterbium ions is unlikely to be very great because the nitrogen centers are relatively far apart in these ligands.

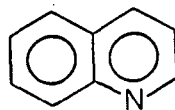
Figure 5 Nitrogenous Bases Used in this Study.



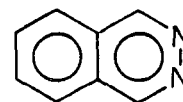
Pyrazine



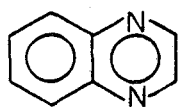
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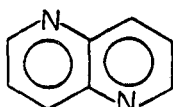
Quinoline



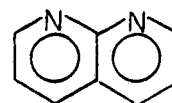
Phthalazine



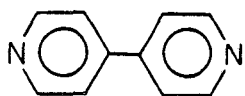
Quinoxaline



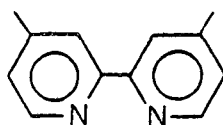
1,5-Naphthyridine



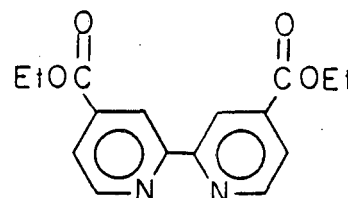
1,8-Naphthyridine



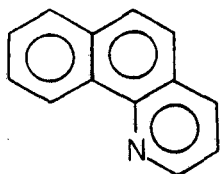
4,4'-Bipyridine



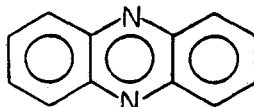
4,4'-Dimethyl-
2,2'-bipyridine



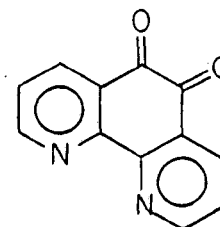
4,4'-Dicarboxylate-
2,2'-bipyridine
diethyl diester



7,8-Benzoquinoline

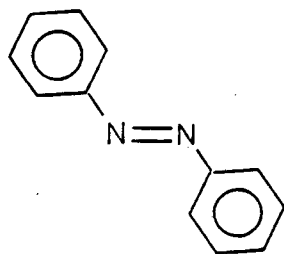


Phenazine

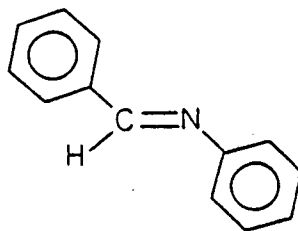


1,10-Phenanthroline-
5,6-dione

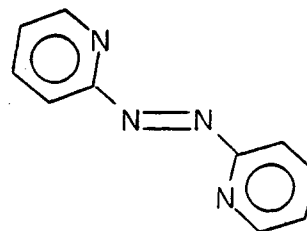
Figure 5 Continued.



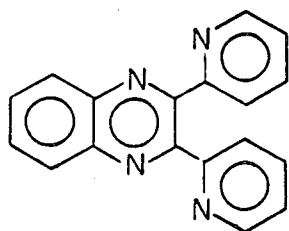
Azobenzene



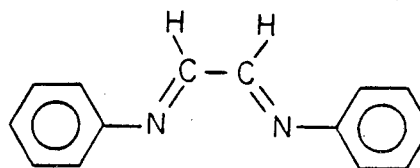
Benzylideneaniline



2,2'-Azopyridine



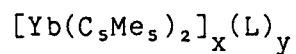
2,3-Di-(2'-pyridino)-
quinoxaline (DPQX)



N,N'-Bis(p-tolyl)-1,4-diaza-
diene (TDAD)

Table 1: Physical Properties of Nitrogenous Base Complexes of

Bis(pentamethylcyclopentadienyl)ytterbium;

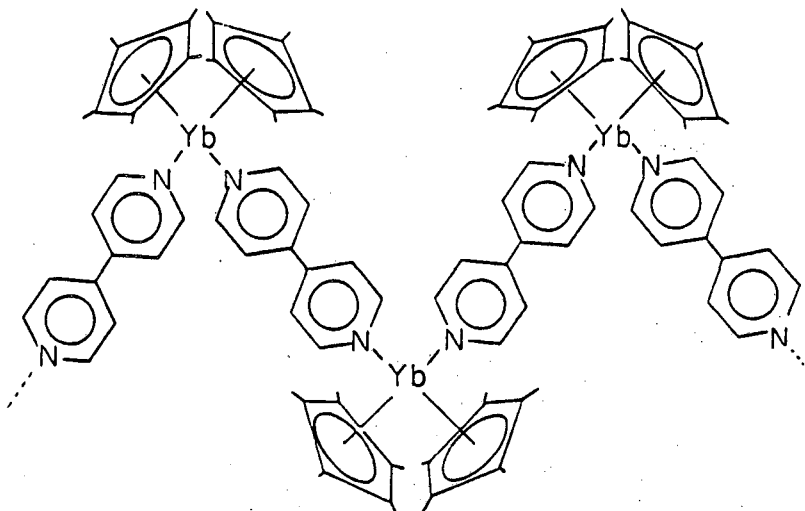


	<u>Base</u>	<u>x</u>	<u>y</u>	<u>Colour</u>	<u>m.p.(°C)</u>
<u>1</u>	Pyridine ^(a)	1	2	dark green	208 - 210
<u>2</u>	Pyrazine	1	1	brown	> 330
<u>3</u>	Pyridazine	1	2	red	176 - 177
<u>4</u>	Quinoline	1	1	red	256 - 259
<u>5</u>	Phthalazine	1	1	red	> 330
<u>6</u>	Quinoxaline	1	1	brown	> 330
<u>7</u>	1,5-Naphthyridine	1	1	brown	> 330
<u>8</u>	1,8-Naphthyridine	1	1	red	dec 220
<u>9</u>	2,2'-Bipyridine ^(a)	1	1	brown	> 330
<u>10</u>	4,4'-Bipyridine	1	1	purple	> 330
<u>11</u>	4,4'-Dimethyl-2,2'- bipyridine	1	1	dark brown	> 330
<u>12</u>	4,4'-Dicarboxylate- 2,2'-bipyridine diethyl diester	1	1	red-brown	> 330
<u>13</u>	2,2'-Bipyrimidine ^(b)	2	1	dark brown	305 - 308
<u>14</u>	7,8-Benzoquinoline	1	1	brown	265 - 267
<u>15</u>	Phenazine	2	1	red-brown	> 330
<u>16</u>	1,10-Phenanthroline- 5,6-dione	2	1	brown	> 330

Table 1 Continued

	<u>Base</u>	<u>x</u>	<u>y</u>	<u>Colour</u>	<u>m.p.</u> (°C)
<u>17</u>	Azobenzene	1	1	blue-green	164 - 167
<u>18</u>	Azobenzene	2	1	dark purple	195 - 197
<u>19</u>	Benzylideneaniline	1	1	dark brown	74 - 77
<u>20</u>	2,2'-Azopyridine	2	1	brown-black	> 330
<u>21</u>	2,3-Di-(2'-pyridino)- quinoxaline	2	1	black	> 330
<u>22</u>	N,N'-Bis(p-tolyl)- 1,4-diazadiene	1	1	dark brown	dec 220

(a) Reference 1 (b) Reference 2

Figure 6 A Polymeric Structure for $\text{Yb}(\text{C}_5\text{Me}_5)_2(4,4'\text{-bipyridine})$ 

It is informative to compare the insoluble nature of 2, 6, 7 and 10 with the soluble, crystalline products obtained in the reactions with pyridazine and phenazine. Phenazine forms a 2:1 complex (15) where the organic ligand bridges two $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units. Here the nitrogen atoms are far enough apart to allow a secondary interaction but the larger phenazine ligand, with a third aromatic ring, effectively blocks off the second coordination site at ytterbium. In the case of pyrazine, a 1:2 adduct (3) is formed. This indicates that there is enough room around the ytterbium for a secondary interaction but the close spatial disposition of the nitrogen atoms prevents a strong interaction with a second $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$ unit. As a result, the coordinative vacancy is satisfied by coordination of a second pyridazine ligand.

Proton NMR data are tabulated in Tables 2 and 3 for all soluble diamagnetic and paramagnetic complexes, respectively. The broad line widths and large chemical shifts indicate very clearly which complexes contain the paramagnetic ytterbium(III) ion. In some cases the paramagnetic shift and line broadening are so extensive that certain ligand resonances are not observable.

The NMR spectra of the diamagnetic complexes (Table 2) are unremarkable. In all cases, the aromatic proton resonances shift slightly upfield (ca. 0.1 - 0.2 ppm) upon complexation to $\text{Yb}(\text{C}_5\text{Me}_5)_2$. This is expected because coordination to an electron poor metal center decreases the deshielding effect of the aromatic ring current. The pentamethylcyclopentadienyl methyl resonance falls between 1.9 and 2.1 ppm for all of these complexes compared with a chemical shift of 1.93 ppm for base-free $\text{Yb}(\text{C}_5\text{Me}_5)_2$ ². The ring methyl resonance is not strongly influenced by coordination of a Lewis base because the protons do not experience a strong deshielding effect due to the ring π -electron density. In addition, the predominantly ionic metal-ring bonding³ implies that the ring π -electron density is itself not greatly dependent upon the Lewis base strength of other ligands in the coordination sphere of the metal.

The NMR spectra of the soluble paramagnetic complexes (Table 3) show line widths ranging from 8 to more than 200 Hz. This is typical for the paramagnetic $4f^{13}$ ytterbium(III) ion⁴. The paramagnetic shift of NMR resonances in lanthanide complexes is primarily due to the pseudocontact shift⁵. This is a through space effect arising from the anisotropy of the molecular magnetic field in low symmetry environments. The magnitude of the pseudocontact shift is dependent on

the distance (as r^{-3}) and angular relationship between the protons of interest and the paramagnetic center. Line broadening due to the pseudocontact term also falls off rapidly with distance (as r^{-6}). This is helpful in assigning the NMR spectra of paramagnetic lanthanide complexes since generally the protons closest to the metal center have the broadest line widths and the largest chemical shifts. For example, in the mono chelate complexes 11 and 12 the furthest downfield resonance is assigned to the 6,6' protons of the 2,2'-bipyridine ring system because these are closest to the metal center. The corresponding resonance is not observed in the unsubstituted analogue 9 presumably because of extreme line broadening. All of these complexes also have resonances integrating to two protons between -10.5 and -13.1 ppm which can be assigned to the comparatively distant 3,3' protons. Assignment of the remaining resonances are less certain.

The strong similarity between the NMR resonances of 9, 11 and 12 implies that 12 is also coordinated through the nitrogen atoms and not through the diester oxygen atoms. The observation of coupling for the ethyl groups also indicates that the ester functionality is far removed from the ytterbium ion. The infrared spectrum of 12 shows a strong carbonyl band at 1708 cm^{-1} which compares well with the free diester carbonyl stretch at 1721 cm^{-1} . The small decrease in stretching frequency is consistent with delocalization of the unpaired electron into the ester groups (Figure 7) and not with coordination through the ester oxygens.

Table 2: ^1H NMR Data for Diamagnetic $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_x(\text{L})_y$ Complexes

<u>Base</u>	<u>^1H NMR</u> ^(a)
<u>1</u> Pyridine ^(b)	δ 2.12 (30H, s)
<u>4</u> Quinoline	δ 8.61 (1H, m); 7.79 (1H, m); 7.35 (4H, m); 6.72 (1H, m); 1.98 (30H, s)
<u>14</u> 7,8-Benzoquinoline	δ 8.67 (1H, d); 7.3 - 7.8 (7H, m); 6.82 (1H, dd); 1.91 (30H, s)
<u>19</u> Benzylideneaniline	δ 8.06 (2H, d); 7.20 (2H, q); 7.0 - 7.2 (7H, m); 1.93 (30H, s)

(a) Recorded in C_6D_6 or C_7D_8 at 32 °C. Chemical shifts in ppm relative to tetramethylsilane. (b) Reference 1

Table 3: ^1H NMR Data for Paramagnetic $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_X(\text{L})_Y$ Complexes

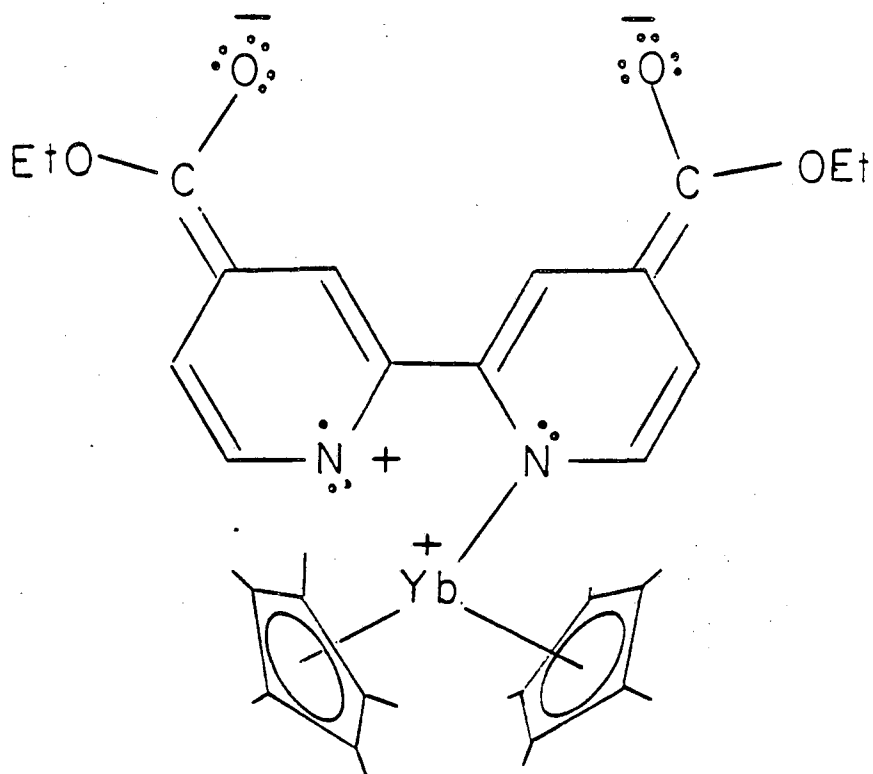
<u>Base</u>	^1H NMR ^(a)
<u>5</u> Phthalazine X = Y = 1	δ 31.2 (15H, 51 Hz); 13.3 (15H, 51 Hz); -3.7 (1H, 15 Hz); -9.1 (1H, 17 Hz); -9.5 (1H, 14 Hz); -15.0 (1H, 27 Hz).
<u>8</u> 1,8-Naphthyridine X = Y = 1	δ 7.9 (30H, 200 Hz); -1.1 (1H, 16 Hz); -7.9 (1H, 15 Hz); -8.6 (1H, 17 Hz); -9.3 (1H, 19 Hz); -23.8 (1H, 26 Hz).
<u>9</u> 2,2'-Bipyridine ^(b) X = Y = 1	δ 25.3 (2H, 41 Hz); 4.1 (30H, 9 Hz); -13.1 (2H, 8 Hz).
<u>11</u> 4,4'-Dimethyl- 2,2'-bipyridine X = Y = 1	δ 143.0 (2H, 84 Hz); 3.8 (30H, 15 Hz); -6.1 (6H, 30 Hz); -10.5 (2H, 14 Hz)
<u>12</u> 4,4'-Dicarboxylate- 2,2'-bipyridine diethyl diester ^(c) X = Y = 1	δ 206.9 (2H, 110 Hz); 4.7, 4.5, 4.1 (40H); -11.8 (2H, 11 Hz); -18.5 (2H, 94 Hz).
<u>13</u> 2,2'-Bipyrimidine ^(b) X = 2, Y = 1	δ 68.5 (2H, 28 Hz); 4.2 (4H, 103 Hz); -4.1 (60H, 61 Hz).

<u>15</u> Phenazine	δ 6.4 (4H, 16 Hz); 5.6 (4H, 16 Hz);
X = 2, Y = 1	-1.9 (60H, 380 Hz).
<u>16</u> 1,10-Phenanthroline-	δ 22.6 (2H, 60 Hz); 11.5 (2H, 30 Hz);
5,6-dione	4.4 (30H, 65 Hz); -2.1 (30H, 61 Hz);
X = 2, Y = 1	-6.1 (2H, 43 Hz).
<u>17</u> Azobenzene (1:1)	δ 79.1 (4H, 24 Hz); 14.1 (30H, 25 Hz);
X = Y = 1	-145.9 (4H, 230 Hz); -186.6 (2H, 97 Hz).
<u>18</u> Azobenzene (2:1)	δ 18.1 (? 4H, 12 Hz); 11.4 (? 4H, 20 Hz);
X = 2, Y = 1	-5.8 (30H, 300 Hz); -15.7 (? 2H, 16 Hz)
<u>20</u> 2,2'-Azopyridine	δ 74.2 (2H, 40 Hz); 61.4 (2H, 35 Hz);
X = 2, Y = 1	18.3 (2H, 21 Hz); -2.1 (30H, 163 Hz);
	-12.6 (30H, 86 Hz).
<u>21</u> 2,3-Di-(2'-pyridino)-	δ 108.9 (2H, 64 Hz); 71.8 (2H, 54 Hz);
quinoxaline	29.6 (2H, 29 Hz); -6.0 (30H, 100 Hz);
X = 2, Y = 1	-6.8 (30H, 100 Hz); -22.0 (2H, 29 Hz).
<u>22</u> N,N'-Bis(p-tolyl)-	δ 113.4 (4H, 500 Hz); 59.8 (6H, 73 Hz);
1,4-diazadiene	50.2 (4H, 49 Hz); 1.8 (30H, 35 Hz);
X = Y = 1	-2.6 (2H, 100 Hz).

(a) Recorded in d_6 -benzene or d_6 -toluene at 32 °C. Chemical shifts are in ppm relative to tetramethylsilane. Relative intensity and line width at half peak height are given in brackets.

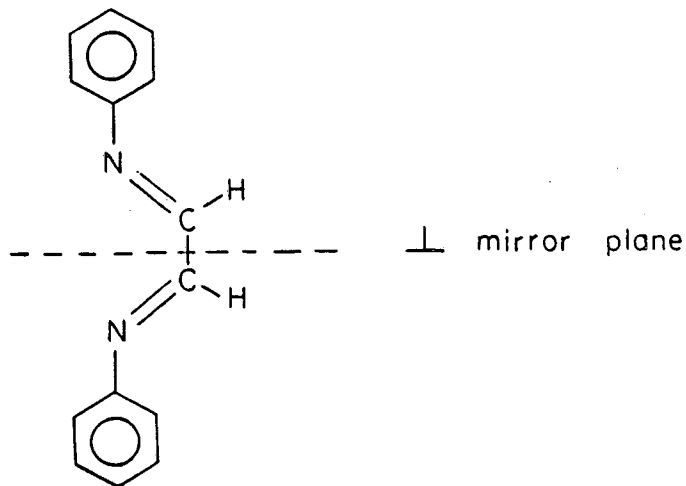
(b) Reference 2 (c) At 59 °C: δ 195.9 (2H, 100 Hz); 5.8 (4H, br q); 4.4 (30H, 25 Hz); 4.1 (6H, br t); -14.0 (2H, 8 Hz); -23.4 (2H, 102 Hz).

Figure 7 One Resonance Form of Complex 12.



The NMR spectrum of 22 is also readily interpreted. The ring methyl resonance is observed at 1.8 ppm, similar to that in the other mono chelate complexes above. A mirror plane passing through the center of the 2,3 carbon-carbon bond and perpendicular to this bond and the 1,4-diazadiene framework renders the two p-tolyl rings equivalent (Figure 8). Rapid rotation about the N-C (p-tolyl) bond at 32 °C is still required to explain the presence of only one type of ortho, meta and para resonance (integration 4:4:6). The downfield resonance is assigned to the ortho protons since these are, on average, closest to the ytterbium center. The resonance at 50.2 ppm is therefore assigned to the meta protons. The protons on carbon 2 and 3 of the 1,4-diazadiene backbone are chemically equivalent due to the mirror plane as shown in Figure 8 and give a single resonance at -2.6 ppm.

Figure 8



The 1:1 azobenzene complex 17 also exhibits a straightforward NMR spectrum. The observation of single ortho, meta and para proton resonances (integration 4:4:2) indicates that rotation about the N-C (phenyl) bond is rapid at 32 °C, just as observed for 22, above. This requires symmetrical coordination of ytterbium to both nitrogen centers on the NMR timescale (Figure 9a) or as in a dimeric structure (Figure 9b). A rapid monomer-dimer equilibrium would also be consistent with the NMR data. This complex gives a mass spectrum with a parent ion at 626 amu corresponding to a monomeric species. A comparison of the calculated and observed isotope pattern for this ion is shown in Figure 10. Dimer fragmentation in the mass spectrometer cannot however be ruled out. Unfortunately this compound is too air and moisture sensitive to allow an accurate solution molecular weight determination to be made.

Figure 9 Possible Solution Structures for Complex 17.

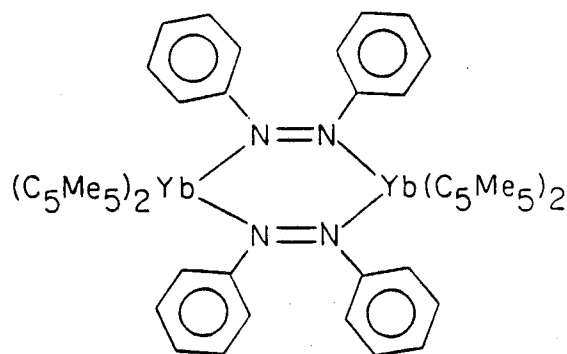
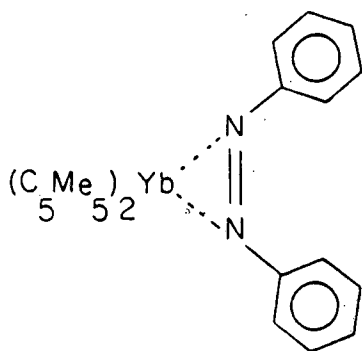
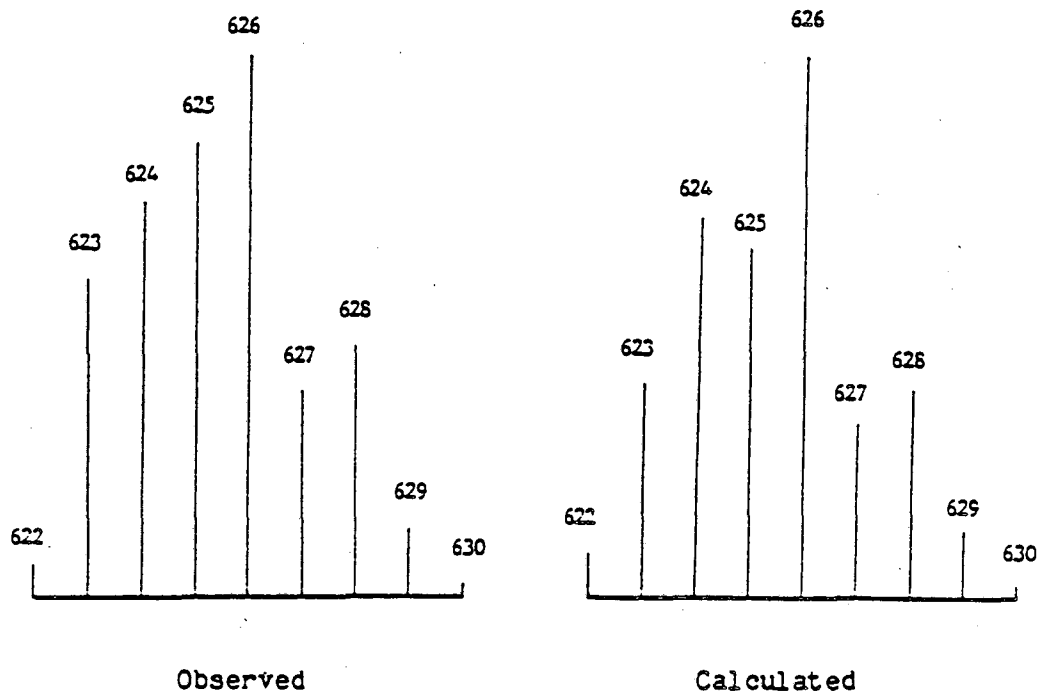


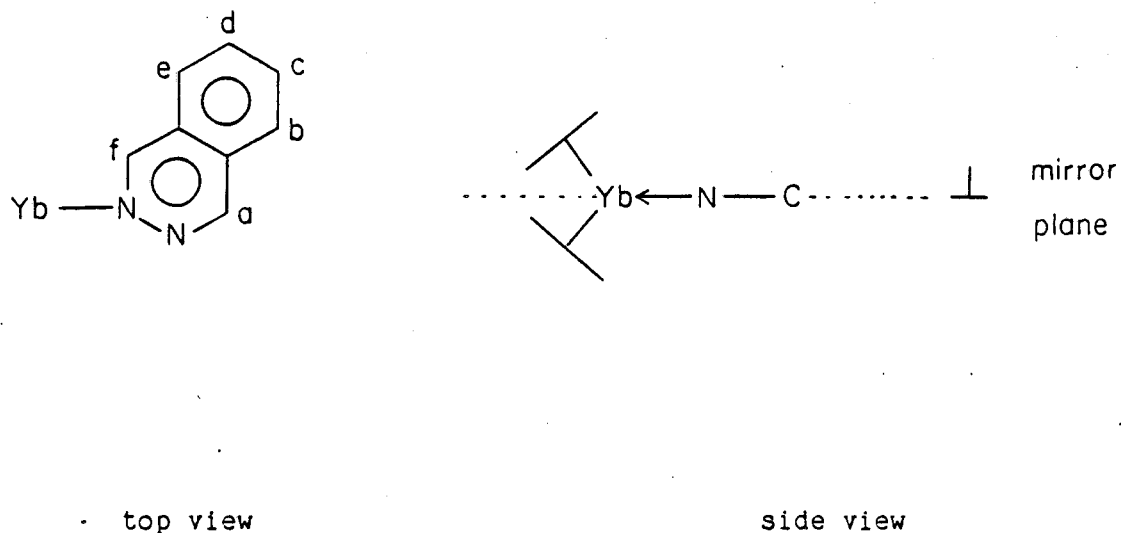
Figure 10 Parent Ion Isotope Distribution for 17

Free azobenzene exists as the trans isomer ⁶ but it does not seem likely that this geometry is maintained in 17. The chemical equivalence of the phenyl rings in the proton NMR would require a rapid dissociative equilibrium of the reduced (and highly basic) ligand from a $\text{Yb}(\text{C}_5\text{Me}_5)_2^+$ cation in a nonpolar medium (d_6 -benzene). A polymeric structure containing equivalent rings can also be ruled out since 17 is very soluble in pentane. The infrared spectrum provides the best evidence for a cis geometry. Cis-azobenzene has four strong bands ⁷ (689, 701, 757 and 779 cm^{-1}) in the 600 to 800 cm^{-1} region while the trans isomer has only two (687 and 771 cm^{-1}). The observation of four strong bands (680, 711, 750 and 783 cm^{-1}) strongly indicates a cis geometry for 17. Isomerization of trans-azobenzene upon coordination to transition metals, especially in cases where reduction occurs, is well

known ⁸. An X-ray crystal structure determination should be performed in order to establish the monomeric or dimeric structure of 17, though suitable crystals have not yet been obtained.

The NMR spectra of the remaining 1:1 complexes, 5 and 8, are not so easily interpreted. Complex 5 exhibits inequivalent pentamethylcyclopentadienyl rings and the phthalazine proton resonances are all inequivalent though only four are observed. Rigid coordination of the $\text{Yb}(\text{C}_5\text{Me}_5)_2$ group to one nitrogen lone pair (Figure 11) would result in inequivalent phthalazine protons, but it would not result in inequivalent rings. This is because the planar phthalazine ligand is restricted to lay in the mirror plane between the rings for steric reasons. Coordination to a single nitrogen would explain the NMR of 8; however the line width of the ring methyl resonance is much greater than that in 5 and varies considerably with temperature suggesting that the rings are in fact inequivalent but have nearly the same chemical shift. Given the similar steric bulk and proximity of the nitrogen centers within each ligand, it is not unreasonable to assume 5 and 8 have the same structural type in solution.

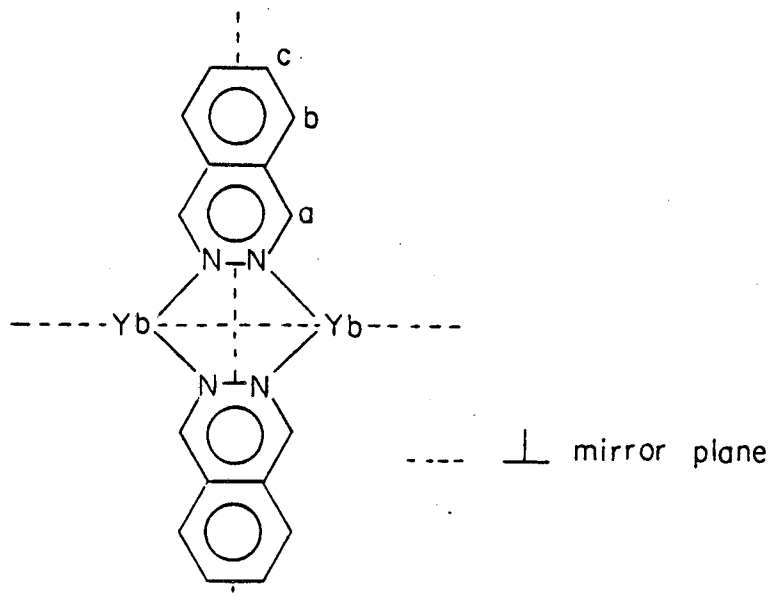
Figure 11 Schematic View of Coordination to One Nitrogen Center in 5.



(rings above and below plane not shown)

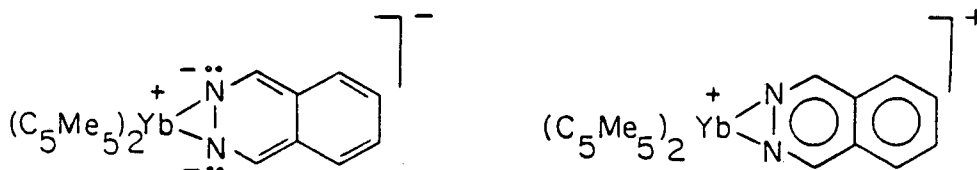
A simple dimer where two ligands bridge two $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units (Figure 12) would still result in equivalent rings and would also render some of the phthalazine or 1,8-naphthyridine protons equivalent. Any dimeric structure would also require unfavourably close contact between $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units because of the close proximity of the nitrogen centers within these ligands.

Figure 12 A Dimeric Structure for 5 (C_5Me_5 rings above and below the plane omitted).



One possible explanation for the NMR spectra of 5 and 8 is the presence of two ytterbium containing species in solution. The simplest postulate involves disproportionation upon reduction of the organic ligand producing dianions and neutral ligands coordinated to $Yb(C_5Me_5)_2^+$ cations (Figure 13).

Figure 13 Disproportionation upon Reduction with $Yb(C_5Me_5)_2$



The inability of phthalazine and 1,8-naphthyridine to form bridges would then result in tight ion pairs of $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})]^+$ cations and $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L}^{2-})]^-$ anions in solution. Provided ligand and electron exchange is not rapid on the NMR timescale, two types of ring protons and two different sets of base protons (six resonances; three each for the anion and cation) are predicted for both 5 and 8. In fact only four phthalazine and five 1,8-naphthyridine resonances are observed for 5 and 8 respectively. This is not unusual even with well behaved ytterbium (III) complexes ². Hydrolysis experiments disclose the presence of the neutral ligand and a mixture of hydrogenated isomers in an approximately 1:1 ratio. This is consistent with a structure made up of coordinated dianions and neutral ligands although it is conceivable that disproportionation could occur during hydrolysis. There is no evidence to indicate that radical coupling occurs either during complex formation or on hydrolysis.

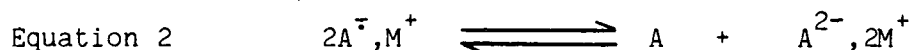
Extensive studies of radical anions in solution have shown that disproportionation occurs in many cases ⁹. In the presence of tightly binding cations, the free energy of disproportionation is given by Equation 1 ⁹.

$$\text{Equation 1} \quad \Delta G_{\text{disp}} = \Delta E_{\text{rep}} - \Delta_B$$

ΔE_{rep} = repulsion energy between electrons in the same orbital.

Δ_B = anion - cation binding energy.

Since Δ_B represents the coulombic attraction between the reduced ligand and the cation it is proportional to $e_a e_c / r$ where e_a and e_c are the anion and cation charges and r is the charge separation. Considering the disproportionation equilibrium in Equation 2,

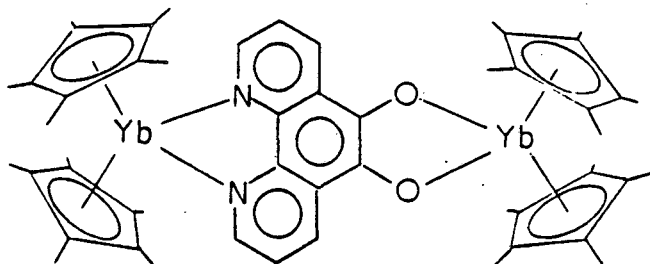


Δ_B is twice as large for the binding of a dianion by two cations as it is for two anions binding two cations. Thus strong cation binding favours disproportionation. In the case of phthalazine and 1,8-naphthyridine the situation is slightly different because it is not possible for two $Yb(C_5Me_5)_2^+$ cations to bind a single dianion. Nevertheless Δ_B should still favour disproportionation because the neutral ligands are also capable of binding strongly to $Yb(C_5Me_5)_2$ through a nitrogen lone pair. This contribution to Δ_B may compensate for the inability of the dianion to bind two cations. Later in this chapter magnetic susceptibility measurements will provide additional evidence to support disproportionation in 5, 8 and some of the less soluble 1:1 complexes.

Phenazine, 2,2'-bipyrimidine and 1,10-phenanthroline-5,6-dione react with two equivalents of $Yb(C_5Me_5)_2(OEt_2)$, regardless of the stoichiometry, to form paramagnetic complexes 15, 13 and 16, respectively. This raises the question of whether a one or two electron reduction has taken place to give a mixed valence-radical anion (Figure 4a) or a ytterbium(III)-dianion complex (Figure 4b). Complex 16 shows

inequivalent ring resonances in the proton NMR spectrum indicating coordination through the nitrogen and the oxygen centers. The strong dione carbonyl stretching frequencies at 1701 and 1684 cm^{-1} are not observed in 16 supporting a two electron reduction to a dialkoxide complex (Figure 14).

Figure 14 Structure of Complex 16.



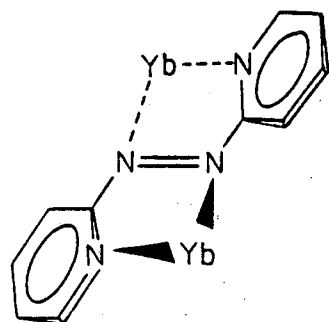
Complexes 13 and 15 show equivalent ring resonances in the NMR spectra. However this can not be taken as evidence for a two electron reduction since the rate of electron exchange between divalent and trivalent ytterbium ions coordinated to the same ligand may very well be rapid on the NMR timescale resulting in an averaged chemical shift for the ring resonances. Only one ring resonance is observed to $-85\text{ }^{\circ}\text{C}$.

Azobenzene reacts with two equivalents of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ to form a 2:1 complex 18. Azobenzene is the only ligand in this study capable of forming 1:1 and 2:1 complexes which gives isolable crystalline products in both stoichiometries. Reduction of heterocycles has been reported ¹⁰ to increase the basicity of the nitrogen atoms towards protons by as much as 20 orders of magnitude so it is not surprising therefore that it is difficult to form 1:1 adducts of 2,2'-bipyrimidine and phenazine since the reduced ligands are much better bases towards $\text{Yb}(\text{C}_5\text{Me}_5)_2$ than the free neutral molecules. Polymeric 1:1 complexes are not formed because the coordination sphere of each ytterbium is sufficiently filled by the ligands. With azobenzene the reaction mixture initially turns deep blue-green, then purple over the course of an hour consistent with rapid formation of 1:1 complex 17, followed by a much slower reaction with a second equivalent of $\text{Yb}(\text{C}_5\text{Me}_5)_2$. The purple 2:1 complex is difficult to isolate free of the 1:1 complex even when excess $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ is used. The markedly different behaviour of azobenzene could be caused by several factors depending on whether 17 has the monomeric (Figure 9a) or dimeric (Figure 9b) structure. If 17 is monomeric, this would indicate that steric crowding between $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units is sufficient to prevent dimer formation. Formation of a 2:1 adduct would therefore be difficult for the same reasons. A dimeric structure for 17 would require a second equivalent of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ to break up a strong interaction between one nitrogen and a $\text{Yb}(\text{C}_5\text{Me}_5)_2^+$ cation in order for formation of the 2:1 complex to occur. Since the cationic ytterbium(III) center is a better Lewis acid than divalent ytterbium by virtue of its smaller size and greater positive charge, this may well be difficult.

Shortly after this work was completed, the synthesis and crystal structure of the samarium(III) analogue was reported ¹¹. The virtually superimposable infrared spectra of this compound and 18 suggests that these complexes are isostructural. The crystal structure shows a distorted trans-azobenzene unit with exceptionally close contact between the samarium centers and the ortho carbon-hydrogen bonds of one phenyl ring (agostic interactions). The observation of only one strong absorption in the 600 to 800 cm^{-1} region at 730 cm^{-1} for both complexes, may be a reflection of the severely distorted trans geometry. It is interesting that reaction of the 1:1 complex 17 with another equivalent of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ results in isomerization of coordinated azobenzene. This is clearly necessary because steric repulsion between pentamethylcyclopentadienyl rings is too large to allow coordination of more than one $\text{Yb}(\text{C}_5\text{Me}_5)_2$ unit in the cis configuration.

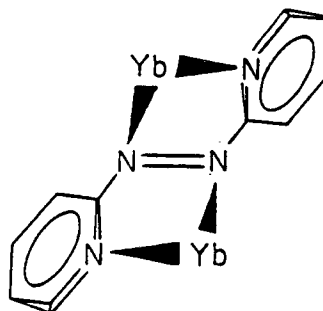
2,2'-Azopyridine and 2,3-di-(2'-pyridino)quinoxaline (DPQX) form intensely coloured 2:1 complexes 20 and 21 respectively. The NMR spectrum of both are remarkably similar and show two inequivalent ring resonances. This is explained by the flexible coordination environment of these ligands. All of the isomers shown in Figures 15 and 16 are consistent with the NMR spectra. Isomers 15b, 15c, 15d and 16b can probably be ruled out for steric reasons. The key requirement for inequivalent rings is the absence of any planar isomers.

Figure 15 Structural Isomers of Complex 20 (Rings omitted)

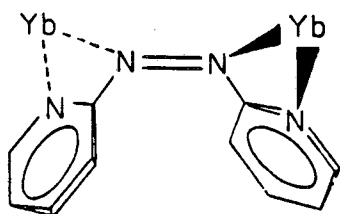


(enantiomeric pair)

a

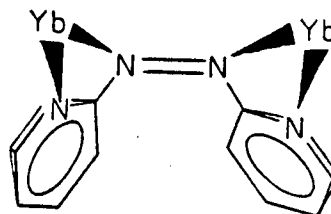


b

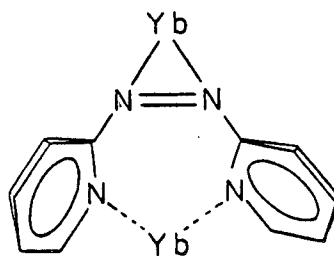


(enantiomeric pair)

c

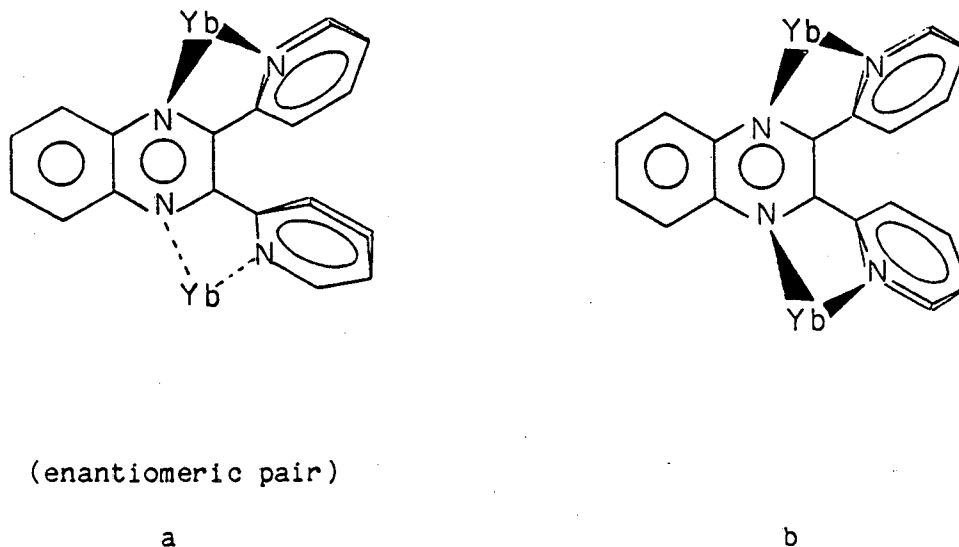


d



e

Figure 16 Structural Isomers of Complex 21 (Rings omitted)



A large number of 2,2'-azopyridine complexes are known ¹², all of which contain the trans isomer coordinated through one or both pyridine nitrogen atoms. Symmetrical coordination of both pyridine units gives rise to a distinctive four band infrared absorption pattern between 1400 and 1600 cm^{-1} . This pattern is observed for 20 (1465, 1479, 1523, 1601 cm^{-1}) consistent with the structures in Figure 15. 1:2-Chelate complexes involving azo nitrogen coordination are formed with two equivalents of copper(II)halides ^{12e} resulting in a decrease of the Raman active (and infrared inactive for symmetrical azo compounds) N=N stretching frequency by 100 cm^{-1} . A larger decrease in frequency would be expected for the azo stretch of 20 because reduction populates the π^* N=N antibonding molecular orbital. Unfortunately no information about the azo stretching frequency can be obtained for 20 because the

compound absorbs intensely throughout the visible spectrum. Recent studies ^{12g} of reduced bis-transition metal carbonyl complexes of 2,2'-azopyridine have shown conclusively by ESR hyperfine coupling, that azo coordination occurs for the reduced ligand. This has been attributed to the greatly enhanced basicity of the azo nitrogen atoms upon reduction. In view of this, it seems likely that azo coordination also occurs in 20. Bis chelate formation places the $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units in close proximity so pyridine ring canting is necessary to minimize steric interactions leading to inequivalent rings in the proton NMR spectrum.

Molecular models show that the pyridine rings of DPQX cannot both be coplanar with the quinoxaline system due to steric interactions between protons at the 6-position of the pyridine rings ¹³. In order to minimize this effect and still maintain a chelate interaction with the metal centers, the pyridine rings are probably canted at ca. 45 ° with respect to the quinoxaline plane. This has been suggested for several transition metal chloride complexes of DPQX which have infrared spectra very similar to that of 21. Steric repulsion between $\text{Yb}(\text{C}_5\text{Me}_5)_2$ is not likely to be significant because the ytterbium centers are much farther apart here than in 2,2'-bipyrimidine complex 13 which has a planar coordination geometry ².

Table 4: Ytterbium-(C₅Me₅) Symmetric Tilting Frequencies

<u>Diamagnetic Complexes</u>		
<u>1</u>	Pyridine ^(a)	265 cm ⁻¹
<u>4</u>	Quinoline	277
<u>14</u>	7,8-Benzoquinoline	275
<u>19</u>	Benzylideneaniline	265
<u>Paramagnetic Complexes</u>		
<u>2</u>	Pyrazine	290 cm ⁻¹
<u>3</u>	Pyridazine	309
<u>5</u>	Phthalazine	311
<u>6</u>	Quinoxaline	294
<u>7</u>	1,5-Naphthyridine	303
<u>8</u>	1,8-Naphthyridine	310
<u>9</u>	2,2'-Bipyridine ^(a)	290
<u>10</u>	4,4'-Bipyridine	290
<u>11</u>	4,4'-Dimethyl-2,2'-bipyridine	308
<u>12</u>	4,4'-Dicarboxylate-2,2'-bipyridine diethyl diester	311
<u>13</u>	2,2'-Bipyrimidine ^(b)	303
<u>15</u>	Phenazine	315
<u>16</u>	1,10-Phenanthroline-5,6-dione	295
<u>17</u>	Azobenzene (1:1)	314
<u>18</u>	Azobenzene (2:1)	299
<u>20</u>	2,2'-Azopyridine	301
<u>21</u>	2,3-Di-(2'-pyridino)quinoxaline	305
<u>22</u>	N,N'-Bis(p-tolyl)-1,4-diazadiene	313

(a) Reference 1 (b) Reference 2

To this point little mention has been made of the mass and infrared spectra of these compounds. The high melting points and low volatilities of these compounds make it difficult to obtain mass spectral data in most cases. Ligand vibrations account for most of the infrared bands and these generally do not change dramatically on reduction and complexation. Perhaps the most noteworthy observation is a strong correlation between the ytterbium - pentamethylcyclopentadienyl ring symmetric tilting frequency ¹⁴ and the metal oxidation state. The metal-ring symmetric tilting frequency varies between 290 and 313 cm⁻¹ for trivalent ytterbium and between 255 and 277 cm⁻¹ for divalent ytterbium (Table 4). The higher ytterbium (III)-ring tilting frequency reflects the stronger coulombic attraction between the smaller, more highly polarizing trivalent metal center and the negatively charged ring compared with the divalent ytterbium-ring interaction. This trend extends beyond nitrogenous base complexes of Yb(C₅Me₅)₂ as will become evident in subsequent chapters.

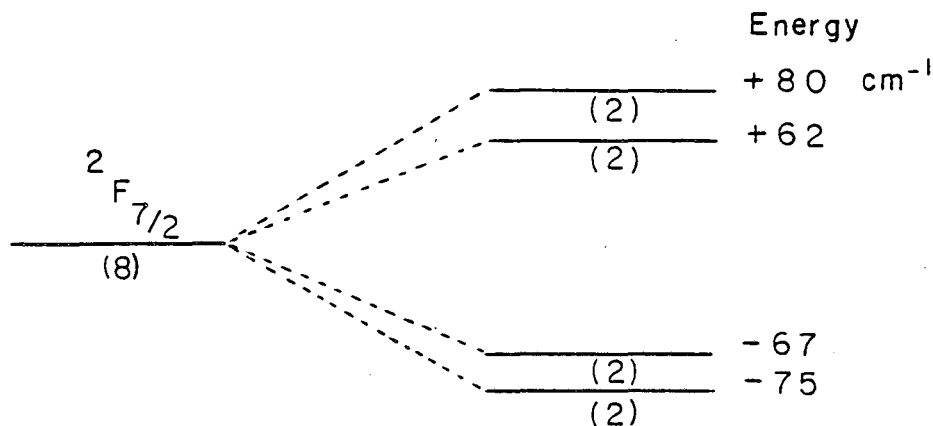
Magnetic Susceptibility Studies

Magnetic susceptibility measurements provide information on the electronic structure of the reduced ligands and the interaction of unpaired ligand spins with the paramagnetic ytterbium(III) ion. NMR spectroscopy is useful in determining the oxidation state of ytterbium but provides little information about the reduced ligand. Boncella ² previously found ESR to be of limited use because a signal could only be observed for 2,2'-bipyridine complex 9 at very low temperatures (ca. 21 K) and low microwave powers. Magnetic susceptibility measurements,

unlike NMR and ESR spectroscopy, provide information over a wide temperature range and in the solid state.

Trivalent ytterbium is a paramagnetic $4f^{13}$ ion. In a low symmetry ligand field the ${}^2F_{7/2}$ free ion ground state is split into four Kramer's doublets ¹⁵ (Figure 17). At low temperatures (< 30 K) only the two lowest levels are populated and contribute to the magnetic moment. As a result, at temperatures between 0 and 30 K, the complex follows the Curie law ($C = \chi T$) with $\mu \approx 3.8$ B.M. At temperatures above 30 K, thermal population of the third and fourth doublet levels becomes increasing significant and the contribution of these levels to the magnetic moment results in a deviation from Curie law behaviour. By 90 K, both levels are easily accessible while the next manifold of states arising from the ${}^2F_{5/2}$ term are 10300 cm^{-1} higher in energy and is not thermally accessible. Thus from 90 to 300 K, the temperature dependence of the magnetic susceptibility follows the Curie-Weiss law ($C = \chi(T-\theta)$) with $\mu \approx 4.5$ B.M. The value of θ is typically -20 to -50 K. A plot of the inverse molar susceptibility ($1/\chi$) as a function of temperature for a typical ytterbium (III) compound therefore has two linear regions (Figure 1b). The slope ($1/C$) for each region is directly related ⁵ to the magnetic moment as $\mu = 2.828 C^{1/2}$.

Figure 17 Splitting of the ${}^2F_{7/2}$ Ytterbium(III) Term in a Low Symmetry Ligand Field.



Free Ion

For the paramagnetic 1:1 complexes containing ytterbium(III) and a reduced ligand, three electronic structural types are possible. If the complex contains a radical anion which is coupled to the unpaired spin on ytterbium then the temperature dependence of the magnetic susceptibility will be drastically different from that of a simple ytterbium(III) ion; complexes showing this type of behaviour are designated here as type A. This was shown to be the case for the 2,2'-bipyridine complex 9 (Figure 1a). In the case of noninteracting ytterbium and radical anion spins (type B), the individual contributions of these spins to the molar magnetic susceptibility (but not to the magnetic moments) are additive. The expected moment per molecule (μ_T) can be calculated as shown:

$$\chi_T = \chi_1 + \chi_2$$

$$\chi_T T = \chi_1 T + \chi_2 T$$

and
$$\mu^2 = (2.828)^2 (\chi T)$$

so
$$\mu_T^2 = \mu_1^2 + \mu_2^2$$

or
$$\mu_T = (\mu_1^2 + \mu_2^2)^{1/2}$$

for a type B complex then,

low temperature:
$$\mu_T = [(3.8)^2 + (1.73)^2]^{1/2} = 4.2 \text{ B.M.}$$

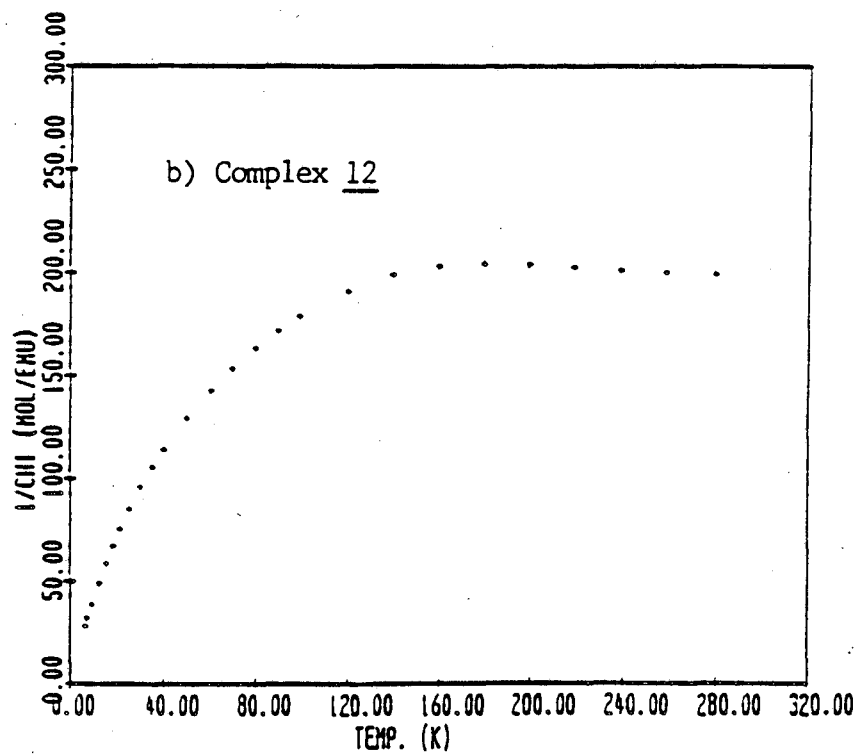
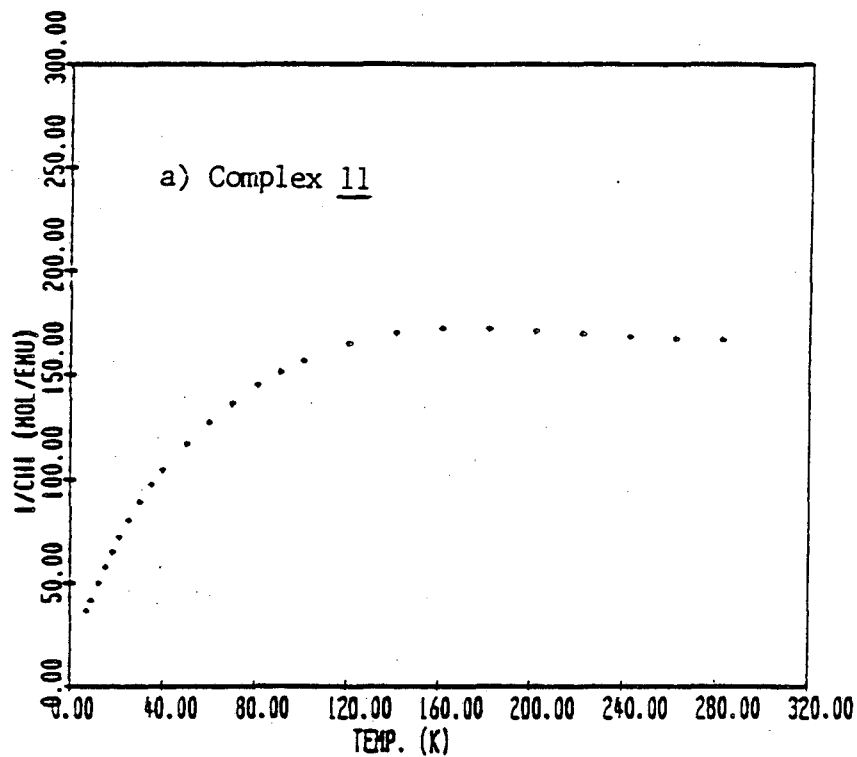
high temperature:
$$\mu_T = [(4.5)^2 + (1.73)^2]^{1/2} = 4.8 \text{ B.M.}$$

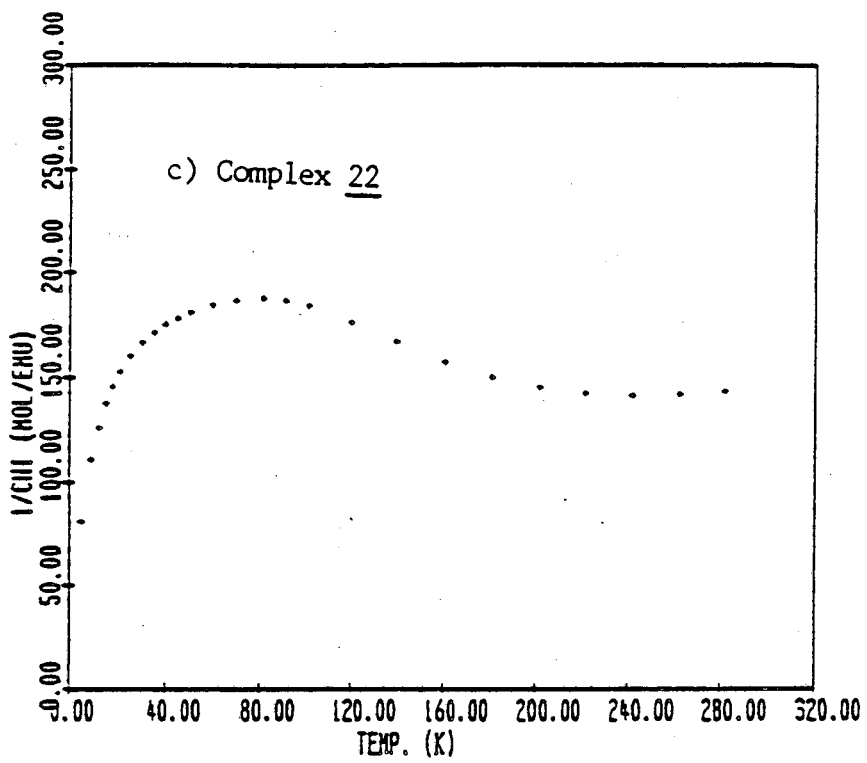
Thus the general shape of a $1/\chi$ versus T plot is the same for a type B complex as a typical ytterbium(III) compound but the slope (and the moment) are different for the low and high temperature regions.

Finally, disproportionation of the radical anions to give a structure composed of $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})]^+ [\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L}^{2-})]^-$ units could also occur. This possibility was suggested earlier to account for the unusual NMR spectra of 5 and 8. Assuming the electrons are paired in the dianion (singlet ground state) then this situation would give rise to the same magnetic susceptibility behaviour as a simple ytterbium(III) compound (type C).

The magnetic susceptibility plots of the mono chelate complexes 11, 12 and 22 are shown in Figure 18. The behaviour of these complexes is similar to that of unsubstituted 2,2'-bipyridine complex 9 (Figure 1a). The unusual temperature dependence of the susceptibility indicates that these are type A complexes. The magnetic moment

Figure 18 Plots of χ_M^{-1} vs. T for Complexes 11, 12 and 22.





decreases rapidly with temperature indicating that the interaction is antiferromagnetic (spin pairing) in nature. Since the Néel temperature is not reached by 5 K, the interaction is very weak; the coupling constant J is on the order of a few wavenumbers. No attempt was made to fit the magnetic susceptibility curves in order to determine a numerical value for J because this would require a more precise expression for the energy of the ytterbium ground state, including excited state contributions, than is currently available.

Changing the energy of the singly occupied molecular orbital (SOMO) by varying the base reduction potential appears to have little effect on the strength of the ytterbium-radical coupling. The reduction potential of the free base varies from -1.4 V for N,N' -bis(*p*-tolyl)-1,4-diazadiene to -2.2 V for 4,4'-dimethyl-2,2'-bipyridine (Table 7). Thus while it may be necessary for the orbitals containing the unpaired spins to be of comparable energy, the nearly identical coupling in these complexes demonstrates that this is not the only factor involved. Boncella ² concluded that the absence of any coupling between the trinuclear cobalt radical and ytterbium(III) in $[(C_5Me_5)_2Yb(III)][(\mu_3-OC)_4Co_3(C_5R_5)_2]$ was due to an energy mismatch between the metal based radical orbitals. It should also be pointed out that intimate contact between the radical spin and the ytterbium(III) ion may also be required.

Table 5: Magnetic Moments of Some $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_x[\text{L}]_y$ Complexes

	<u>Base</u>	μ (θ) ^(a)	
		<u>5 - 40 K</u>	<u>90 - 280 K</u>
<u>3</u>	Pyridazine	3.37 (-6)	4.49 (-57)
<u>5</u>	Phthalazine	3.76 (-2)	4.79 (-34)
<u>8</u>	1,8-Naphthyridine	3.72 (-2)	4.29 (-26)
<u>10</u>	4,4'-Bipyridine	2.91 (-7)	4.64 (-89)
<u>13</u>	2,2'-Bipyrimidine ^(b)		5.97 (-15)
<u>15</u>	Phenazine	5.55 (-3)	6.12 (-25)
<u>17</u>	Azobenzene (1:1)		
<u>18</u>	Azobenzene (2:1)		5.95 (-25)
<u>20</u>	2,2'-Azopyridine	5.40 (-4)	6.18 (-32)
<u>21</u>	2,3-Di-(2'-pyridino)quinoxaline		5.75 (-16)

(a) Magnetic moments in B.M. per molecule (θ in K) at 5 kGauss; data fit to the Curie - Weiss law $C = \chi(T-\theta)$ for the temperature ranges indicated. (b) Reference 2.

Table 6: Néel Temperatures for $[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2[\text{L}]$ Complexes.

<u>Base</u>	T_N
<u>13</u> 2,2'-Bipyrimidine ^(a)	12 K
<u>18</u> Azobenzene (2:1)	15
<u>21</u> 2,3-Di-(2'-pyridino)quinoxaline	18

(a) Reference 2.

The remaining 1:1 complexes, 3, 5, 8, and 10 show magnetic susceptibility behaviour more typical of simple ytterbium(III) compounds. The magnetic moments in the low (5 - 30 K) and high (90 - 280 K) temperature regions are given in Table 5. The results suggest that only ytterbium(III) is contributing to the observed moments. In the low temperature regime all four complexes show moments significantly lower than the 4.2 B.M. expected for a type B complex. In the high temperature region the moment of phthalazine complex 5 is closer to that expected for a type B complex, however the remaining three are all reasonable for type C compounds. The rather small difference in moment (0.3 B.M.) between type B and C complexes makes it impossible to completely rule out a type B radical anion complex. Nevertheless, this result does lend some support to NMR data suggesting disproportionation for the soluble phthalazine and 1,8-naphthyridine complexes and it places the less soluble pyridazine and 4,4'-bipyridine complexes in the same class.

Magnetic susceptibility is more useful in distinguishing between one and two electron reductions for 2:1 complexes because a larger difference in magnetic moment is involved. Transfer of a single electron produces a mixed valence-radical anion complex (Figure 4a) with an expected moment of 4.2 B.M. at low temperatures and 4.8 B.M. at high temperatures assuming noninteracting spins (type B). A two electron reduction produces a ytterbium(III)-dianion species (Figure 4b) with an expected moment of 5.4 B.M. at low temperatures and 6.3 B.M. at high temperature assuming the dianion has a singlet ground state (type D). Interacting spins in a ytterbium(III)-dianion complex are also possible (type E).

Figure 19 Plots of χ_M^{-1} vs. T for Complexes 15 and 20.

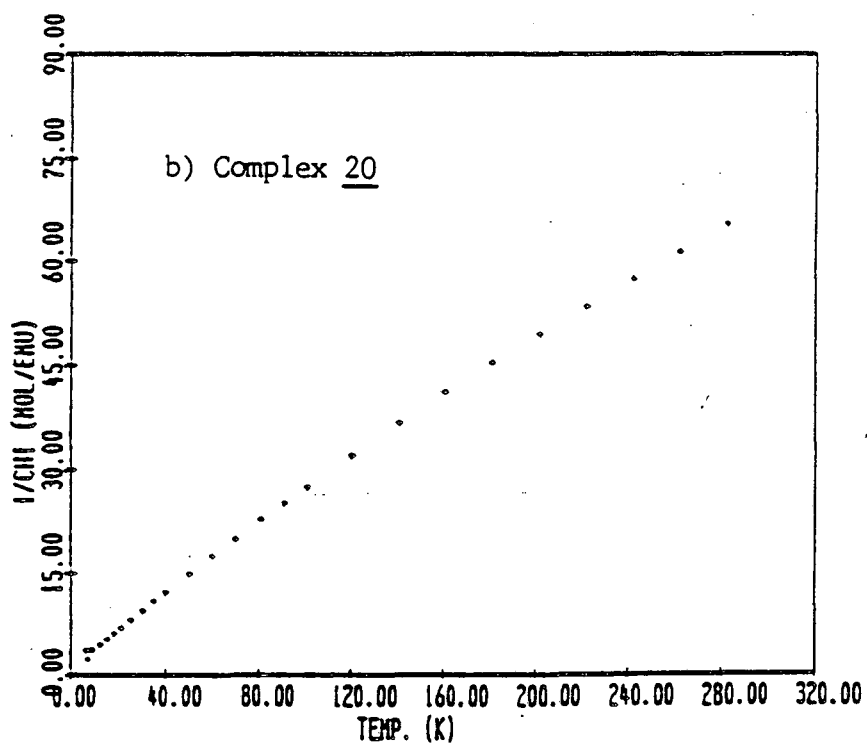
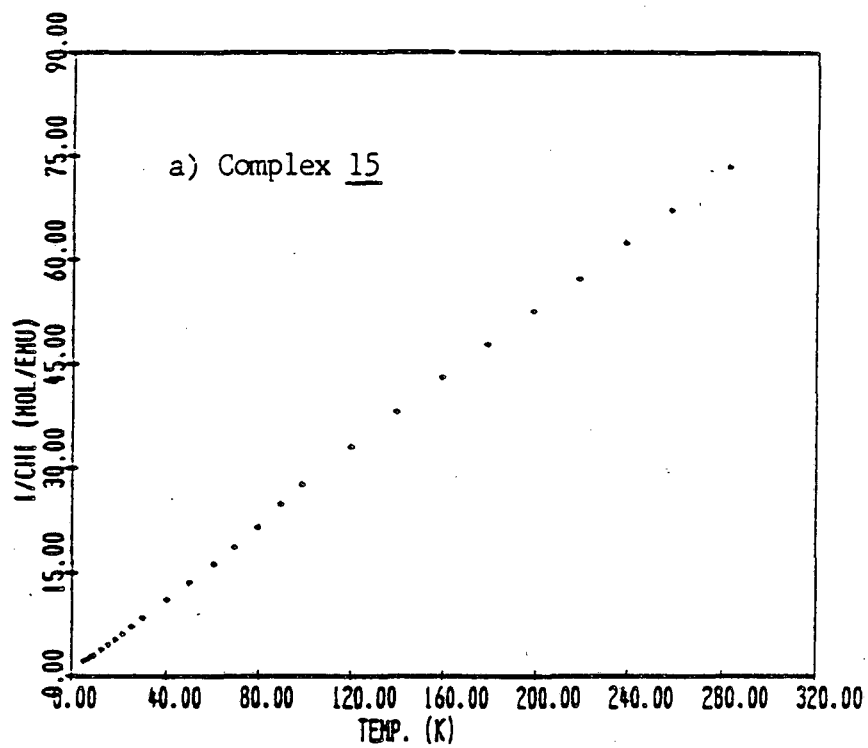
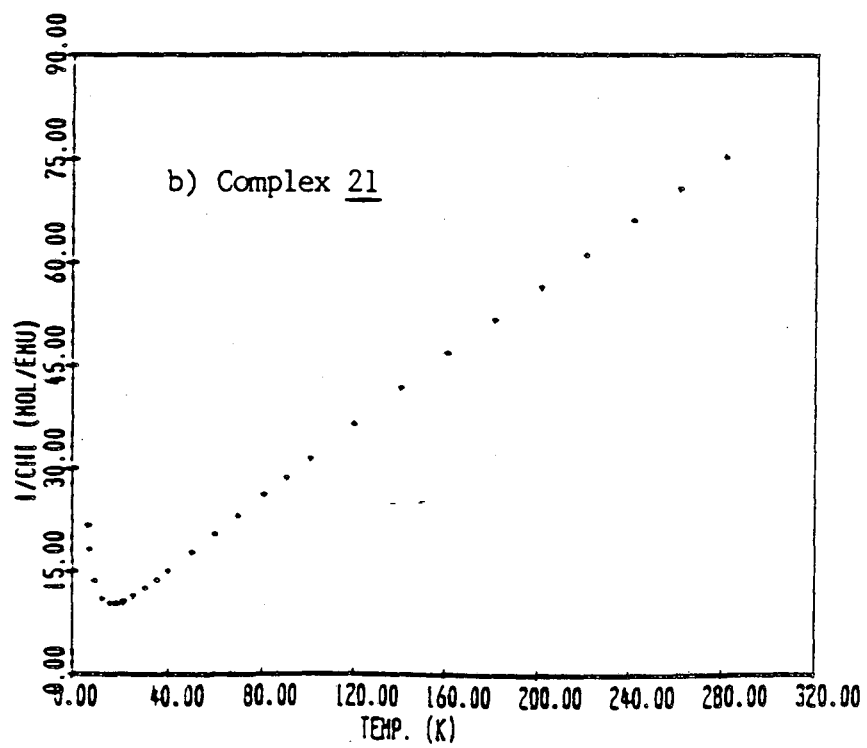
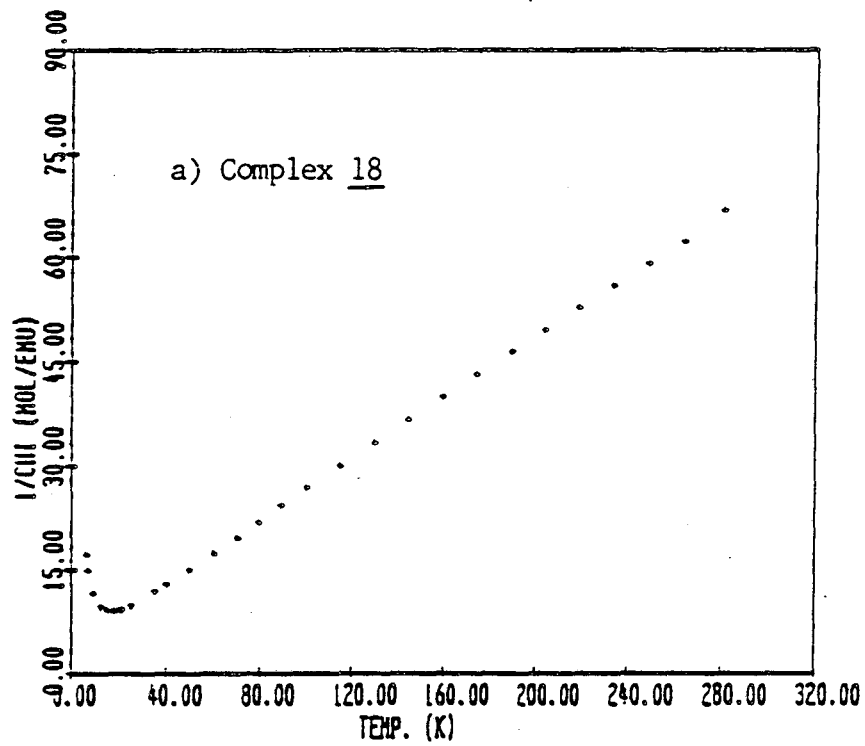


Table 5 and Figure 19 show conclusively that phenazine and 2,2'-azopyridine form type D complexes (15 and 20). This is not surprising since the second reduction potential of the free ligands (Table 7; -1.8 V for phenazine and -1.6 V for 2,2'-azopyridine) are considerably less negative than the first reduction potential of pyrazine (-2.1 V) which is also easily reduced by $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$. The 2:1 complexes of 2,2'-bipyrimidine (13), azobenzene (18) and DPQX (21) also exhibit high temperature moments around 6.0 B.M. and should therefore be classified as ytterbium(III)-dianion complexes. Boncella ² assigned 13 as a mixed valence-radical anion complex (type A). This conclusion was based largely on an incorrect calculation of the expected moment and the observation of disorder in the X-ray crystal structure thought to result from divalent and trivalent ytterbium ions occupying the same crystallographic sites in different unit cells. Since no other supporting evidence such as low temperature ESR or visible spectroscopy was obtained, this conclusion would appear to be incorrect.

The low temperature behaviour of 13, 18 and 21 differs from that of other 2:1 complexes. In these compounds, the molar susceptibility reaches a maximum then declines with decreasing temperature (Figure 20). This is characteristic of antiferromagnetically coupled spins making these type E complexes. The interactions are weak as demonstrated by the low Néel temperatures (Table 6).

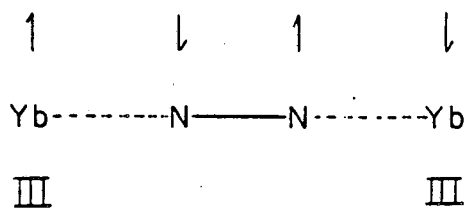
The mechanism of spin pairing cannot be determined from the magnetic susceptibility data. Two possible mechanisms are shown in Figure 21. The first involves pairing of the ytterbium spins via the bridging organic dianion in a superexchange mechanism (Figure 21a). The

Figure 20 Plots of χ_M^{-1} vs. T for Complexes 18 and 21.

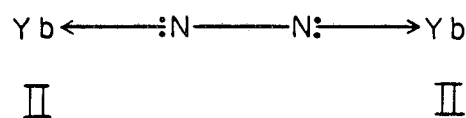


second involves a reversible electron transfer process where the ground state consists of divalent ytterbium ions coordinated to a neutral ligand (Figure 21b). It should be possible to distinguish between these alternatives by examining the f-f transitions in the visible spectrum at liquid helium temperature. No attempt has been made to carry out this experiment. Without some knowledge of the spin pairing mechanism it is not possible to explain the difference in Néel temperature between these complexes or the absence of this effect in the phenazine and 2,2'-azopyridine complexes. Electron delocalization within the ligand, coordination geometry and ligand reduction potential may all play a role. The classification of complexes by electronic structural type is summarized in Table 8.

Figure 21 Spin Pairing Mechanisms for 2:1 Dianion Complexes.



(a)



(b)

Table 7: Reduction Potentials of Nitrogenous Bases^(a)

<u>Base</u>	$-\xi_{1/2}^1$	$-\xi_{1/2}^2$	<u>Reference</u>
Pyridine	2.6 V		16 17 19 20
Pyrazine	2.1		16 17 19 20
Pyridazine	2.2		16 17 19 20
Quinoline	2.1		17 19 20
Phthalazine	2.0		17 19 20
Quinoxaline	1.8	2.2	17 19 20
1,5-Naphthyridine	1.8		20
2,2'-Bipyridine	2.1		10b 20
4,4'-Bipyridine	1.9		10b 20
4,4'-Dimethyl-2,2'-bipyridine	2.2		24
4,4'-Dicarboxylate-2,2'-bipyridine diethyl diester	1.6	2.0	22
2,2'-Bipyrimidine	1.8		23
7,8-Benzoquinoline	2.2	2.7	19 20
Phenazine	1.2	1.8	17 19 20
1,10-Phenanthroline-5,6-dione	0.4	1.3	21
Azobenzene	1.4	2.0	18 20 26
Benzylideneaniline	1.9	2.4	20
2,2'-Azopyridine	1.0	1.6	20 26
N,N'-Bis(p-tolyl)-1,4-diazadiene	1.4		25

(a) Relative to the saturated calomel electrode (S.C.E.) in dimethyl formamide or acetonitrile.

Table 8: Classification of Complexes by Electronic Structural Type

Type A

2,2'-Bipyridine

4,4'-Dimethyl-2,2'-bipyridine

4,4'-Dicarboxylate-2,2'-bipyridine diethyl diester

N,N'-Bis(p-tolyl)-1,4-diazadiene

Type C

Pyrazine

Pyridazine

Phthalazine

1,8-Naphthyridine

4,4'-Bipyridine

Azobenzene (1:1)

Type D

Phenazine

2,2'-Azopyridine

Type E

2,2'-Bipyrimidine

Azobenzene (2:1)

2,3-Di-(2'-pyridino)quinoxaline

Ligand Reduction Potentials

The reduction potentials of all ligands used in this study are tabulated in Table 7. The reduction potential of DPQX has not been measured but is assumed to be less negative than that of quinoxaline (-1.8 V) because of greater radical anion electron delocalization. The reduction potential of 1,8-naphthyridine is also unknown but is probably similar to 1,5-naphthyridine (-1.8 V). With the exception of benzylideneaniline, it appears that $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ is capable of reducing coordinated nitrogenous bases with free ligand reduction potentials as high as ca. -2.1 V versus S.C.E. Since the oxidation potential of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{CH}_3\text{CN})_2$ has been measured as +1.3 V in acetonitrile ²⁷, coordination must greatly decrease (ca. 0.8 V) the reduction potential of the base. This is expected because reduction increases the base strength of the reduced ligand ¹⁰, dramatically increasing its affinity for the electropositive ytterbium center. Coordination therefore stabilizes the reduced species more than the neutral ligand which should make reduction easier. This effect is well known in transition metal chemistry; for example, the ligand reduction potential is -0.83 V in $[\text{Ir}(\text{bipy})_3]^+$ compared with -2.1 V for free 2,2'-bipyridine ²⁸.

It is noteworthy that for ligands with reduction potentials in the -2.0 to -2.2 V range, all those with two nitrogen centers (pyrazine, pyridazine, phthalazine, 2,2'-bipyridine and 4,4'-dimethyl-2,2'-bipyridine) are reduced while those with only one nitrogen atom (benzylideneaniline, quinoline and 7,8-benzoquinoline) are not. Stabilization of the complexed radical anion is greater when the negative charge can be delocalized over more than one nitrogen center

because this increases the strength of more than one ytterbium - nitrogen interaction. As a result, the reduction potential is not lowered as much by complex formation for ligands with only one nitrogen as it is for those with two or more. A comparison of the reduction potential of benzylideneaniline (-1.9 V) with the oxidation potential of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{CH}_3\text{CN})_2$ (+1.3 V) indicates that bases containing only one nitrogen are stabilized by less than 0.6 V relative to the free ligand.

Quinoline and 7,8-benzoquinoline form diamagnetic complexes (4 and 14) in which one aromatic carbon atom is forced into close proximity with the metal. Since thermal reactions of uranium (III) are known where the metal attacks a nearby carbon-hydrogen or nitrogen-hydrogen bond with liberation of hydrogen gas and oxidation to a uranium (IV) compound ²⁹, the thermal reactivity of 4 and 14 was investigated. Despite the similarity in oxidation potential ³⁰ between uranium (III) (+1.5 V for $(\text{C}_5\text{H}_4\text{Me})_3\text{U}$) and ytterbium (II), no paramagnetic products are formed on heating. Sublimation of the intact complexes occurs at 250 to 300 °C in 75 to 80 % yield.

Summary

Bis(pentamethylcyclopentadienyl)ytterbium diethyl etherate acts as a reducing agent towards nitrogenous bases with reduction potentials of ca. -2.0 V or less forming paramagnetic coordination complexes. The stoichiometry and electronic structure of the complex formed depends on the ability of the ligand to fill the coordination sphere of the ytterbium ion. Mono chelate complexes of 2,2'-bipyridine and 1,4-diazadiene derivatives form soluble, monomeric, radical anion complexes. In other 1:1 compounds, disproportionation of the radical

anion occurs to give coordinated dianions and neutral ligands in the same compound. When the ligand is incapable of filling the coordination sphere of the ytterbium ion, secondary interactions with other available nitrogen atoms will result. If the ligand itself contains another nitrogen atom which cannot coordinate to the same ytterbium, yet is far enough removed from the coordinated nitrogen to allow for a bridging interaction then insoluble polymers are formed. If the nitrogen atoms are too close together to allow this type of interaction then a second base may fill the coordinative vacancy giving a 1:2 complex.

Complexes of 2:1 stoichiometry are formed when the ligand is capable of chelating two $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units without steric crowding or when the ligand bulk is sufficient to prevent secondary interactions between the $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units and other nitrogen centers. All of the 2:1 complexes examined contain trivalent ytterbium and organic dianions. This last result is in accord with the reducing ability $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ compared with the second reduction potentials of these ligands.

Experimental

Manipulation of air sensitive compounds was carried out using standard Schlenk techniques. All solvents were dried and deoxygenated by distillation from sodium benzophenone ketyl under nitrogen prior to use. The preparation of bis(pentamethylcyclopentadienyl)ytterbium (II) diethyl etherate has been reported elsewhere ³¹. Unless otherwise stated, all nitrogenous bases used in this study were commercial samples used as received.

Infrared spectra were recorded on a Nicolet FT - IR. Nuclear magnetic resonance spectra were recorded on a JEOL FX90-Q 90 MHz spectrometer. Mass spectra and elemental analyses were performed by the University of California, Berkeley mass spectral and microanalytical laboratories. Uncorrected melting points were obtained on sealed samples using a Thomas - Hoover capillary melting point apparatus.

Magnetic susceptibility measurements were made using a S.H.E. model 905 superconducting magnetometer (SQUID). Sample containers made from two tightly fitting KEL-F halves were used for air sensitive samples; no significant decomposition was noted during the course of measurement, ca. 1 day. In a typical experiment 50 - 75 mg of the compound to be studied was ground and weighed into a KEL-F container in an argon dry box. The two halves of the container were sealed with the aid of a small amount of silicone grease. After removal from the dry box, the container was wired closed with nylon monofilament thread and suspended in the sample chamber by a cotton thread. The sample chamber was then alternately evacuated to 30 microns Hg and refilled with high purity helium three times. Samples were measured automatically at two

fields and at temperatures between 5 and 280 K. Measurements were taken at 5 and 40 kG using the following temperature intervals: 3 K from 6 - 21 K; 5 K from 25 - 50 K; 10 K from 50 - 100 K; 20 K from 100 - 280 K. Sample data was corrected for container (including grease) and sample diamagnetism. Samples exhibiting Curie - Weiss behaviour were fit to the Curie - Weiss law $1/\chi = (T - \theta)/C$ using a linear least squares program written by Dr. E. Gamp. Effective magnetic moments were then calculated as $\mu = 2.828 C^{1/2}$.

Yb(C₅Me₅)₂(Pyrazine) · (C₇H₈); 2

A solution of pyrazine (0.06 g, 0.8 mmol) in 20 mL toluene was added to a solution of Yb(C₅Me₅)₂(OEt₂) (0.84 g, 1.6 mmol) in 40 mL of toluene by canula. The solution immediately turned deep brown with slow (4 h) precipitation of a muddy brown solid. The solid was allowed to settle overnight then the brown supernatant was filtered, the filtrate was concentrated and cooled at -10 °C. A second crop of the muddy precipitate was isolated from the mother liquors by canula filtration. The combined precipitate was washed with hexane and dried under reduced pressure leaving a free flowing, pyrophoric brown powder. Hydrolysis of a small sample with D₂O / CD₂Cl₂ disclosed the presence of one molar equivalent of toluene of solvation and confirmed the 1:1 stoichiometry by proton NMR. Yield: 0.55 g (56 %). m.p. > 330 °C. IR (Nujol, CsI): 3180 (br w), 2725 (m), 1005 (s), 970 (w), 755 (m), 720 (vs), 690 (w), 460 (w), 400 (br s), 290 (vs) cm⁻¹. Anal. Calcd for C₂₄H₃₄N₂Yb: C, 60.5; H, 6.88; N, 4.55 %. Found: C, 59.7; H, 6.82; N, 4.22 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Pyridazine})_2$; 3

Neat pyridazine (0.20 mL, 2.2 mmol) was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.51 g, 0.99 mmol) in 100 mL of ether by syringe. The resulting deep red solution was stirred 2 h and the solution cooled directly to $-10\text{ }^\circ\text{C}$ overnight. Dark red crystals were isolated from the mother liquors by filtration but these immediately collapsed to a rust coloured powder on exposure to vacuum. The powdery product was difficult to redissolve in toluene or ether. Yield: 0.45 g (75 %). m.p. 176 - 178 $^\circ\text{C}$. IR (Nujol, CsI): 3100 (vw), 3075 (vw), 3045 (vw), 3010 (w), 2720 (w), 1600 (s), 1571 (m), 1565 (w), 1550 (s), 1410 (m-s), 1315 (m-s), 1294 (s), 1278 (w), 1230 (m), 1215 (vs), 1195 (vw), 1155 (w), 1111 (vs), 1065 (s), 1020 (m-s), 990 (vw), 976 (s), 965 (vw), 916 (vs), 902 (vs), 825 (w-m), 800 (w), 760 (vs), 740 (vs), 708 (vs), 670 (m-s), 660 (m), 632 (m), 628 (w-m), 620 (vw), 579 (vw), 472 (s), 388 (s), 309 (vs) cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{N}_4\text{Yb}$: C, 55.7; H, 6.34; N, 8.93 %. Found: C, 55.8; H, 6.72; N, 8.84 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Quinoline})$; 4

Quinoline was predried by storage over KOH for 4 days, followed by distillation from BaO. Purified quinoline was stored over 3 Å molecular sieves in the dark prior to use.

Purified quinoline (0.10 mL, 0.84 mmol) was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.41 g, 0.79 mmol) in 20 mL of ether by syringe. The deep red solution was stirred 1 h, filtered and concentrated to 5 mL. Cooling at $-10\text{ }^\circ\text{C}$ overnight gave an excellent yield of shiny red prisms. Yield: 0.40 g (88 %). m.p. 256 - 259 $^\circ\text{C}$. IR (Nujol, CsI): 3046 (vw), 3036 (vw), 2723 (w), 1618 (w), 1589 (w-m), 1577 (w-m), 1530 (vw),

1504 (s), 1398 (sh w), 1308 (m), 1218 (vw), 1153 (vw), 1139 (vw), 1127 (w-m), 1098 (vw), 1018 (w), 988 (vw), 949 (w), 854 (vw), 812 (vs), 805 (vs), 783 (vs), 767 (vw), 735 (m), 623 (w-m), 587 (vw), 529 (vw), 520 (vw), 485 (m), 470 (vw), 400 (vw), 375 (br m), 303 (vw), 277 (br vs) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32 °C): Diamagnetic, δ 8.61 ppm (1H, m), 7.79 (1H, m), 7.35 (4H, m), 6.72 (1H, m), 1.98 (30H, s). Anal. Calcd for $\text{C}_{29}\text{H}_{37}\text{NYb}$: C, 60.8; H, 6.51; N, 2.44 %. Found: C, 61.0; H, 6.44; N, 2.43 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Phthalazine})$; 5

A solution of phthalazine (0.17 g, 1.3 mmol) in 40 mL of ether was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.67 g, 1.3 mmol) in 20 mL of ether with rapid stirring. The deep red solution was stirred 30 min., filtered and the filtrate was concentrated to 20 mL. Cooling at -10 °C produced very fine red crystals. Yield: 0.62 g (84 %). m.p. > 300 °C. IR (Nujol, CsI): 2720 (vw), 1590 (w), 1550 (vw), 1360 (w), 1328 (m), 1300 (vw), 1280 (m), 1211 (w), 1170 (br w), 1123 (w), 1070 (vw), 1020 (w), 970 (br w), 891 (s), 718 (vs), 680 (vw), 535 (vw), 470 (vw), 385 (br w), 351 (w), 311 (vs) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32 °C): δ 31.2 (15H, $\nu_{1/2} = 51$ Hz), 13.3 (15H, $\nu_{1/2} = 51$ Hz), -3.7 (1H, $\nu_{1/2} = 15$ Hz), -9.1 (1H, $\nu_{1/2} = 17$ Hz), -9.5 (1H, $\nu_{1/2} = 14$ Hz), -15.0 (1H, $\nu_{1/2} = 27$ Hz) The other ligand resonances were not observed. Anal. Calcd for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{Yb}$: C, 58.6; H, 6.33; N, 4.88 %. Found: C, 58.8; H, 6.41; N, 4.90 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Quinoxaline})$; 6

Quinoxaline (Aldrich) was sublimed twice and then stored in the dark under nitrogen prior to use. A solution of purified quinoxaline (0.10 g, 0.77 mmol) in 20 mL of ether was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.79 g, 1.5 mmol) in 30 mL of ether with stirring. Immediate precipitation of a sparkling brown solid occurred. After settling, the green supernatant was filtered and discarded. The residue was washed twice with pentane and dried under reduced pressure. Yield: 0.35 g (80 %). m.p. > 330 °C. IR (Nujol, CsI): 2720 (w), 1587 (w), 1531 (w), 1493 (vw), 1438 (sh vw), 1422 (vw), 1367 (sh vw), 1350 (vw), 1322 (m), 1272 (w), 1210 (m), 1148 (s), 1126 (s), 1076 (vw), 1060 (vw), 1021 (m), 961 (vs), 936 (w), 819 (vw), 779 (m-s), 771 (sh w), 744 (m-s), 722 (sh vw), 612 (vw), 598 (w), 542 (w-m), 411 (m), 375 (br m), 327 (w), 294 (br s) cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{Yb}$: C, 58.6; H, 6.33; N, 4.88 %. Found: C, 58.7; H, 6.57; N, 4.59 %. The 1:1 stoichiometry of this complex was confirmed by hydrolysis.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(1,5\text{-Naphthyridine})$; 7

A solution of 1,5-naphthyridine (0.07 g, 0.6 mmol) in 10 mL of ether was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.61 g, 1.2 mmol) in 40 mL of ether. Immediate precipitation of a dark brown solid occurred. Stirring was continued 2 h, then the precipitate was allowed to settle overnight. The green supernatant was filtered and discarded. The muddy brown residue was washed twice with hexane then dried under reduced pressure. The resulting brown free-flowing powder was insoluble in aromatic and aliphatic hydrocarbons and ether. Attempts to recrystallize this material from tetrahydrofuran gave glassy brown

solids containing solvent. Yield: 0.31 g (92 %). m.p. > 330 °C. IR (Nujol, CsI): 2720 (w), 1619 (s), 1569 (s), 1554 (s), 1489 (m), 1426 (m), 1349 (m), 1304 (vs), 1256 (m), 1224 (w), 1206 (m-s), 1156 (w), 1129 (m), 1100 (vw), 1081 (s), 1019 (m), 966 (m), 945 (w), 906 (vw), 859 (vw), 835 (vw), 817 (w), 796 (s), 776 (s), 758 (m), 743 (s), 704 (vw), 665 (vw), 651 (m), 631 (m), 600 (w), 565 (w), 492 (vw), 430 (w), 380 (br m), 303 (br vs), 250 (vw) cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{Yb}$: C, 58.6; H, 6.33; N, 4.88 %. Found: C, 59.5; H, 6.43; N, 4.34 %.

Yb(C₅Me₅)₂(1,8-Naphthyridine); 8

1,8-Naphthyridine was prepared by the oxidative condensation of 2-aminopyridine and glycerol with nitrobenzenesulphonic acid according to a literature procedure ³².

A solution of 1,8-naphthyridine (0.12 g, 0.93 mmol) in 20 mL of toluene was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.48 g, 0.93 mmol) in 30 mL of toluene with rapid stirring. The deep red solution was stirred 2 h, filtered, and the filtrate was concentrated to 35 mL and cooled at -10 °C for several days. Fine red crystals were isolated from the mother liquors but these rapidly collapsed to a rust coloured powder on exposure to vacuum. Yield: 0.33 g (62 %). m.p. dec. 220 °C. IR (Nujol, CsI): 3062 (vw), 3030 (vw), 2720 (w), 1610 (vs), 1582 (vs), 1549 (m), 1520 (m), 1420 (vs), 1388 (m), 1350 (w), 1338 (s), 1300 (s), 1265 (m), 1253 (m), 1238 (m), 1210 (m), 1195 (w-m), 1179 (m), 1120 (m), 1100 (vs), 1050 (w), 1020 (w), 962 (w), 942 (w), 931 (s), 920 (w), 830 (w), 800 (w), 759 (vs), 722 (vs), 618 (w), 595 (w), 550 (w-m), 530 (vw), 520 (w), 498 (vw), 421 (w-m), 390 (m), 310 (s), 250 (s) cm^{-1} . ¹H NMR (C_7D_8 , 32 °C): δ 7.9 ppm (30H, $\nu_{1/2}$ = 200 Hz), -1.1 (1H, $\nu_{1/2}$ = 16

Hz), -7.9 (1H, $\nu_{1/2}$ = 15 Hz), -8.6 (1H, $\nu_{1/2}$ = 17 Hz), -9.3 (1H, $\nu_{1/2}$ = 19 Hz), -23.8 (1H, $\nu_{1/2}$ = 26 Hz) The other ligand resonances were not observed. Anal. Calcd for $C_{28}H_{36}N_2Yb$: C, 58.6; H, 6.33; N, 4.88 %. Found: C, 58.5; H, 6.48; N, 4.87 %.

Hydrolysis of a small sample of this compound with D_2O / C_6D_6 showed the presence of 1,8-naphthyridine as well as a very large number of other resonances due to unidentifiable species. The presence of resonances between 5 and 8 ppm suggested that the hydrolysate contained hydrogenated 1,8-naphthyridine isomers.

$Yb(C_5Me_5)_2(4,4'$ -Bipyridine); 10

A solution of $Yb(C_5Me_5)_2(OEt_2)$ (0.45 g, 0.87 mmol) in 50 mL of ether was added to a solution of 4,4'-bipyridine (0.07 g, 0.4 mmol) in 10 mL of ether with stirring. Immediate precipitation of a purple solid occurred on mixing. After stirring for 1 h, the suspension was allowed to settle and the green supernatant was filtered and discarded. The precipitate was washed twice with hexane and vacuum dried yielding a free-flowing purple powder. The product was completely insoluble in toluene, hexane, ether, tetrahydrofuran and sparingly soluble in acetonitrile, though it could not be crystallized from the latter solvent. Yield: 0.25 g (93 %). m.p. > 330 °C. IR (Nujol, CsI): 3180 (vw), 3070 (w), 2725 (w-m), 2550 (vw), 1720 (w), 1595 (vs), 1550 (s), 1495 (s), 1340 (m), 1279 (w), 1260 (m), 1215 (m), 1195 (s), 1160 (w), 1090 (m), 1035 (w), 1015 (s), 960 (vs), 795 (s), 770 (m), 750 (w), 718 (m), 695 (vw), 680 (vw), 650 (br w), 611 (vs), 590 (w), 570 (vw), 370 (br s), 290 (vs) cm^{-1} . Anal. Calcd for $C_{30}H_{38}N_2Yb$: C, 60.1; H, 6.39; N, 4.67 %. Found: C, 58.0; H, 6.36; N, 5.22 %.

Hydrolysis of a small sample of this compound with D_2O / C_6D_6 indicated the presence of 2.2 pentamethylcyclopentadienyl rings per 4,4'-bipyridine by proton NMR of the benzene phase, thus confirming the 1:1 stoichiometry suggested by elemental analysis.

$Yb(C_5Me_5)_2(4,4'$ -Dimethyl-2,2'-bipyridine); 11

$Yb(C_5Me_5)_2(OEt_2)$ (0.80 g, 1.6 mmol) and 4,4'-dimethyl-2,2'-bipyridine (0.28 g, 1.6 mmol) were weighed into a Schlenk flask and dissolved in 40 mL of toluene with stirring. The brown solution was stirred overnight, filtered and the filtrate was concentrated to 20 mL. Cooling at $-10\text{ }^\circ\text{C}$ overnight produced large brown crystals. Yield: 0.67 g (69 %). m.p. $> 300\text{ }^\circ\text{C}$. IR (Nujol, CsI): 2720 (vw), 1595 (s), 1519 (br m), 1399 (w), 1365 (sh w), 1294 (s), 1240 (s), 1177 (s), 1018 (w), 944 (br vs), 900 (m), 872 (w), 825 (m), 799 (w), 737 (vw), 727 (vw), 591 (vw), 536 (m), 509 (w), 308 (s), 271 (br s) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , $32\text{ }^\circ\text{C}$): δ 143.0 ppm (2H, $\nu_{1/2} = 84\text{ Hz}$), 3.8 (30H, $\nu_{1/2} = 15\text{ Hz}$), -6.1 (6H, $\nu_{1/2} = 30\text{ Hz}$), -10.5 (2H, $\nu_{1/2} = 14\text{ Hz}$) No other resonances were observed.

Anal. Calcd for $C_{32}H_{42}N_2Yb$: C, 61.2; H, 6.74; N, 4.46 %. Found: C, 60.8; H, 6.72; N, 4.42 %.

$Yb(C_5Me_5)_2(4,4'$ -Dicarboxylate-2,2'-bipyridine diethyl diester); 12

4,4'-Dicarboxylate-2,2'-bipyridinediethyl diester was prepared by esterification of the diacid according to the literature ³³. The crude diester was recrystallized twice from boiling ethanol.

$Yb(C_5Me_5)_2(OEt_2)$ (0.63 g, 1.2 mmol) and the diester (0.36 g, 1.2 mmol) were weighed into a Schlenk flask and dissolved in 60 mL of hexane with stirring. The orange - red solution was stirred 1 h,

filtered and the filtrate was concentrated to 10 mL. Cooling at $-78\text{ }^{\circ}\text{C}$ for several days produced deep red crystals which collapsed to a brick red powder on exposure to vacuum. Yield: 0.70 g (79 %). m.p. $> 330\text{ }^{\circ}\text{C}$. IR (Nujol, CsI): 2730 (w), 2626 (w), 2540 (w), 1732 (m), 1708 (vs), 1611 (m), 1534 (vs), 1502 (vs), 1372 (s), 1365 (m), 1284 (s), 1267 (vs), 1202 (vs), 1161 (w), 1134 (sh m), 1116 (s), 1037 (s), 963 (vs), 920 (vw), 862 (br m-s), 800 (br vs), 748 (m-s), 724 (w), 686 (br m), 663 (w), 536 (w), 443 (s), 390 (br s), 311 (s), 294 (w) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , $32\text{ }^{\circ}\text{C}$): δ 206.9 ppm (2H, $\nu_{1/2} = 110\text{ Hz}$), 4.7, 4.5, 4.1 (40H, overlapping resonances), -11.8 (2H, $\nu_{1/2} = 11\text{ Hz}$), -18.5 (2H, $\nu_{1/2} = 94\text{ Hz}$). $59\text{ }^{\circ}\text{C}$: δ 195.9 ppm (2H, $\nu_{1/2} = 100\text{ Hz}$), 5.8 (4H, br q), 4.4 (30H, $\nu_{1/2} = 25\text{ Hz}$), 4.1 (6H, br t, partially obscured), -14.0 (2H, $\nu_{1/2} = 8\text{ Hz}$), -23.4 (2H, $\nu_{1/2} = 102\text{ Hz}$). Anal. Calcd for $\text{C}_{36}\text{H}_{46}\text{N}_2\text{O}_4\text{Yb}$: C, 58.1; H, 6.23; N, 3.76 %. Found: C, 54.7; H, 6.19; N, 3.62 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(7,8\text{-Benzoquinoline})$; 14

A solution of sublimed 7,8-benzoquinoline (0.20 g, 1.1 mmol) in 10 mL of ether was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.58 g, 1.1 mmol) in 40 mL of ether by canula. The deep green - brown solution was stirred 20 minutes, filtered, and the filtrate was concentrated to 15 mL and cooled at $-15\text{ }^{\circ}\text{C}$ for several days. Fine brown crystals were isolated from the mother liquor by filtration. Sublimation at $150\text{ }^{\circ}\text{C} / 10^{-1}\text{ torr}$ afforded large brown-black crystals of higher purity. Yield (after sublimation): 0.42 g (62 %). m.p. $265 - 267\text{ }^{\circ}\text{C}$. IR (Nujol, CsI): 2721 (m), 1650 (m), 1600 (w-m), 1595 (w-m), 1550 (m), 1516 (w), 1404 (s), 1180 (w), 1175 (w), 1151 (m), 1135 (m), 1096 (s), 1065 (w), 831

(vs), 746 (s), 720 (s), 625 (m), 380 (w), 315 (br s), 275 (vs) cm^{-1} . ^1H NMR (C_6D_6 , 32 °C): Diamagnetic, δ 8.67 ppm (1H, d), 7.3 - 7.8 (7H, m), 6.82 (1H, dd), 1.91 (30H, s). Anal. Calcd for $\text{C}_{33}\text{H}_{39}\text{NYb}$: C, 63.7; H, 6.31; N, 2.25 %. Found: C, 63.8; H, 6.28; N, 2.29 %.

$[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2(\text{Phenazine})$; 15

A solution of phenazine (0.07 g, 0.4 mmol) in 20 mL of ether was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.42 g, 0.81 mmol) in 20 mL of ether. The resulting deep red solution was cooled without further agitation at -10 °C overnight. Fine red crystals were isolated from the mother liquors by filtration. Yield: 0.38 g (87 %). m.p. > 330 °C. IR (Nujol, CsI): 3056 (vw), 2727 (w), 2620 (vw), 1860 (vw), 1596 (s), 1555 (w), 1330 (vs), 1306 (w), 1282 (vs), 1233 (sh w), 1213 (s), 1164 (vw), 1128 (m), 1052 (vw), 1023 (w-m), 896 (vs), 800 (vw), 749 (vw), 720 (vs), 685 (vw), 591 (w), 385 (br m), 354 (w), 315 (br vs), 280 (vw) cm^{-1} . ^1H NMR (C_7D_8 , 32 °C): δ 6.4 ppm (4H, $\nu_{1/2} = 16$ Hz), 5.6 (4H, $\nu_{1/2} = 16$ Hz), -1.9 (60H, $\nu_{1/2} = 380$ Hz). Anal. Calcd for $\text{C}_{52}\text{H}_{68}\text{N}_2\text{Yb}$: C, 58.5; H, 6.42; N, 2.62 %. Found: C, 58.2; H, 6.51; N, 2.62 %.

$[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2(1,10\text{-Phenanthroline-5,6-dione})$; 16

A solution of 1,10-phenanthroline-5,6-dione (0.09 g, 0.4 mmol) in 30 mL of toluene was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.47 g, 0.91 mmol) in 20 mL of toluene with stirring. The solution slowly turned brown and deposited a brown crystalline solid. Cooling at -10 °C overnight, followed by filtration gave 0.30 g (64 %) of fine brown crystals. m.p. > 330 °C. IR (Nujol, CsI): 3090 (vw), 2720 (w), 1575 (s), 1430 (sh w), 1325 (w), 1310 (vw), 1272 (vw), 1260 (w), 1114 (w),

1063 (s), 1028 (s), 930 (w), 825 (sh w), 800 (s), 723 (s), 690 (w), 640 (br m), 620 (sh w), 516 (w), 400 (s), 295 (br s) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 $^\circ\text{C}$): δ 22.6 ppm (2H, $\nu_{1/2}$ = 60 Hz), 11.5 (2H, $\nu_{1/2}$ = 30 Hz), 4.4 (30H, $\nu_{1/2}$ = 65 Hz), -2.1 (30H, $\nu_{1/2}$ = 61 Hz), -6.1 (2H, $\nu_{1/2}$ = 43 Hz). Anal. Calcd for $\text{C}_{52}\text{H}_{66}\text{N}_2\text{O}_2\text{Yb}_2$: C, 56.9; H, 6.06; N, 2.55 %. Found: C, 56.0; H, 5.96; N, 2.29 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Azobenzene})$; 17

A solution of azobenzene (0.40 g, 2.2 mmol) in 20 mL of pentane was added to a suspension of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (1.15 g, 2.22 mmol) in 60 mL of pentane with stirring. The deep blue-green solution was stirred 1 h, the solution filtered, and the filtrate was concentrated to 10 mL and cooled at -20°C for several days. Very dark blue-green crystals were isolated from the mother liquors by filtration. Further concentration of the filtrate followed by cooling at -78°C produced a second crop of crystals. Yield: 0.65 g (47 %). m.p. 164 - 167 $^\circ\text{C}$. IR (Nujol, CsI): 3080 (w), 3050 (w), 2730 (w-m), 1905 (vw), 1855 (vw), 1835 (vw), 1765 (vw), 1580 (s), 1560 (m-s), 1341 (m), 1324 (vw), 1300 (w), 1282 (vw), 1227 (m), 1161 (w), 1151 (w), 1091 (s), 1075 (m), 1018 (s), 986 (m-s), 975 (sh w), 884 (w-m), 879 (m), 819 (w), 783 (s), 750 (vs), 711 (s), 680 (vs), 571 (m-s), 525 (m), 516 (w), 489 (w-m), 380 (s), 314 (vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 31 $^\circ\text{C}$): δ 79.1 ppm (4H, $\nu_{1/2}$ = 24 Hz), 14.1 (30H, $\nu_{1/2}$ = 25 Hz), -145.9 (4H, $\nu_{1/2}$ = 230 Hz), -186.6 (2H, $\nu_{1/2}$ = 97 Hz). M.S. (C.I.): m/e = 626 amu (M^+), 491 ($\text{M}^+ - (\text{C}_5\text{Me}_5)$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 183 (PhNNPh^+), 135 (C_5Me_5^+). Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_2\text{Yb}$: C, 61.4; H, 6.44; N, 4.47 %. Found: C, 61.6; H, 6.48; N, 4.53 %.

[Yb(C₅Me₅)₂]₂(Azobenzene); 18

A solution of azobenzene (0.20 g, 1.2 mmol) in 30 mL of pentane was added to a suspension of Yb(C₅Me₅)₂(OEt₂) (1.2 g, 2.3 mmol) in 50 mL of pentane with rapid stirring. The initially blue-green solution changed colour to dark purple over the course of 1 h. The purple-black solution was stirred 4 h, filtered and the filtrate was concentrated to 10 mL. Cooling at -78 °C produced small dark purple prisms. Yield: 0.25 g (20 %). m.p. 195 - 197 °C. IR (Nujol, CsI): 2725 (w), 1582 (s), 1530 (m), 1330 (m), 1296 (m-s), 1272 (w), 1176 (br m), 1096 (w), 1020 (s), 969 (m), 948 (vw), 929 (vw), 850 (w), 820 (w), 797 (w), 750 (sh w), 730 (vs), 708 (sh w), 620 (m), 590 (vw), 580 (m), 531 (w), 511 (sh vw), 500 (w), 423 (w), 380 (br m), 299 (br s), 275 (sh w) cm⁻¹. ¹H NMR (C₆D₆, 32 °C): δ 18.1 ppm (? 4H, $\nu_{1/2}$ = 12 Hz), 11.4 (? 4H, $\nu_{1/2}$ = 20 Hz), -5.8 (60H, $\nu_{1/2}$ = 300 Hz), -15.7 (? 2H, $\nu_{1/2}$ = 16 Hz). Anal. Calcd for C₅₂H₇₀N₂Yb₂: C, 58.4; H, 6.60; N, 2.62 %. Found: C, 57.9; H, 6.64; N, 2.55 %.

Yb(C₅Me₅)₂(Benzylideneaniline); 19

Benzylideneaniline was prepared by the Schiff base condensation of aniline with benzaldehyde following a literature procedure ³⁴. A solution of benzylideneaniline (0.32 g, 1.8 mmol) in 40 mL of ether was added to a solution of Yb(C₅Me₅)₂(OEt₂) (0.90 g, 1.7 mmol) in 40 mL of ether. The solution slowly changed colour to deep green-brown over a period of 2 h. After stirring overnight, the solution was concentrated to 20 mL and cooled at -10 °C for several days. Brown-black crystals were isolated from the mother liquor by filtration. Yield: 0.85 g (78 %) m.p. 74 - 77 °C. IR (Nujol, CsI): 3080 (vw), 3030 (vw), 2725 (w),

1605 (w), 1590 (w), 1580 (vw), 1568 (m), 1558 (sh w), 1485 (sh w), 1300 (br w), 1260 (vw), 1190 (m), 1170 (vw), 1159 (w), 1080 (w), 1020 (w), 1000 (vw), 968 (w), 920 (vw), 880 (w-m), 760 (vs), 748 (s), 719 (w-m), 694 (vs), 650 (vw), 619 (vw), 586 (vw), 542 (w), 530 (vw), 520 (vw), 452 (br w), 360 (br w), 265 (br vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 °C): Diamagnetic. δ 8.06 ppm (2H, d), 7.20 (2H, q), 7.0 - 7.2 (7H, m), 1.93 (30H, s). M.S.(C.I.) m/e = 625 amu (M^+), 490 ($\text{M}^+ - (\text{C}_5\text{Me}_5)$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 182 ($\text{PhNCH}(\text{Ph})^+$). Anal. Calcd for $\text{C}_{33}\text{H}_{41}\text{NYb}$: C, 63.4; H, 6.62; N, 2.24 %. Found: C, 63.1; H, 6.59; N, 2.19 %.

[Yb(C₅Me₅)₂]₂(2,2'-Azopyridine); 20

2,2'-Azopyridine was prepared by oxidative coupling of 2-aminopyridine with NaOCl according to a literature procedure ³⁵. The crude product was purified by chromatography on silica gel using hexane followed by diethyl ether as eluant. The red ether fraction containing 2,2'-azopyridine was evaporated to dryness and the red-orange residue recrystallized from hot hexane.

A solution of 2,2'-azopyridine (0.18 g, 0.98 mmol) in 20 mL of toluene was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (1.03 g, 1.99 mmol) in 40 mL of toluene with stirring. The red-brown solution was stirred 1 h, filtered, and the filtrate was concentrated to 40 mL and cooled at -10 °C overnight. Large dark brown crystals were isolated from the mother liquor by filtration. Yield: 0.80 g (75 %). m.p. > 330 °C. IR (Nujol, CsI): 2722 (w-m), 1601 (vs), 1558 (w), 1523 (m), 1479

(vs), 1465 (vs), 1296 (m), 1275 (w-m), 1210 (w), 1156 (m-s), 1097 (w-m), 1063 (vw), 1022 (m), 988 (vs), 838 (vw), 800 (w), 774 (w), 751 (s), 723 (w-m), 648 (w), 623 (w), 584 (w), 556 (w), 519 (w), 413 (w), 378 (br m), 350 (w), 301 (br s) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 °C): δ 74.2 ppm (2H, $\nu_{1/2}$ = 40 Hz), 61.4 (2H, $\nu_{1/2}$ = 35 Hz), 18.3 (2H, $\nu_{1/2}$ = 21 Hz), -2.1 (30H, $\nu_{1/2}$ = 163 Hz), -12.6 (30H, $\nu_{1/2}$ = 86 Hz) The other resonances were not observed. M.S.(E.I.): m/e = 1072 amu (M^+), 937 ($\text{M}^+ - (\text{C}_5\text{Me}_5)$), 802 ($\text{M}^+ - 2(\text{C}_5\text{Me}_5)$), 666 ($\text{M}^+ - 3(\text{C}_5\text{Me}_5)$), 531 ($\text{M}^+ - 4(\text{C}_5\text{Me}_5)$), 358 ($\text{Yb}(2,2'\text{-azopyridine})^+$). Anal. Calcd for $\text{C}_{50}\text{H}_{68}\text{N}_4\text{Yb}_2$: C, 56.1; H, 6.40; N, 5.23 %. Found: C, 56.5; H, 6.47; N, 5.19 %.

$[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2(2,3\text{-Di-(2'-pyridino)quinoxaline)}$; 21

2,3-Di-(2'-pyridino)quinoxaline (DPQX) was made by the Schiff base condensation of 2,2'-pyridil [$(\text{C}_5\text{H}_5\text{N})\text{C}(=\text{O})\text{C}(=\text{O})(\text{NC}_5\text{H}_5)$] with *o*-phenylenediamine according to a literature procedure ³⁶. The crude product was recrystallized from boiling methanol.

A solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.67 g, 1.3 mmol) in 250 mL of pentane was added to a flask containing DPQX (0.18 g, 0.63 mmol) with rapid stirring. The green-black mixture was stirred for 1 h after which time no solids remained. Filtration and concentration of the filtrate to 50 mL followed by cooling at -10 °C for several days produced shiny black needles. Yield: 0.41 g (61 %). m.p. >330 °C. IR (Nujol, CsI): 3050 (w), 2715 (w), 1718 (w), 1585 (m), 1560 (m), 1533 (m), 1420 (sh w), 1333 (m), 1310 (m), 1272 (m), 1251 (m-s), 1240 (sh w), 1210 (w), 1191 (m), 1162 (w), 1155 (w), 1140 (s), 1096 (s), 1072 (sh w), 1046 (w), 1020 (w), 1008 (w), 970 (vs), 852 (m-s), 798 (br s),

775 (w), 768 (s), 732 (s), 712 (s), 702 (s), 639 (w), 610 (w-m), 550 (vs), 472 (br m), 430 (m), 355 (w), 305 (vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 $^\circ\text{C}$): δ 108.9 ppm (2H, $\nu_{1/2}$ = 64 Hz), 71.8 (2H, $\nu_{1/2}$ = 54 Hz), 29.6 (2H, $\nu_{1/2}$ = 29 Hz), -6.0 (30H, $\nu_{1/2}$ = 100 Hz), -6.8 (30H, $\nu_{1/2}$ = 100 Hz), -22.0 (2H, $\nu_{1/2}$ = 29 Hz) Only resonances observed. Anal. Calcd for $\text{C}_{58}\text{H}_{72}\text{N}_4\text{Yb}_2$: C, 59.5; H, 6.20; N, 4.78 %. Found: C, 55.8; H, 6.20; N, 4.31 %.

Yb(C₅Me₅)₂(N,N'-Bis(p-tolyl)-1,4-diazadiene); 22

N,N'-Bis(p-tolyl)-1,4-diazadiene (TDAD) was prepared by the Schiff base condensation of glyoxal and p-toluidine as reported ³⁷. The crude TDAD was recrystallized from hot isopropanol.

TDAD (0.27 g, 1.1 mmol) and $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.59 g, 1.1 mmol) were weighed into a Schlenk flask under nitrogen, dissolved in 200 mL of hexane and the dark green-black solution was stirred for 2 h. Filtration and cooling of the filtrate at -10 $^\circ\text{C}$ overnight gave dark brown crystals. Yield: 0.58 g (75 %). m.p. dec. 220 $^\circ\text{C}$. IR (Nujol, CsI): 2720 (w), 1604 (vs), 1553 (m), 1497 (vs), 1328 (s), 1313 (sh w), 1274 (vs), 1181 (m), 1143 (s), 1113 (vw), 1026 (m), 1000 (m), 897 (br s), 830 (vw), 796 (s), 722 (w), 700 (vw), 647 (vw), 616 (vw), 591 (vw), 513 (m), 415 (br w), 384 (br w), 313 (vs), 303 (vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 $^\circ\text{C}$): δ 113.4 ppm (4H, $\nu_{1/2}$ = 500 Hz), 59.8 (6H, $\nu_{1/2}$ = 73 Hz), 50.2 (4H, $\nu_{1/2}$ = 49 Hz), 1.8 (30H, $\nu_{1/2}$ = 35 Hz), -2.6 (2H, $\nu_{1/2}$ = 100 Hz). 98 $^\circ\text{C}$: δ 78.8 ppm (4H, $\nu_{1/2}$ = 180 Hz), 65.5 (6H, $\nu_{1/2}$ = 77 Hz), 48.8 (4H, $\nu_{1/2}$ = 34 Hz), 2.2 (30H, $\nu_{1/2}$ = 34 Hz), -1.6 (2H, $\nu_{1/2}$ = 100

Hz). M.S.(E.I.): $m/e = 680$ amu (M^+), 545 ($M^+ - (C_5Me_5)$), 444

($Yb(C_5Me_5)_2^+$), 410 ($M^+ - 2(C_5Me_5)$), 309 ($Yb(C_5Me_5)^+$). Anal. Calcd for $C_{36}H_{46}N_2Yb$: C, 64.6; H, 6.82; N, 4.12 %. Found: C, 64.2; H, 7.02; N, 4.08 %.

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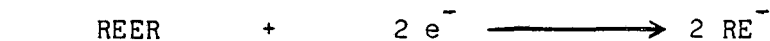
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Chapter 2: Reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$ with Organic Dichalcogenides and Related Molecules.

Reactions with Organic Dichalcogenides.

The ability of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ to reduce nitrogenous bases with reduction potentials as high as -2.1 V, shown in the previous chapter, indicated that it should be possible to reduce other organic substrates containing coordinating heteroatoms. The well known tendency of organic dichalcogenides to undergo a facile two electron reduction to the corresponding alkyl or aryl chalcogenide anions ¹ (Equation 1) made these compounds particularly attractive as substrates. It was expected that the reaction of two equivalents of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with one equivalent of the dichalcogenide would produce a ytterbium(III) organic chalcogenide complex (Equation 2). This was of some interest because at the time this study was initiated, only three reports of molecular lanthanide alkoxides had appeared in the literature ², while the thiolate, selenolate and tellurolate complexes were unknown.

Equation 1



E = O, S, Se, Te

R = alkyl, aryl

Equation 2



Diethyl Ether Complexes

The reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with the reducible organic dichalcogenides shown in Table 1 proceeds rapidly on mixing in diethyl ether or hydrocarbon solvents according to Equation 2. The physical properties of the crystalline complexes are given in Table 2. The reactions with *t*-butyl- and trimethylsilyl peroxide also proceed rapidly as shown by the colour change from deep green to bright orange on mixing, however the alkoxide complexes can only be isolated as pentane soluble oils which do not crystallize even with agitation and prolonged cooling at -78°C . Further characterization of the alkoxide complexes has not been carried out.

The colour of the complexes depends strongly on the identity of the heteroatom. As mentioned above, the alkoxide complexes are orange while the thiolates and selenolates are purple and the tellurolate is olive green. The intense colours of these complexes may be due to a ligand lone pair to metal charge transfer band. The observed colours suggest that the energy of this transition decreases in the order: oxygen \gg sulphur = selenium $>$ tellurium.

All complexes give mass spectra where the parent ion represents loss of diethyl ether. Weak diethyl ether coordination may also be responsible for the consistently poor analyses obtained for these compounds. It is noteworthy in this regard that the base-free mesitylthiolate complex 4 gives a satisfactory analysis. No explanation is offered for the low melting point of the phenylthiolate complex 1.

The proton NMR spectra of the diethyl ether complexes are assigned in Table 3. The pentamethylcyclopentadienyl methyl resonance is unusually broad (300 - 600 Hz width at half peak height) for all of the

Table 1 Reducible Organic Dichalcogenides Used in this Study.

<u>Substrate</u>	<u>$-\xi_{1/2}$ (V) ^(a)</u>	<u>Reference</u>
-S-S-	1.7	3
-S-S-	1.7	3
-S-S-	(b)	
-S-S-	(b)	
-CH ₂ -S-S-CH ₂ -	1.8	3
CH ₃ -S-S-CH ₃	1.8	4
-Se-Se-	1.2	3
-Te-Te-	1.1	5
Me ₃ CCC{{{O-CMe ₃	(b)	
Me ₃ Si-O-O-SiMe ₃	(b)	

(a) Measured at a rotating platinum electrode in dimethylformamide or acetonitrile. Potentials are relative to the saturated calomel electrode. (b) Not reported.

Table 2 Physical Properties of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{OEt}_2)$ Complexes.

	<u>ER</u>	<u>Colour</u>	<u>m.p. (°C)</u>
<u>1</u>	$\text{C}_6\text{H}_5\text{S}$	purple	62 - 65
<u>2</u>	p- $\text{C}_7\text{H}_7\text{S}$	purple	127 - 129
<u>3</u>	m- $\text{C}_7\text{H}_7\text{S}$	purple	130 - 132
<u>4</u>	mesityl-S (a)	dark purple	159 - 163
<u>5</u>	$\text{C}_6\text{H}_5\text{CH}_2\text{S}$	purple	152 - 156
<u>6</u>	$\text{C}_6\text{H}_5\text{Se}$	purple	156 - 160
<u>7</u>	$\text{C}_6\text{H}_5\text{Te}$	olive green	142 - 145

(a) isolated base-free.

aryl complexes. This could be caused by slow exchange of coordinated diethyl ether (Equation 3) or by slow pentamethylcyclopentadienyl ring rotation. Rotation about the E-C(aryl) bond occurs in solution as shown by the equivalent ortho and meta resonances in the proton NMR spectra of the phenyl, p-tolyl and mesityl chalcogenide complexes (Figure 1). Inversion at the chalcogenide atom decreases from greater than 125 kJ mole⁻¹ in free R₂E to 40 - 80 kJ mole⁻¹ in transition metal chalcogenide complexes ⁶, however it seems unlikely that the barrier to inversion is low enough to account for this observation. Rotation about the E-C bond does not necessarily rule out slow pentamethylcyclopentadienyl ring rotation because rotation about the E-C bond could occur in a "cog-wheel" fashion with respect to the methyl groups of the C₅Me₅ rings.

Equation 3



Figure 1

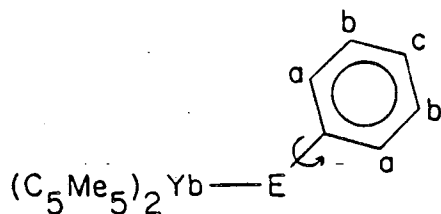


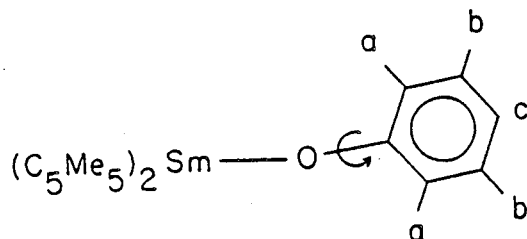
Table 3: ^1H NMR Assignments for $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{OEt}_2)$ Complexes ^(a)

	<u>ER</u>	<u>ortho</u>	<u>meta</u>	<u>para</u>	<u>C₅Me₅</u>	<u>other</u>
<u>1</u>	C ₆ H ₅ S	5.5	73.2	42.6	9.7	
<u>2</u>	p-C ₆ H ₄ S	5.5	76.4	<u>Me</u> 30.3	8.5	
<u>3</u>	m-C ₆ H ₄ S	9.2	78.4	44.7	9.2	
		5.9	<u>Me</u> 56.0			
<u>4</u>	mesityl-S ^(b)	<u>Me</u> 3.7	(c)	<u>Me</u> 18.6	9.2	
<u>5</u>	C ₆ H ₅ CH ₂ S	-14.2 ^(d)	-16.0 ^(d)	-25.9	4.2	CH ₂ -6.8
<u>6</u>	C ₆ H ₅ Se	9.7 ^(e)	62.7	37.9	9.7	
<u>7</u>	C ₆ H ₅ Te	11.9	46.2	16.4	8.5	

(a) Recorded in C₆D₆ at 32 °C. Chemical shifts relative to tetramethylsilane. Coordinated diethyl ether not observed. (b) base-free (c) not observed (d) arbitrary assignment (e) on the basis of integrated intensity.

A relatively narrow (ca. 100 Hz) ring resonance is observed for the benzylthiolate complex 5. The additional carbon atom between sulphur and the aromatic ring increases the distance of this ring from the metal center, making hindered rotation of the C₅Me₅ rings less likely. On the other hand, diethyl ether is probably more tightly bound because steric interactions between the ether ethyl groups and the aryl ring are not as great. Both of these factors favour narrower ring resonances so the observation of a sharp resonance for 5 provides no insight into the cause of line broadening for the aryl chalcogenide complexes.

The mesitylthiolate complex 4 is isolated without coordinated diethyl ether. Presumably this is because the ortho methyl substituents of the mesitylthiolate ligand block the second coordination site at ytterbium. Despite the presence of methyl groups in the ortho position of the aryl ring, rotation about the S-C(aryl) bond occurs to -80 °C, as shown by the single ortho resonance in the proton NMR. The closely related samarium(III) alkoxide I, recently reported in the literature ⁷, also shows equivalent ortho resonances. The crystal structure of I shows an extremely large Sm-O-C angle of 174° which has been attributed to steric repulsion between the ortho methyl substituents of the alkoxide and the methyl groups of the C₅Me₅ rings. Unfortunately the line width of the pentamethylcyclopentadienyl resonance was not reported for I so the presence or absence of hindered C₅Me₅ ring rotation in this complex cannot be ascertained. From these findings it is evident that rotation about the E-C(aryl) bond occurs even in extremely congested environments.

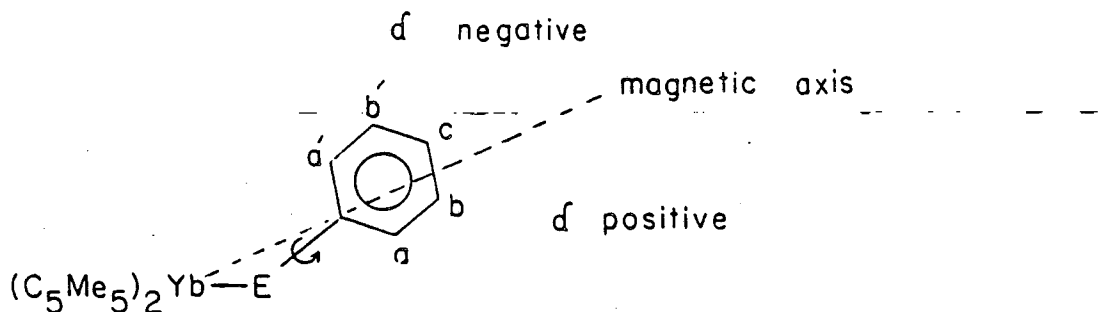


I

The aromatic proton resonances follow similar trends for all diethyl ether complexes synthesized. A comparison of several substituted arylthiolate complexes allows assignment of the resonances downfield of tetramethylsilane in the order: ortho < para < meta (Table 3). The chemical shifts in paramagnetic lanthanide complexes have been attributed to the through-space pseudocontact term ^o (Chapter 1). Thus it is predicted that the magnitude of the chemical shift should decrease with distance from the paramagnetic center. In fact the ortho protons appear to be the least shifted of the aromatic resonances. This apparent anomaly can be rationalized by noting that the pseudocontact term also contains an angular dependence which need not average to zero in low symmetry systems. Rotation about the E-C(aryl) bond causes the ortho and meta protons to travel in a circular path through space about the E-C(para) vector. Obviously, the angle between these protons and

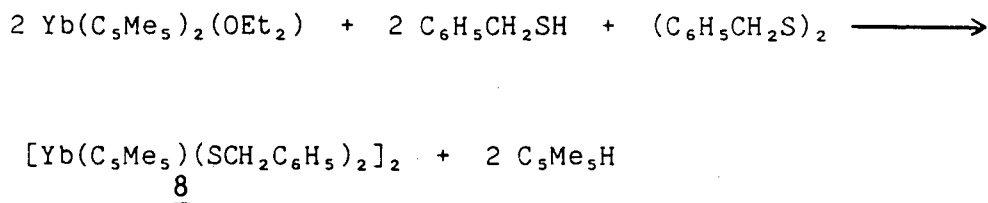
the magnetic axis will vary with rotation. In this case, the distance between these protons and the metal center will also vary because the Yb-E-C(aryl) angle is not linear. Since the sign of the paramagnetic shift depends on the angular term, it is possible that the ortho and para protons travel through regions of both negative and positive shift during rotation (Figure 2). As a result, an averaged chemical shift is observed which may be considerably smaller in magnitude than that observed for a particular orientation. The paramagnetic shift need not average to zero unless the magnetic axis coincidentally corresponds to the E-C(para) vector. The para protons are not displaced by such a rotation and may therefore exhibit a larger chemical shift than either the ortho or meta protons. Clearly, the observed chemical shifts will depend very strongly on the coordination geometry. It is interesting to note in this regard, that the base-free mesitylthiolate complex 4 exhibits proton chemical shifts similar to those of the diethyl ether complexes. This is consistent with dissociation of diethyl ether in hydrocarbon solvents.

Figure 2

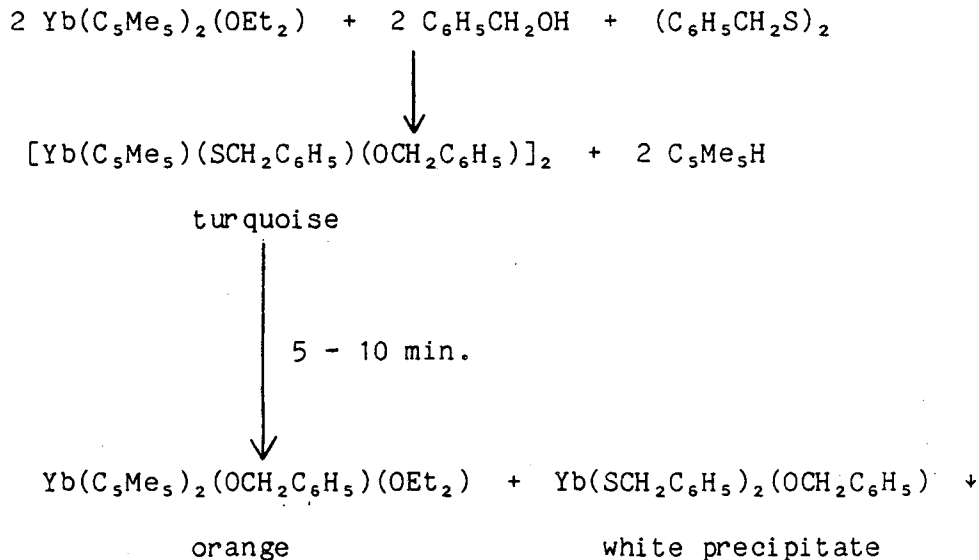


The reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with benzyl disulphide produces a small yield of turquoise crystals 8 in addition to the more soluble benzylthiolate diethyl etherate 5. The proton NMR of this compound shows two benzylthiolate ligands for each C_5Me_5 ring. Analysis confirms the stoichiometry of this complex as $\text{Yb}(\text{C}_5\text{Me}_5)(\text{S}-\text{CH}_2\text{C}_6\text{H}_5)_2$. The observation of a one ring product suggests that benzylthiol is present as an acidic impurity in the benzyl disulphide. Repeated recrystallization of the disulphide does lower the yield, but a small amount of 8 (ca. 10 %) is always isolated. As expected 8 can be synthesized in high yield according to Equation 4. Attempts to prepare the analogous complexes for other thiolates produces turquoise oils. Substitution of an alcohol for the thiol in Equation 4 leads to turquoise solutions which turn bright orange and deposit white powders after 10 to 20 minutes. It would appear from this observation that ligand redistribution reactions similar to those in Scheme 1 are taking place.

Equation 4

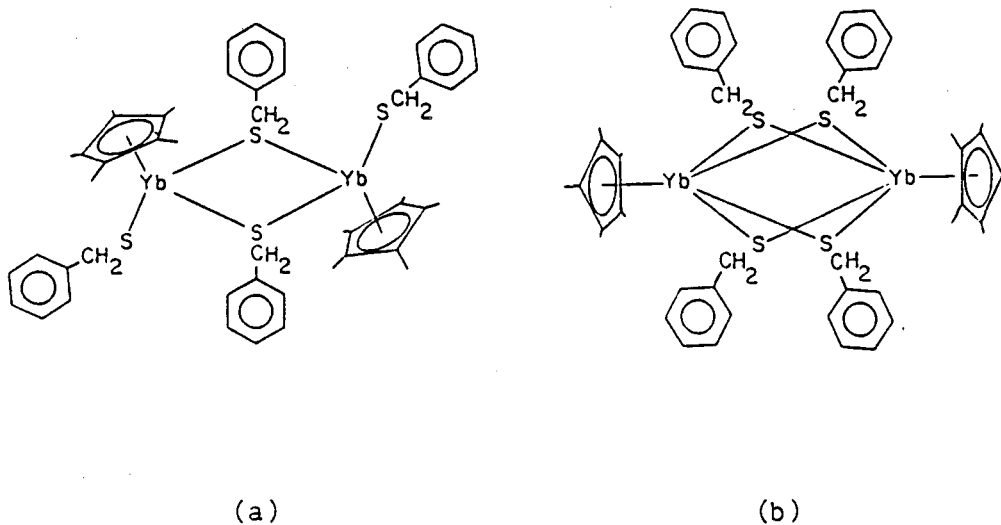


Scheme 1



The absence of any coordinated diethyl ether strongly suggests an aggregate because a simple monomer would only be five-coordinate. This is an important point because even in the sterically crowded mesitylthiolate complex 4, a coordination number of seven is attained. Furthermore other $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ complexes are eight coordinate with ligands less sterically demanding than mesitylthiolate. A dimer is more likely than an oligomeric or polymeric structure because the complex is hydrocarbon soluble. Two possible structures are shown in Figure 3. The benzylthiolate ligands are chemically equivalent in the proton NMR spectrum to -85°C , however since no information is available on the rate of bridge-terminal benzylthiolate exchange in similar species, this observation does not necessarily rule out the structure in Figure 3a. Nevertheless Figure 3b is probably more reasonable because the ytterbium ions are seven-coordinate here while they are only six-coordinate in Figure 3a. Unfortunately crystals suitable for a structural study have not yet been obtained.

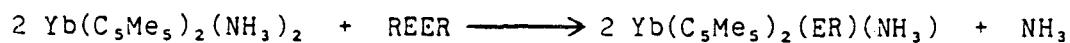
Figure 3



Ammonia Complexes

In order to avoid the broad NMR line widths and poor analyses which characterize the diethyl ether complexes, $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{OEt}_2)$, adducts of more strongly coordinating bases have been investigated. Since ammonia provides crystalline products which exhibit sharp resonances in the NMR spectrum, these complexes have been studied in detail. Much better yields and cleaner products are obtained when the ammonia complexes are prepared directly from $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ and the dichalcogenide (Equation 5) rather than by displacement of diethyl ether with ammonia (Equation 6).

Equation 5



Equation 6



The reaction shown in Equation 5 proceeds rapidly on mixing in diethyl ether or toluene with dissolution of sparingly soluble $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$. The physical properties of the ammonia adducts are given in Table 4. In general, the ammonia complexes are less soluble than the corresponding diethyl etherates. This property allows isolation of orange, hexane-soluble alkoxide complexes, 16 and 17, when only oils could be obtained with diethyl ether as the coordinating base. The mesitylthiolate complex does not form a base adduct for steric reasons.

The melting points of the ammonia complexes are typically 40 - 80 °C higher than the corresponding diethyl ether adducts, reflecting more efficient crystal packing with the compact ammonia molecule as the base. In keeping with the higher melting points, the ammonia adducts are less volatile and consequently much more difficult to obtain mass spectra of than their diethyl ether counterparts. However when it is possible to obtain a mass spectrum, coordinated ammonia is lost.

The colours of the ammonia adducts are similar to the diethyl etherates, supporting the theory that the colour is primarily dependent upon the identity of the heteroatom. This is only a rough guideline and at least one exception is observed: the phenyltelluroolate diethyl etherate 7 is olive green while the ammonia complex 15 is purple. The thiolate and selenolate ammonia complexes 9 - 12 and 14 respectively, are isolated as red crystals from the reaction mixture which rapidly

Table 4: Physical Properties of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{NH}_3)$ Complexes.

	<u>ER</u>	<u>Colour</u>	<u>m.p. (°C)</u>
<u>9</u>	$\text{C}_6\text{H}_5\text{S}$	magenta	206 - 208
<u>10</u>	p- $\text{C}_7\text{H}_7\text{S}$	magenta	208 - 211
<u>11</u>	m- $\text{C}_7\text{H}_7\text{S}$	magenta	206 - 207
<u>12</u>	$\text{C}_6\text{H}_5\text{CH}_2\text{S}$	magenta	221 - 223
<u>13</u>	CH_3S	red	174 - 177
<u>14</u>	$\text{C}_6\text{H}_5\text{Se}$	magenta	195 - 198
<u>15</u>	$\text{C}_6\text{H}_5\text{Te}$	purple	190 - 191
<u>16</u>	Me_3CO	red-orange	184 - 186
<u>17</u>	Me_3SiO	orange	221 - 222

turn magenta and opaque on exposure to vacuum. Recrystallization from toluene yields burgundy crystals which do not change colour on exposure to vacuum. This suggests that the crystals isolated directly from the reaction mixture contain a second, weakly coordinated molecule of ammonia which is easily lost under reduced pressure.

The proton NMR spectra of the ammonia complexes are assigned in Table 5. Variable temperature NMR is useful in identifying overlapping resonances because the chemical shifts of protons in simple ytterbium(III) complexes vary linearly with inverse temperature (Curie-Weiss law) over the accessible NMR temperature range (-85 to 150 °C).⁹ Since the change in chemical shift with temperature usually varies for different types of protons, resonances which overlap at one temperature may become distinguishable at another. Plots of chemical shift (δ) versus inverse temperature (T^{-1}) are shown in Figures 4 and 5 for the overlapping resonances of 10 and 11 respectively, which illustrate the utility of variable temperature NMR in locating and assigning resonances.

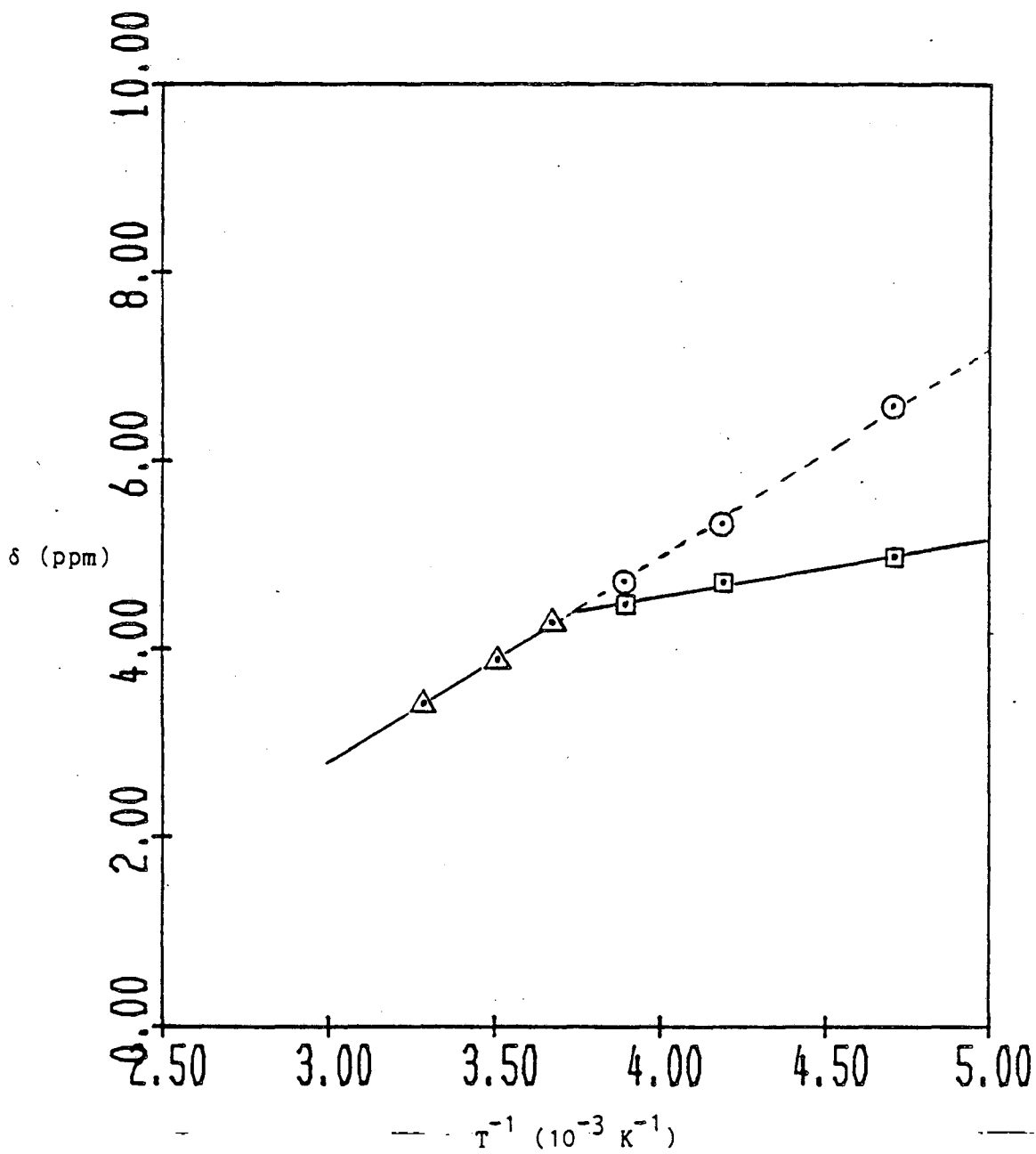
The pentamethylcyclopentadienyl resonance is only 40 to 80 Hz wide for the thiolate, selenolate and tellurolate ammonia complexes. The strong dependence of line width on the coordinated base implies that base dissociation is at least partially responsible for the broad line widths of the diethyl etherates. The alkoxide complexes 16 and 17 do exhibit line widths on the order of 250 Hz. However, since no information is available for the corresponding diethyl etherates, no valid comparison can be made. The combined results for the ammonia and diethyl ether complexes suggest that line broadening can be caused by

Table 5: ^1H NMR Assignments for $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{NH}_3)$ Complexes ^(a)

	<u>ER</u>	<u>ortho</u>	<u>meta</u>	<u>para</u>	<u>C₅Me₅</u>	<u>other</u>
<u>9</u>	C ₆ H ₅ S	44.0	12.8	8.7	3.8	
<u>10</u>	p-C ₇ H ₇ S	38.8	12.7	<u>Me</u> 3.8 ^(b)	3.8 ^(b)	
<u>11</u>	m-C ₇ H ₇ S	51.6	14.0	9.8 ^(c)	3.8	
		41.7	<u>Me</u> 9.8 ^(c)			
<u>12</u>	C ₆ H ₅ CH ₂ S	-2.4	9.1	11.2	4.0	CH ₂ -16.0
<u>13</u>	CH ₃ S				4.1	<u>Me</u> -5.9
<u>14</u>	C ₆ H ₅ Se	25.1	9.6	7.4	4.3	
<u>15</u>	C ₆ H ₅ Te	16.5	6.7	6.0	4.0	
<u>16</u>	Me ₃ CO				6.1	<u>Me</u> -57.5
<u>17</u>	Me ₃ SiO				4.8	<u>Me</u> -37.4

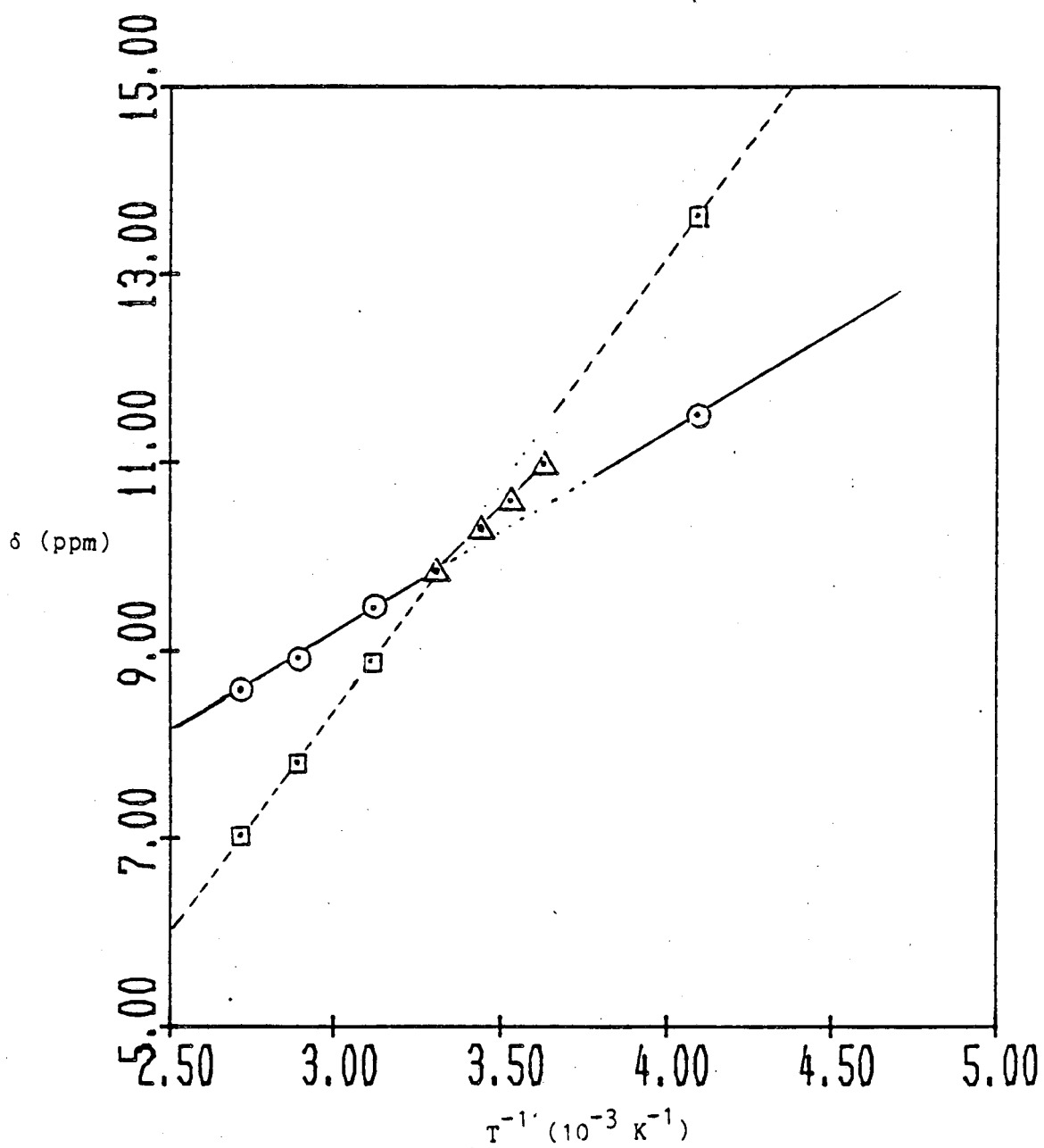
(a) Recorded in C₆D₆ at 32 °C. Chemical shifts in ppm relative to tetramethylsilane. Coordinated ammonia is not observed. (b) Distinguishable by variable temperature (VT) NMR, Figure 4. (c) VT-NMR, Figure 5.

Figure 4 Chemical Shift (δ) versus Inverse Temperature (T^{-1})
for the Overlapping para-CH₃ and C₅Me₅ Resonances of 10. (a)



(a) Para-CH₃, \square ; C₅Me₅, \circ ; overlapping resonances Δ .

Figure 5 Chemical Shift (δ) versus Inverse Temperature (T^{-1})
for the Overlapping meta-CH₃ and para-H Resonances of 11.^(a)



(a) Meta-CH₃ \square ; para-H \circ ; overlapping resonances Δ .

either hindered C_5Me_5 ring rotation or by base dissociation. The primary cause is base dissociation for the diethyl etherates while hindered ring rotation is probably responsible for line broadening in the sterically crowded base-free mesitylthiolate and alkoxide ammoniates 4, 16, and 17, respectively.

The chemical shift of the aromatic ring proton resonances of $Yb(C_5Me_5)_2(ER)(NH_3)$ decrease in the order: ortho > meta > para. The magnitude of the observed chemical shift decreases with increasing distance from the paramagnetic center as the heteroatom is changed from sulphur to selenium to tellurium. This is in the order predicted by the pseudocontact shift term. The drastic change in order relative to the diethyl etherates seems to suggest a difference in structure. The simplest explanation is that ammonia remains coordinated in solution while diethyl ether does not. The benzyl- and methylthiolate complexes, 12 and 13 respectively, do not follow the same trend since in these complexes the protons on the carbon bound to sulphur appear upfield of tetramethylsilane. The important point to be derived from these NMR studies is that the proton chemical shifts follow well behaved patterns within the same structural group. Thus the diethyl etherates and ammoniates follow independent but predictable trends for all substituted aryl chalcogenide complexes. The pattern for alkoxides and alkylthiolates is internally consistent but differs markedly from the aryl chalcogenides.

The X-ray crystal structure of 9 was obtained by Zalkin, Henly and Andersen ¹⁰ although ammonia was not identified as the coordinated base until later. This is because the complex was originally prepared from $Yb(C_5Me_5)_2(OEt_2)$ and the dichalcogenide. However $Yb(C_5Me_5)_2(NH_3)_2$ is

sometimes present as an impurity in the diethyl etherate if excess ytterbium metal is not used in the preparation of YbI_2 (see Introduction). The structure of 9 consists of a pseudotetrahedral arrangement of two C_5Me_5 rings, one phenylthiolate ligand and one ammonia molecule about the ytterbium(III) ion.

The X-ray crystal structure of 15 has been carried out by Zalkin¹¹. An ORTEP plot of this molecule is shown in Figure 6. Selected bond distances and angles are given in Table 6. The coordination environment about ytterbium is pseudotetrahedral and similar to that in 9. The C_5Me_5 rings show rotational disorder due to thermal motion. The Yb-Te-C(aryl) angle of $113.0(3)^\circ$ is larger than the Te-Te-C(aryl) angle found in organic ditellurides ($100 - 102^\circ$)^{12 13} and smaller than the corresponding Yb-S-C(aryl) angle in 9 ($123.0(3)^\circ$)¹⁰. The Yb-N distance of $2.45(1)$ Å is slightly greater than the corresponding distance in 9 ($2.423(8)$ Å). The Yb-Te distance is $3.039(1)$ Å. Since this is the first complex containing a Yb-Te bond, no structural comparisons can be made.

Figure 6 ORTEP Plot of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Te}-\text{C}_6\text{H}_5)(\text{NH}_3)$ 15.

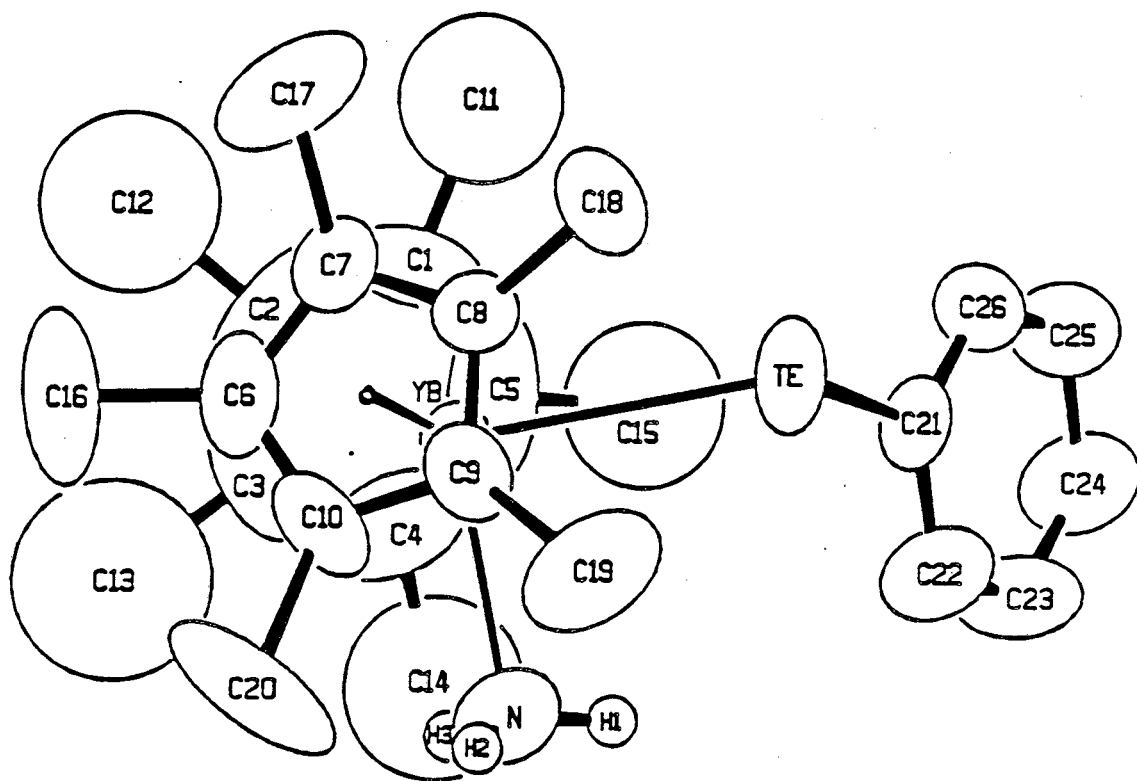
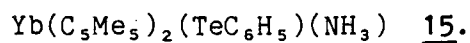


Table 6: Selected Distances (Å) and Angles (°) for



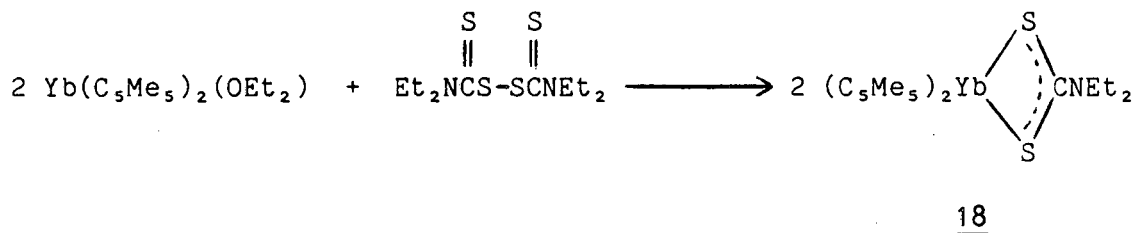
Yb - Cp(1) (a)	2.334
Yb - Cp(2)	2.366
<Yb - C(Cp)>	2.63(3)
<C(Cp) - C(Cp)>	1.39(3)
<C(Cp) - C(Me)>	1.55(2)
Yb - N	2.45(1)
Yb - Te	3.039(1)
Te - C(aryl)	2.12(1)
Cp(1) - Yb - Cp(2)	136.9
Cp(1) - Yb - Te	113.0
Cp(2) - Yb - Te	100.9
Cp(1) - Yb - N	102.9
Cp(2) - Yb - N	103.5
Te - Yb - N	89.0(3)
Yb - Te - C(aryl)	113.0(3)

(a) Cp(1) and Cp(2) are the centroids of the C_5Me_5 rings (atoms C(1) - C(5) and C(6) - C(10)).

Reactions with Related Molecules

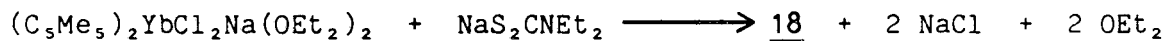
The sulphur-sulphur bond of tetraethylthiuram disulphide is readily cleaved by $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ to form the diethyldithiocarbamate complex 18 :

Equation 7



This complex has been prepared previously ¹⁴ from the anionic dichloride complex, $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Cl}_2\text{Na}(\text{OEt}_2)_2$, and $\text{NaS}_2\text{CNET}_2$ (Equation 8). It is not surprising that cleavage occurs so readily since the reduction potential of tetraethylthiuramdisulphide is only -0.5 V ¹⁵. Chelate formation through the sulphur atoms also helps to stabilize the product and lower the reduction potential of the substrate.

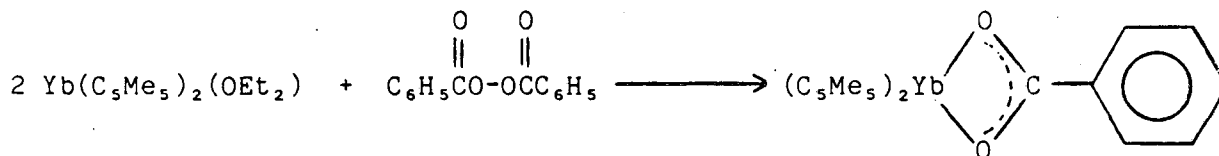
Equation 8



Benzoyl peroxide reacts rapidly with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ at $-78 \text{ }^\circ\text{C}$ to form a red benzoate complex 19 (Equation 9). The reaction is extremely vigorous and exothermic as might be expected given the ease of reduction of benzoyl peroxide ($\xi_{1/2} = +0.15 \text{ V}$ versus SCE) ¹⁶. The NMR spectrum of 19 appears to show three different species in solution .

This conclusion is based on the observation of three sets of resonances (30:2:2:1) in approximately 1:2:1 ratio. Since it is not possible for a simple monomer or dimer to have inequivalent C₅Me₅ ring resonances, the three large resonances must be due to different species. The NMR spectrum could be explained by an equilibrium between monomeric, dimeric and trimeric species in solution if exchange of benzoate ligands is slow on the NMR timescale (Figure 7). Assignment of the three sets of resonances to the individual species is difficult without a detailed examination of the concentration dependence of the NMR spectrum. However it is probably reasonable to assign the broadest C₅Me₅ resonance and the most shifted benzoate proton signals to the monomer. The results discussed earlier in this chapter suggest that line broadening is probably caused by hindered C₅Me₅ ring rotation in this complex. Since the monomer is expected to be more sterically congested than the dimer or trimer, it seems likely that the broadest C₅Me₅ resonance is due to this species. The benzoate protons are closer, on average, to the paramagnetic ytterbium(III) center in the monomer so these resonances are likely to be the most shifted of the three sets observed. Similar logic can be used to assign the resonances of the dimer and trimer. Tentative assignments for 19 are given in Table 7.

Equation 9



The remarkable difference in behaviour between complexes 18 and 19 may be attributable to a shorter Yb-O bond length in 19 compared to the Yb-S bond distance in 18. The shorter Yb-O bond distance could cause steric interactions between the C₅Me₅ and the aryl ring of the benzoate group. Formation of benzoate bridges moves the aryl ring further away from the ytterbium center, while the three atom O-C-O bridge is sufficiently long to prevent unfavourable steric crowding between Yb(C₅Me₅)₂ units. Strictly speaking, a comparison with the sulphur analogue would be more meaningful because the steric and electronic effects of a NEt₂ group differ considerably from those of a phenyl group.

The reaction of Yb(C₅Me₅)₂(OEt₂) with tetraalkyldiphosphine-disulphides proceeds rapidly on mixing in ethereal or hydrocarbon solvents to produce the purple dialkyldithiophosphate complexes 20 and 21 :

Equation 10

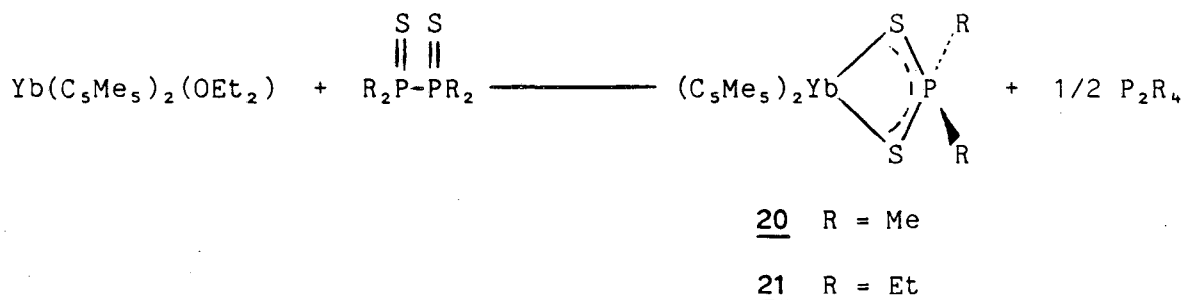


Figure 7 Possible Solution Equilibria for $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{O}_2\text{C}_6\text{H}_5)$ 19

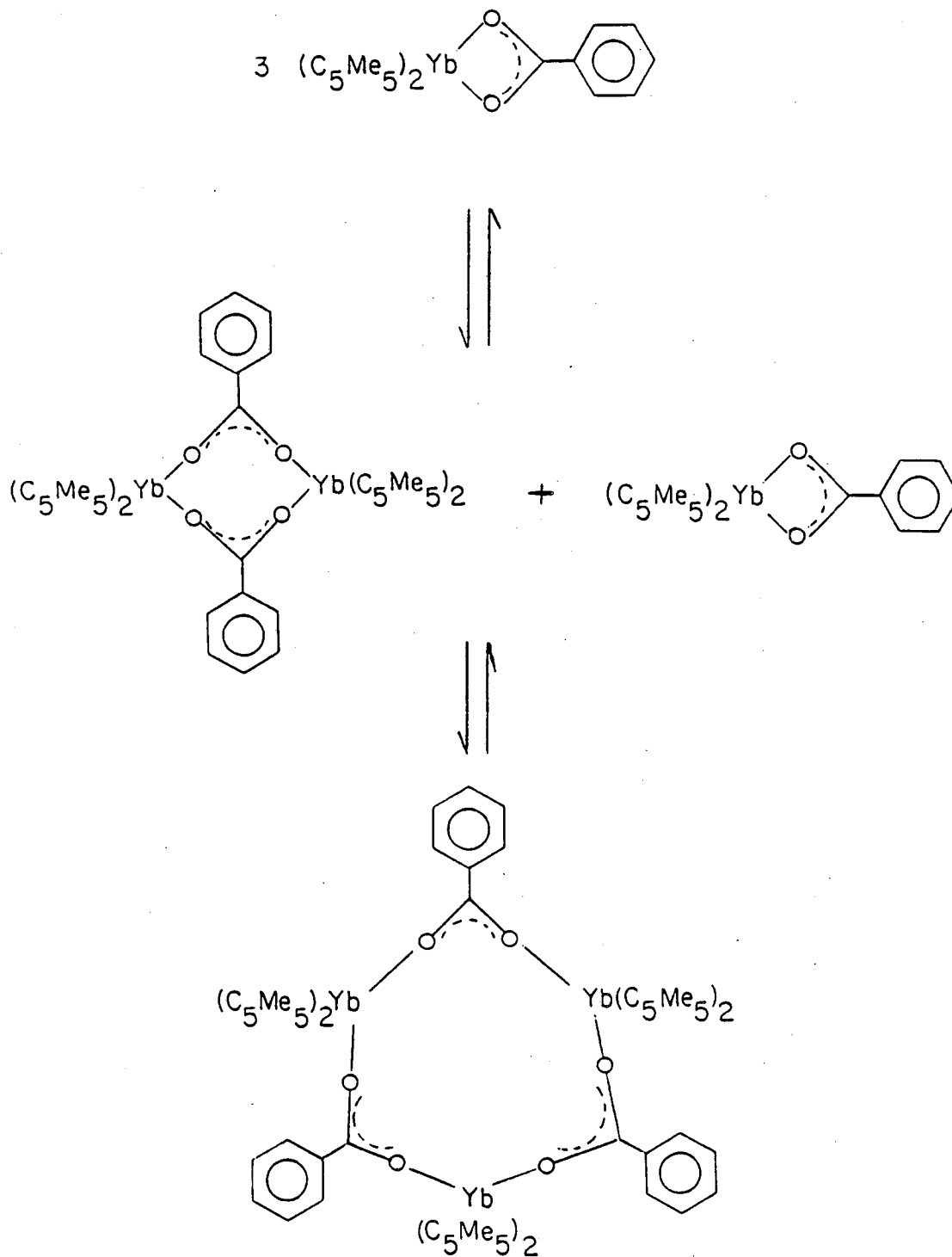


Table 7: ^1H NMR^(a) Assignments for $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{O}_2\text{CC}_6\text{H}_5)$ 19

	<u>ortho</u> ^(b)	<u>meta</u>	<u>para</u>	<u>C₅Me₅</u>
<u>A</u> : Monomer ^(c)	δ 175.0 (85)	-5.9 (40)	-8.2 (35)	11.1 (260)
<u>B</u> : Dimer	54.2 (25)	26.0 (45)	2.1 (18)	-1.9 (65)
<u>C</u> : Trimer	38.1 (16)	18.7 (16)	3.5 (15)	2.3 (55)

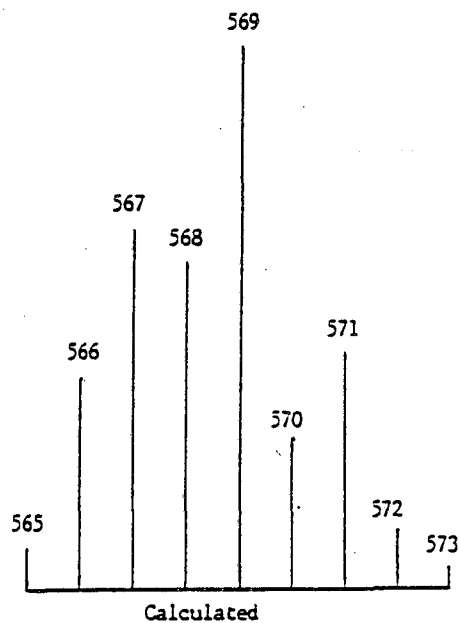
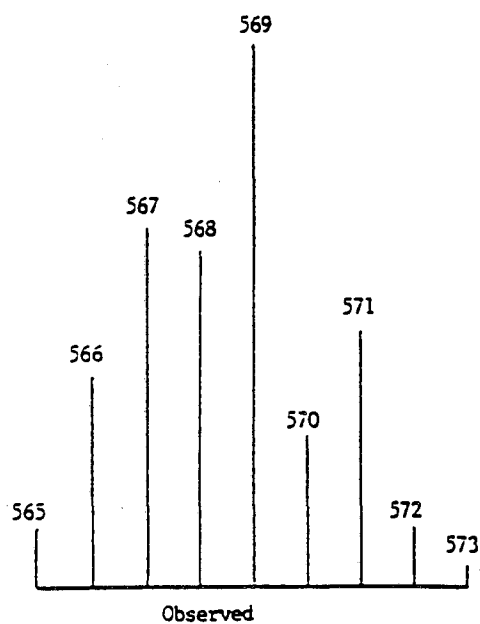
(a) Recorded in C_6D_6 at 21 °C. Chemical shifts in ppm relative to external tetramethylsilane; width at half peak height is given in brackets in Hertz. (b) assignment uncertain. (c) relative integrated intensity for A:B:C is ca. 1:2:1.

The formation of 20 and 21 is conclusively established from the infrared and mass spectra. A number of anionic, tetrakis dialkyldithiophosphate complexes have been synthesized ¹⁷ and the praseodymium complex has been structurally characterized ¹⁸. This structure contains an antiprismatic arrangement of chelating $R_2PS_2^-$ anions about the metal center. Characteristic infrared bands due to the symmetric ($600 - 620\text{ cm}^{-1}$) and asymmetric ($500 - 510\text{ cm}^{-1}$) P-S stretching modes of the chelating dialkyldithiophosphate ligand have been assigned in these complexes ¹⁷. The corresponding bands are observed in the infrared spectrum of 20 (590 and 495 cm^{-1}) and 21 (616 and 507 cm^{-1}). Molecular ions are observed for both 20 and 21 in the mass spectrum. The calculated and observed isotope patterns are shown in Figure 8. The paramagnetic proton and phosphorous NMR spectra are consistent with a simple chelate complex; assignments are given in Table 8.

The formation of a dialkyldithiophosphate complex from the tetraalkyldiphosphine disulphide starting material suggests that P-P bond cleavage occurs with formation of a dialkylphosphine radical ($\cdot PR_2$). In order to test this theory, the reaction mixture was examined by NMR spectroscopy. These experiments show that the predominant phosphorous byproduct is the tetraalkyldiphosphine; the product of dialkylphosphine radical coupling. Some tetraalkyldiphosphine sulphide is also observed. This product can be formed in the reaction of dialkylphosphine radicals with the tetraalkyldiphosphine disulphide starting material. The total integrated intensity of all trivalent phosphorous resonances is approximately equal to that of coordinated

Figure 8 Calculated and Observed Isotope Patterns for
 $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{PR}_2)$ Complexes, 20 and 21.

a) 20



b) 21

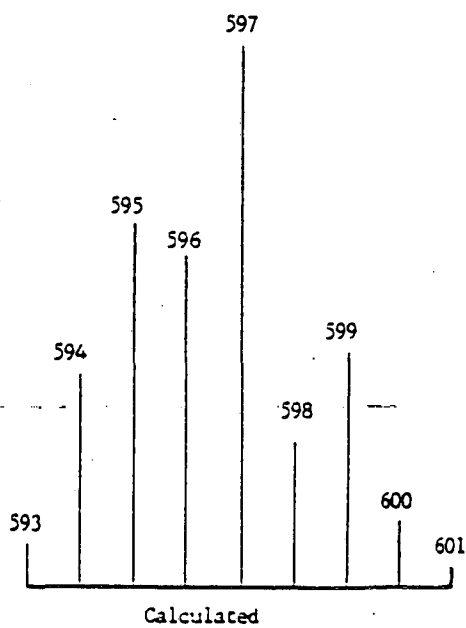
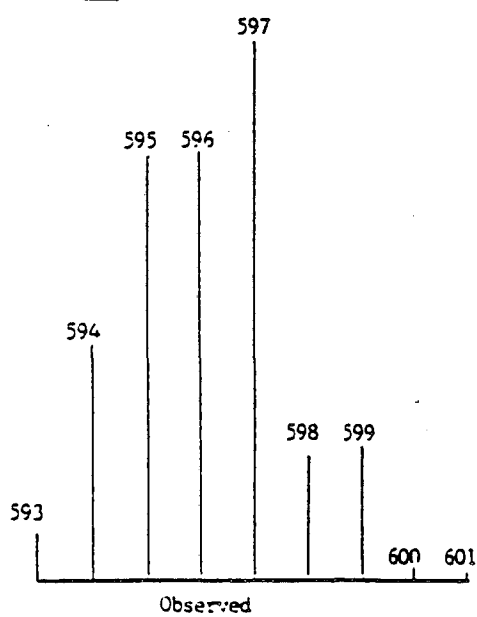


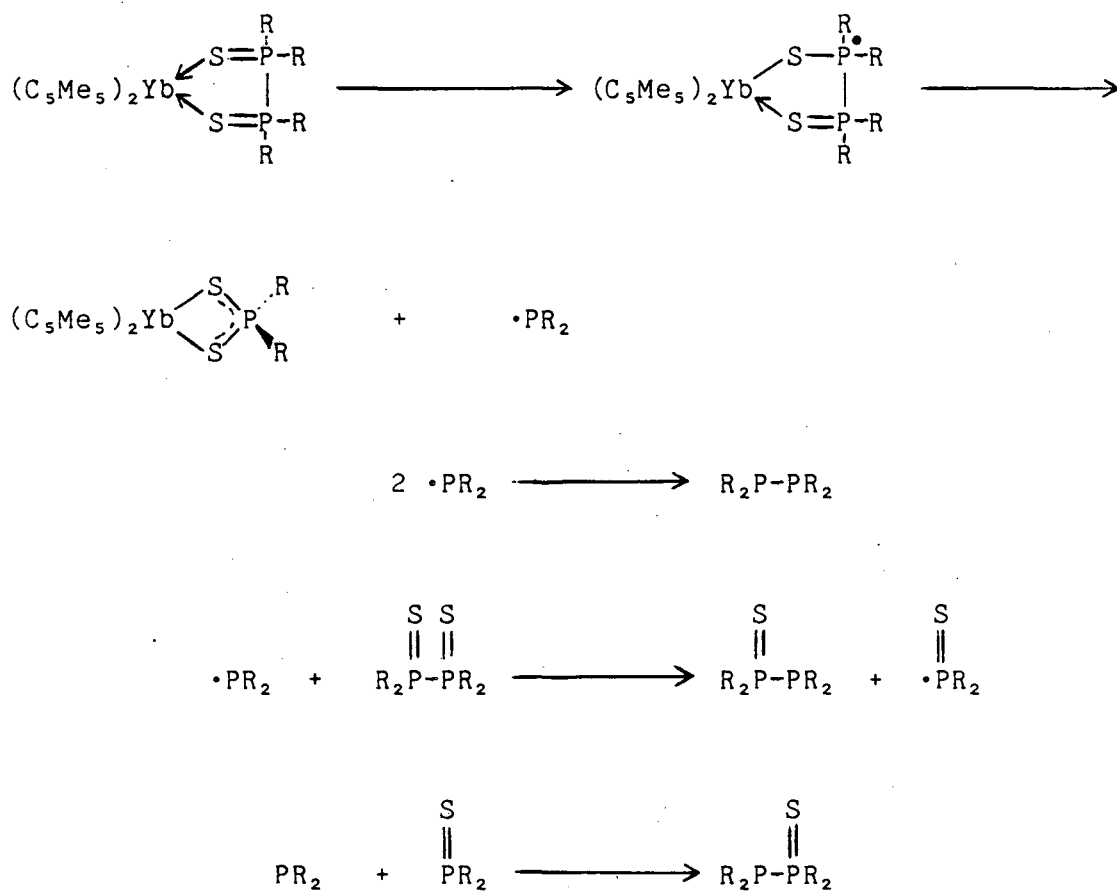
Table 8: Physical Properties of Yb(C₅Me₅)₂(S₂PR₂) Complexes.

	<u>R</u>	<u>m.p. (°C)</u>	NMR (a)	
			<u>¹H (b)</u>	<u>³¹P (c)</u>
<u>20</u>	Me	78 - 82	δ 7.5 (30H, 70 Hz) , -23.5 (6H, 30 Hz)	δ -28.2
<u>21</u>	Et	75 - 77	7.4 (30H, 71 Hz) -7.5 (6H, 31 Hz) -27.9 (4H, 32 Hz)	-5.1

(a) Recorded in C₆D₆ at 32 °C. (b) Chemical shifts in ppm relative to external tetramethylsilane (c) Chemical shifts in ppm relative to external 85 % H₃PO₄.

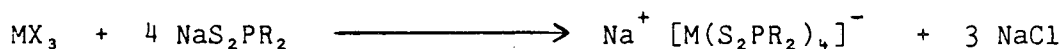
phosphorous indicating that all reduced phosphorous species are accounted for. The NMR spectra of the reaction mixtures clearly support the formation of diakylphosphine radicals. A possible mechanism for this reaction is outlined in Scheme 2.

Scheme 2



Despite the rich transition metal chemistry of tetraalkyldiphosphine disulphides ¹⁹, relatively few reactions are known where cleavage of the phosphorous-phosphorous bond occurs. This is surprising because cleavage of the P-P bond is known to occur electrochemically at ca. -2.5 V versus S.C.E. for the parent organic molecules ²⁰. When cleavage does occur, R₂P=S complexes are isolated ²¹. The transition metal chemistry of dialkyldithiophosphinates is well developed ^{22 23} and the preparation of a wide range of lanthanide complexes has also been reported ^{17 18}. However, in nearly every case these complexes were synthesized from the sodium dialkyldithiophosphate salt ¹⁸ (Equation 11) or by cleavage of the bis(diorganothiophosphoryl)disulphane ²³ (Equation 12).

Equation 11



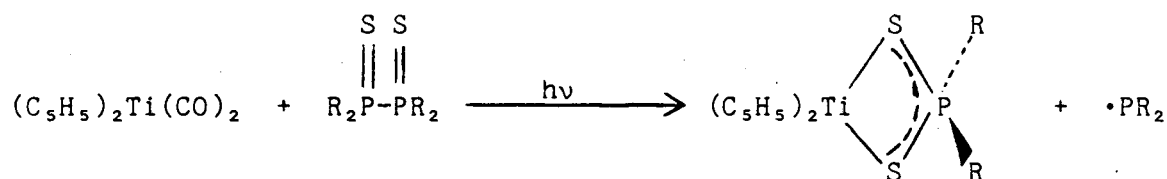
Equation 12



The only previous report of dialkyldithiophosphate complex formation from a tetraalkyldiphosphine disulphide appeared earlier this year ²⁴. Interestingly this reaction also involves oxidation of a divalent metallocene to a trivalent chelate complex (Equation 13). This reaction is thought to involve photochemical dissociation of CO followed by coordination of the diphosphine disulphide to form an unstable titanium(II) species. Oxidation of titanium to the trivalent product

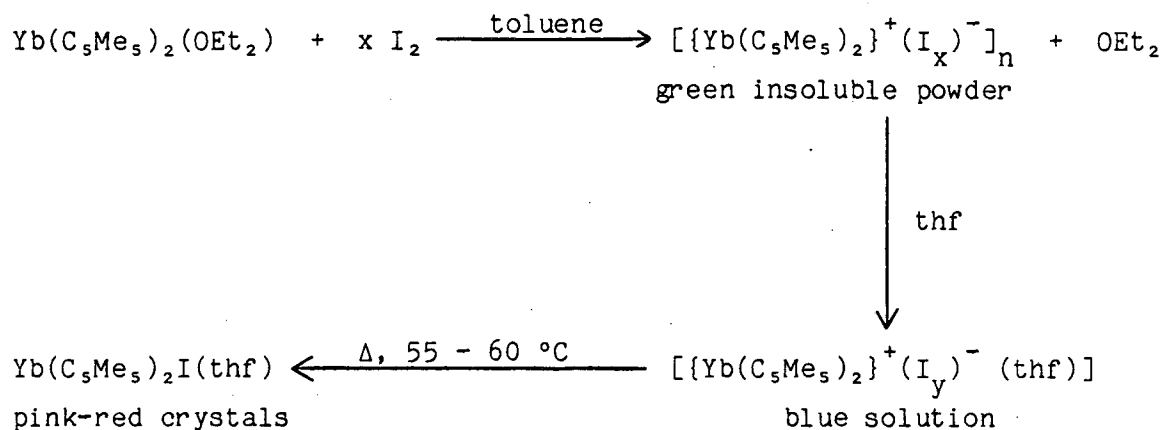
then occurs with loss of a dialkylphosphine radical. The driving force for these reactions is the formation of very strongly bonded chelate complexes of the stable dialkyldithiophosphate ligand with electrophilic metal centers.

Equation 13



The reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with iodine in toluene rapidly produces a bright green, sparingly soluble powder. This material redissolves in tetrahydrofuran to give a deep blue solution. Warming this solution results in an irreversible colour change to golden brown. A very small quantity of red crystals is isolated from this solution which can be identified as the previously prepared $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{I}(\text{thf})$ 22 ²⁵. The various colour changes and the insoluble nature of the initial green powder suggest that a polymeric polyiodide complex is formed which, on warming in tetrahydrofuran, breaks down to 22 (Scheme 3). The tendency of iodine to form polyiodide chains is well known ²⁶ with the most common being the familiar triiodide anion, I_3^- .

Scheme 3



No reaction is observed between $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ and tetraphenyldiphosphine in toluene at room temperature or at reflux for several days. Base-free $\text{Yb}(\text{C}_5\text{Me}_5)_2$ also fails to react with this diphosphine in hexane or toluene. This is almost certainly due to the large size of the diphosphine since formation of a simple coordination is expected with base-free $\text{Yb}(\text{C}_5\text{Me}_5)_2$ even if reductive cleavage of the P-P bond does not occur. The reduction potential of tetraphenyldiphosphine is -2.05 V^{20} so reduction should occur if coordination is able to take place. The reaction with tetraphenyldibismuth also fails to yield any identifiable products, although a reaction with $\text{Yb}(\text{C}_5\text{Me}_5)_2$ does occur in this case. Given the small number of ytterbium phosphide complexes known, it would be worthwhile to investigate the reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ with the smaller tetramethyl- and tetraethyldiphosphines.

Bridging Chalcogenide Complexes

The observation that $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ reduces triphenylphosphine sulphide to form $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-S}]$ ²⁷ suggested that $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ might also be able to reduce phosphine chalcogenides because the oxidation potential of ytterbium(II) is similar to that of uranium(III) in these compounds (-1.35 ²⁸ and -1.5 V²⁹ respectively). The uranium compound has the shortest U-S bond distance reported and yet no magnetic exchange is observed between the sulphide-bridged uranium centers. It was of some interest to determine whether these behaviour patterns also apply to related lanthanide complexes.

The reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with triphenyl or tri-n-butylphosphine sulphide, selenide and telluride produces the bridging chalcogenide complexes:

Equation 14



where R = phenyl, n-butyl
E = S, Se, Te

23 (E = S)
24 (E = Se)
25 (E = Te)

Formation of 23 requires 5 to 8 hours to complete at toluene reflux while the bridging selenide 24 and telluride 25 form rapidly at room temperature. The slow reaction of triphenylphosphine sulphide is probably a reflection of the more negative reduction potential of this molecule compared with the phosphine selenide and telluride since the

reduction potential decreases down group 16 as shown in Table 9. No reduction potentials have been reported for phosphine tellurides, however tri-n-butylphosphine telluride decomposes to the phosphine and elemental tellurium if allowed to warm to room temperature.

Table 9: Reduction Potentials of $(C_6H_5)_3P=E$ Compounds.

<u>E</u>	<u>$-\xi_{1/2}$ (V)^(a)</u>	<u>Reference</u>
O	2.5	30, 31
S	2.4	30
Se	2.1	30

(a) Measured at a dropping mercury electrode relative to S.C.E.

The rate of reaction of $Yb(C_5Me_5)_2(OEt_2)$ with $R_3P=S$ does not depend on diethyl ether dissociation because base-free $Yb(C_5Me_5)_2$ reacts just as slowly as the diethyl etherate.

Some physical properties of the bridging chalcogenide complexes are given in Table 10. The bridging oxide complex cannot be prepared by this route because the reduction potential of the phosphine oxide is too large. This complex has been prepared by Burns³² using a different synthetic strategy and is included for the purpose of comparison. The infrared spectra of all four complexes are superimposable with the exception of one strong band which has been assigned to the Yb-E-Yb asymmetric stretching frequency. The symmetric Yb-E-Yb stretch is not infrared active for a linear molecule but may gain some intensity in a

Table 10: Physical Properties of $[(C_5Me_5)_2Yb]_2[\mu-E]$.

E	m.p.(°C)	Colour	$\nu_{Yb-E-Yb}(cm^{-1})^{(a)}$	1H NMR ($\nu_{1/2}$) ^(b)
O ^(c)	334 - 337	orange	673	24.4 (980)
S	278 - 282	red	379	13.4 (640)
Se	265 - 270	purple	247	12.1 (500)
Te	235 - 238	green	< 225	12.6 (290)

(a) The asymmetric stretching frequency. The band is of strong intensity. (b) Recorded in C_7D_8 at 32 °C. Chemical shifts in ppm downfield of tetramethylsilane; width at half height expressed in Hertz. (c) Prepared by C. Burns, reference 32.

bent geometry. In any event, this band is apparently too weak to observe in these compounds. The asymmetric stretching frequency decreases down the group as expected (Table 10); this stretch is too low in energy to observe in the tellurium compound. The melting point also decreases from oxygen to tellurium. The solubility of the complexes in hydrocarbons follows the inverse trend: the oxide is insoluble while the telluride is very soluble. Similar trends have been observed for the related uranium(IV) compounds, $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-E}]$ ²⁷.

The C_5Me_5 resonance shifts upfield in the proton NMR going from oxygen to selenium but then moves slightly downfield again for tellurium (Table 10). The width of this resonance decreases steadily from oxygen to tellurium. This may be an indication of hindered C_5Me_5 ring rotation, as mentioned earlier in this chapter, because the interference between the rings of the two ytterbium ions must decrease as the Yb-E bond length increases from oxygen to tellurium.

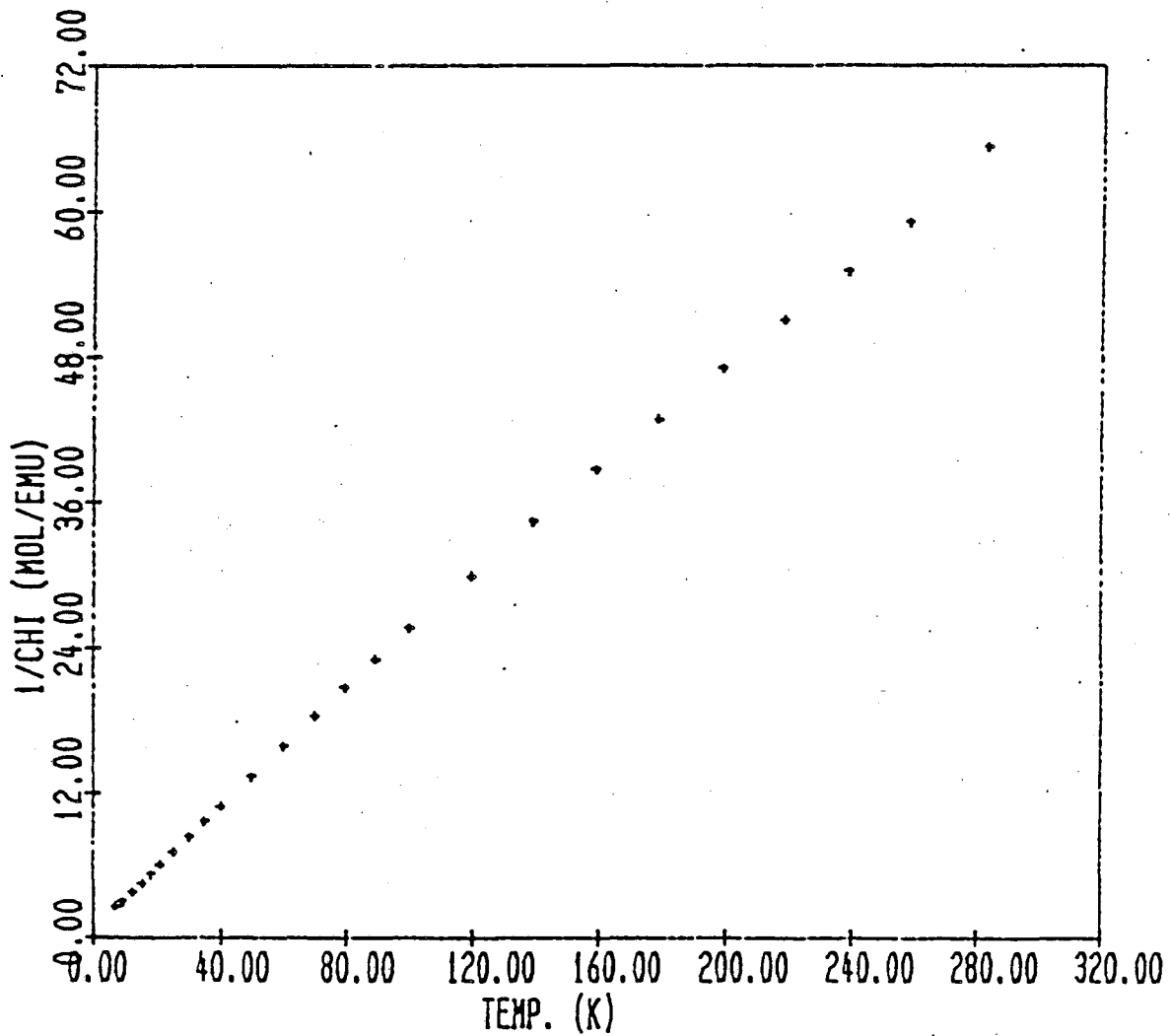
The magnetic susceptibility data for the bridging chalcogenide complexes are summarized in Table 11. The magnetic susceptibility behaviour of all four complexes is typical of non-interacting ytterbium(III) ions in a low symmetry environment as discussed in Chapter 1. The temperature dependence of the magnetic susceptibility is shown in Figure 9 for the bridging selenide complex **24**. Here, as in the uranium(IV) bridging chalcogenide complexes ²⁷, no magnetic interaction is detectable between the ytterbium(III) centers across the chalcogenide dianion. This argues against a significant π contribution to the Yb-E bond.

Table 11: Magnetic Susceptibility Data for $[(C_5Me_5)_2Yb]_2[\mu-E]$.

E	6 - 35 K		100 - 280 K	
	μ (a)	θ (b)	μ	θ
$O^{(c)}$	4.07	-2	4.31	-14
<u>23</u> S	3.86	-2	4.32	-23
<u>24</u> Se	4.14	-1	4.45	-15
<u>25</u> Te	4.20	-2	4.42	-10

(a) The magnetic moment, μ , is calculated as $\mu = 2.828 C^{1/2}$ where C, the Curie constant, is the reciprocal slope from the plot of $[\chi_M(\text{corr})]^{-1}$ vs. T. Moments are expressed in Bohr magnetons per Yb(III). The values of μ and θ are averaged over two field strengths (5 and 40 kGauss). The $\chi(\text{corr})$ values are corrected for container and sample diamagnetism. (b) in degrees Kelvin. (c) prepared by C. Burns, reference 32.

Figure 9 Plot of χ^{-1} versus T for $[(C_5Me_5)_2Yb]_2[\mu-Se]_{24}$.



A single crystal x-ray diffraction study has been performed by Zalkin on the bridging selenide complex 24³². Selected bond distances and angles are given in Table 12 and an ORTEP plot is shown in Figure 10. The molecule has a crystallographic two-fold axis with an Yb-Se-Yb angle of 171.09(6)°. The average Yb-C(ring) distance of 2.2609 ± .007 Å and the Yb-ring centroid distance of 2.32 Å are consistent with seven-coordinate ytterbium(III)³³. The Yb-Se distance of 2.621(1) Å is considerably shorter than that in CdYb₂Se₄ (2.89 Å)³⁴ or Yb₂Se₃ (2.83 Å)³⁵, the only other ytterbium-selenium distances known. The samarium(III) bridging oxide complex [Sm(C₅Me₅)₂]₂[μ-O] has been structurally characterized³⁶. After correcting for the bond length differences going from oxygen to selenium³⁷ and from samarium(III) to ytterbium(III) in seven-coordination³⁸, the Yb-Se distance is predicted to be 0.40 Å greater than the Sm-O distance. The observed Yb-Se distance is 0.63 Å larger. Thus by one comparison the Yb-Se bond length is long while by another it is short. The short Yb-Se bond length, as compared with the inorganic ytterbium selenides, and the near linear Yb-Se-Yb angle could imply some Yb-Se π-bonding. It is much more likely however that this angle is a function of the bulky C₅Me₅ rings on ytterbium. Repulsion between the rings prevents further bending and hinders development of the lone pairs at selenium.

Figure 10 ORTEP Plot of $[(C_5Me_5)_2Yb]_2[\mu-Se]$ 24.

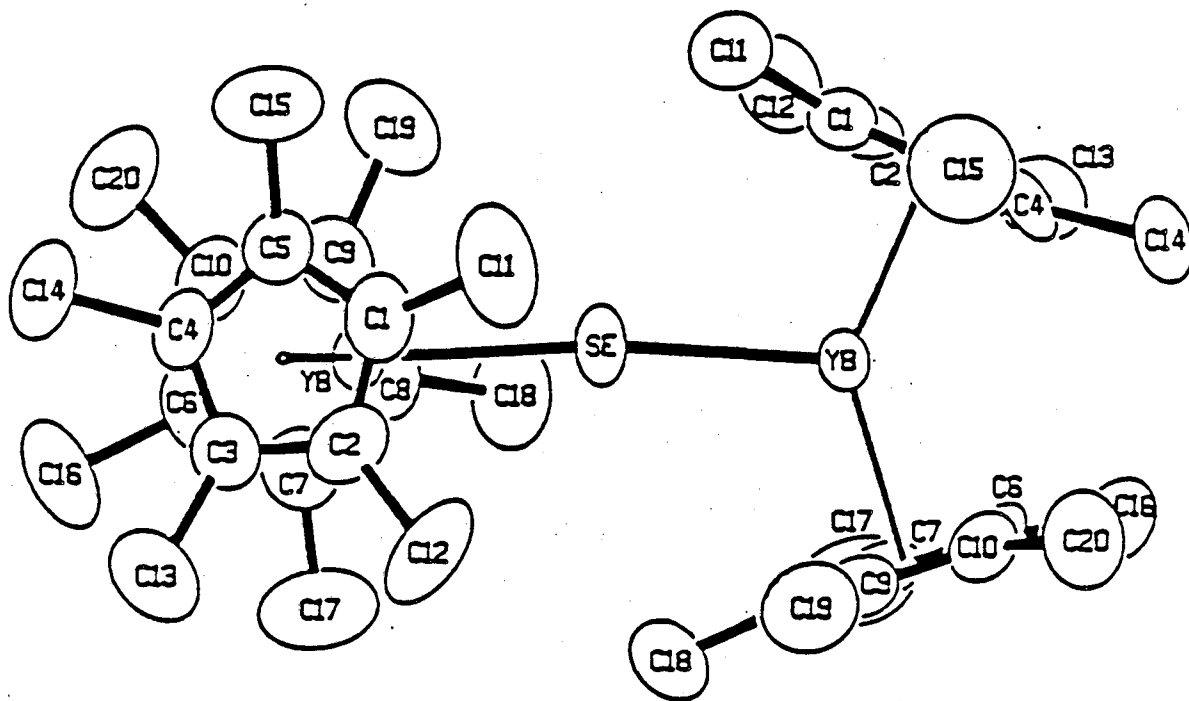
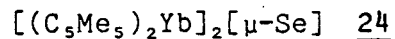


Table 12: Selected Distances (Å) and Angles (°) in



Yb - Cp(1) ^(a)	2.317
Yb - Cp(2)	2.321
Yb - Se	2.621(1)
<Yb - C(Cp)>	2.610(8)
<C(Cp) - C(Cp)>	1.41(2)
<C(Cp) - C(Me)>	1.54(1)
Yb - Se - Yb	171.09(6)
Cp(1) - Yb - Se	110.39
Cp(2) - Yb - Se	110.63
Cp(1) - Yb - Cp(2)	138.94

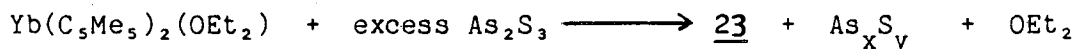
(a) Cp(1) and Cp(2) are the centroids of the C₅Me₅ rings (atoms C(1) - C(5) and C(6) - C(10)).

The bridging sulphide complex 23 can also be synthesized from inorganic sulphur sources such as carbonyl sulphide gas (Equation 15) or As_2S_3 (Equation 16) although the yields are lower. The bridging selenide 24 and bridging telluride 25 can be prepared by reaction with the powdered non-metals (Equation 17). The analogous reaction with elemental sulphur (S_8) does not produce 23 although a reaction does occur. Instead a blue-green solution is obtained initially which changes colour on standing to purple and then brown with deposition of sulphur. The colour is dependent on stoichiometry but the reaction products appear to be unstable with respect to elemental sulphur. No ytterbium containing species are obtained as crystalline products. The series of colour changes and slow decomposition to elemental sulphur suggest that the reaction produces a complex mixture of polysulphide anions which slowly decompose to smaller, unknown, ytterbium sulphide species since polysulphide anions are known to be highly coloured ³⁹. Presumably, the much lower tendency to catenate ⁴⁰ allows isolation of the selenium and tellurium complexes.

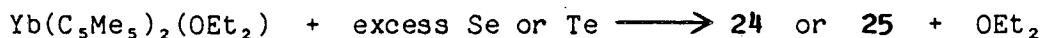
Equation 15



Equation 16



Equation 17



The crystal structure of a novel bridging ditelluride complex 26 has been performed by Zalkin ¹¹. This crystal was obtained from the reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with an excess of tellurium metal. Melting point, analysis and the infrared and mass spectra all indicate that this crystal is not representative of the bulk reaction product; the principle product is the single tellurium bridged complex 25 discussed earlier in this chapter. Attempts to isolate quantities of 26 sufficient for characterization have been unsuccessful. At the present time, this compound must only be considered as an interesting structure. Some selected bond distances and angles are given in Table 13. An ORTEP plot of this molecule is shown in Figure 11.

The structure consists of a Te_2^{2-} unit, formally analogous to a peroxide group, bridging two $\text{Yb}(\text{C}_5\text{Me}_5)_2$ units. The ditelluride bridge is located midway between the ytterbium centers and the Te-Te bond is very nearly normal to the Yb-Yb vector. This vector passes through the midpoint of the Te-Te bond such that the two unique Yb-Te distances are almost identical at 3.1512(9) and 3.1598(7) Å. No lanthanide complexes containing the ditelluride unit have been reported in the literature, so there is no basis for comparison. The Te-Te distance of 2.7685(11) Å compares well with the Te-Te single bond distance of 2.712 Å in diphenyl ditelluride ¹². A Te-Te bond length of 2.81 Å has been reported for elemental tellurium while a value of 2.61 Å has been determined for gaseous Te_2 ¹¹. Only three reports of transition metal- ditelluride complexes have appeared in the literature ^{12 13} and only $[\{\text{MeC}(\text{CH}_2\text{PPh}_2)_3\}\text{Ni}]_2[\mu\text{-Te}_2]\cdot 2\text{C}_4\text{H}_8\text{O}$ ¹³ contains the same bridging geometry as 26. The Te-Te distance in this complex is 2.802(1) Å.

Transition metal complexes containing the analogous disulphide and diselenide units are also known ⁴⁴.

Figure 11 ORTEP Plot of $[(C_5Me_5)_2Yb]_2[\mu-Te_2]$ 26.

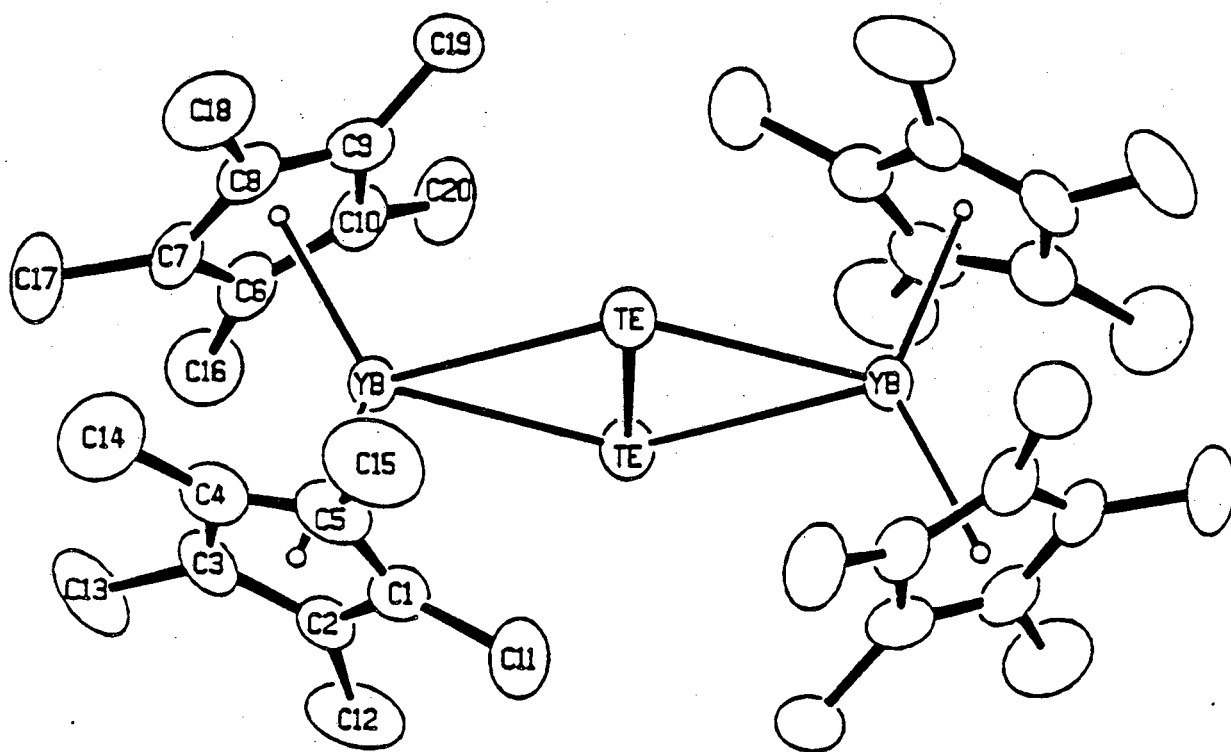
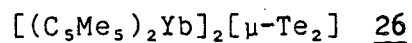


Table 13: Selected Distances (Å) and Angles (°) in

Yb - Cp(1) ^(a)	2.320
Yb - Cp(2)	2.344
<Yb - C(Cp)>	2.63(2)
<C(Cp) - C(Cp)>	1.42(1)
<C(Cp) - C(Me)>	1.52(1)
Yb - Te	3.1512(9)
Yb - Te' ^(b)	3.1598(7)
Te - Te'	2.769(1)
Cp(1) - Yb - Cp(2)	133.26
Yb - Te - Yb'	127.96(2)
Yb - Te - Te'	63.82(2)
Yb' - Te - Te'	64.14(2)
Te - Yb - Te'	52.04(2)

(a) Cp(1) and Cp(2) are the centroids of the C₅Me₅ rings.

(b) ' designates an atom at -x, -y, -z.

Experimental

Standard Schlenk techniques were used in the manipulation of all air sensitive compounds. Unless otherwise specified, all starting materials were commercial samples used as received. The preparation of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ and $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ have been previously reported ⁴⁵.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S-C}_6\text{H}_5)(\text{OEt}_2)$; 1

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.84 g, 1.6 mmol) and diphenyl disulphide (0.18 g, 0.81 mmol) were weighed into a Schlenk tube under nitrogen. Approximately 60 mL of dry ether was added to the solids by canula with vigorous stirring. An immediate colour change to deep purple was observed. After 1 h the solution was canula filtered, and the filtrate was concentrated to 20 mL, and cooled to -10°C overnight. Filtration afforded dark purple needles. Hydrolysis of a small amount of the compound with $\text{D}_2\text{O} / \text{C}_6\text{D}_6$ disclosed the presence of one equivalent of diethyl ether in the organic phase by proton NMR. Yield: 0.37 g (40 %). m.p. $62 - 65^\circ\text{C}$. IR (Nujol, CsI): 2720 (w), 1576 (w), 1142 (w), 1082 (s), 1020 (s), 732 (vs), 690 (s), 472 (w), 420 (vw), 375 (br w), 300 (br s), 225 (br m) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32°C): δ 73.2 ppm (2H, $\nu_{1/2} = 300$ Hz), 42.6 (1H, $\nu_{1/2} = 100$ Hz), 9.7 (30H, $\nu_{1/2} = 540$ Hz), 5.5 (2H, $\nu_{1/2} = 50$ Hz). M.S. (E.I.) $m/e = 553$ amu ($\text{M}^+ - \text{OEt}_2$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 418 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{S-C}_6\text{H}_5)^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 283 ($\text{Yb}(\text{S-C}_6\text{H}_5)^+$). Anal. Calcd for $\text{C}_{30}\text{H}_{45}\text{OSYb}$: C, 57.5; H, 7.24; S, 5.12 %. Found: C, 56.3; H, 6.74; S, 5.28 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S-p-C}_7\text{H}_7)(\text{OEt}_2)$; 2

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.50 g, 0.97 mmol) and di-p-tolyl disulphide (0.11 g, 0.46 mmol) were weighed into a Schlenk flask under nitrogen and dissolved in 75 mL of diethyl ether. The resulting purple solution was stirred for 2 h, filtered and the filtrate was concentrated to 30 mL. Cooling to $-15\text{ }^\circ\text{C}$ yielded dark purple prisms. Yield: 0.53 g (70 %). m.p. $127 - 129\text{ }^\circ\text{C}$. IR (Nujol, CsI): 2730 (w), 1595 (w), 1480 (m), 1220 (w), 1085 (m), 1072 (m), 1012 (m), 800 (s), 788 (sh w), 720 (w), 625 (w), 490 (m), 390 (w), 380 (w), 310 (s) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , $32\text{ }^\circ\text{C}$): δ 76.4 ppm (2H, $\nu_{1/2} = 300\text{ Hz}$), 30.3 (3H, $\nu_{1/2} = 50\text{ Hz}$), 8.5 (30H, $\nu_{1/2} = 500\text{ Hz}$), 5.5 (2H, $\nu_{1/2} = 35\text{ Hz}$). M.S. (E.I.): $m/e = 567\text{ amu}$ ($\text{M}^+ - \text{OEt}_2$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 432 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{S-p-C}_7\text{H}_7)^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 297 ($\text{Yb}(\text{S-p-C}_7\text{H}_7)^+$). Anal. Calcd for $\text{C}_{31}\text{H}_{47}\text{OSYb}$: C, 58.1; H, 7.40; S, 5.01 %. Found: C, 57.7; H, 7.21; S, 3.90 %.

 $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S-m-C}_7\text{H}_7)(\text{OEt}_2)$; 3

Di-m-tolyl disulphide was prepared by the oxidative coupling of m-thiocresol with iodine in diethyl ether according to a literature procedure ⁶. $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (1.43 g, 2.76 mmol) and di-m-tolyl disulphide (0.34 g, 1.38 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 150 mL of dry ether. The purple solution was stirred for 1 h, filtered and the filtrate was concentrated to 40 mL. Cooling the concentrated filtrate to $-20\text{ }^\circ\text{C}$ produced dark purple prisms. Yield: 1.52 g (86 %). m.p. $130 - 132\text{ }^\circ\text{C}$. IR (Nujol, CsI): 3080 (vw), 3045 (w), 2720 (m), 1585 (s), 1569 (s), 1260 (w), 1212 (w), 1160

(m), 1098 (m), 1076 (s), 1019 (m), 862 (w), 849 (s), 800 (w), 760 (vs), 684 (s), 679 (sh s), 591 (w-m), 518 (vw), 490 (vw), 441 (vw), 420 (vw), 375 (br vs) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32 °C): δ 78.4 ppm (1H, $\nu_{1/2}$ = 250 Hz), 56.0 (3H, $\nu_{1/2}$ = 130 Hz), 44.7 (1H, $\nu_{1/2}$ = 60 Hz), 9.2 (31H, $\nu_{1/2}$ = 330 Hz), 5.9 (1H, $\nu_{1/2}$ = 100 Hz). M.S. (E.I.): m/e = 567 amu ($\text{M}^+ - \text{OEt}_2$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 432 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{S-m-C}_7\text{H}_7)^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 297 ($\text{Yb}(\text{S-m-C}_7\text{H}_7)^+$).

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S-mesityl})$; 4

Dimesityl disulphide was prepared by the reaction of iodomesitylene with CuSCN in HMPA at 195 °C ⁴⁷. Iodomesitylene ⁴⁸ and CuSCN ⁴⁹ were prepared according to a literature procedure. $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.63 g, 1.2 mmol) and dimesityl disulphide (0.18 g, 0.61 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 80 mL of diethyl ether. The dark purple solution was stirred for 2 h, filtered and the filtrate concentrated to 20 mL. Cooling to -20 °C gave dark purple blocks. Hydrolysis of small samples of this compound repeatedly failed to disclose the presence of any diethyl ether by proton NMR. Yield: 0.65 g (89 %). m.p. 159 -163 °C. IR (Nujol, CsI): 3060 (vw), 3020 (vw), 2725 (w), 1717 (w), 1600 (w), 1560 (br w), 1345 (w), 1295 (w), 1171 (m), 1150 (m), 1090 (s), 1051 (s), 1018 (s), 962 (vw), 948 (w-m), 923 (vw), 843 (vs), 799 (m), 710 (m), 703 (w-m), 669 (w), 619 (s), 560 (w), 549 (m), 395 (s), 323 (vs), 312 (sh w), 300 (sh w) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32 °C): δ 18.6 ppm (3H, $\nu_{1/2}$ = 80 Hz), 9.2 (30H, $\nu_{1/2}$ = 460 Hz), 3.7 (6H, $\nu_{1/2}$ = 25 Hz). M.S. (E.I.): m/e =

595 amu (M^+), 460 ($Yb(C_5Me_5)(S\text{-mesityl})^+$), 444 ($Yb(C_5Me_5)_2^+$), 324 ($Yb(S\text{-mesityl})^+$), 309 ($Yb(C_5Me_5)^+$). Anal. Calcd for $C_{29}H_{41}SYb$: C, 58.6; H, 6.95; S, 5.39 %. Found: C, 58.3; H, 6.95; S, 5.25 %.

$Yb(C_5Me_5)_2(S\text{-CH}_2C_6H_5)(OEt_2)$; 5

$Yb(C_5Me_5)_2(OEt_2)$ (0.76 g, 1.5 mmol) and dibenzyl disulphide (0.18 g, 0.73 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 100 mL of ether. The burgundy coloured solution was stirred 1 h, filtered and the filtrate concentrated to 20 mL. Cooling to $-20\text{ }^\circ\text{C}$ overnight produced purple crystals. Yield: 0.59 g (61 %). m.p. $152 - 156\text{ }^\circ\text{C}$. IR (Nujol, CsI): 3063 (vw), 2720 (w), 1600 (w), 1492 (m), 1322 (vw), 1289 (vw), 1262 (w), 1221 (w), 1187 (w), 1143 (w), 1121 (vw), 1090 (br w), 1067 (w), 1039 (m), 1033 (m), 998 (w), 915 (w), 890 (w-m), 850 (vw), 803 (br s), 768 (br s), 709 (vs), 697 (vs), 680 (w), 623 (vw), 595 (vw), 563 (m), 523 (w-m), 468 (w), 377 (br m), 350 (w), 310 (vs), 301 (vs), 290 (sh s) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , $32\text{ }^\circ\text{C}$): δ 36.4 ppm (2H, $\nu_{1/2} = 60\text{ Hz}$), 17.0 (2H, $\nu_{1/2} = 40\text{ Hz}$), 14.7 (1H, $\nu_{1/2} = 30\text{ Hz}$), 4.2 (30H, $\nu_{1/2} = 165\text{ Hz}$), -6.8 (2H, $\nu_{1/2} = 34\text{ Hz}$). M.S. (E.I.): $m/e = 595\text{ amu}$ ($M^+ - OEt_2$), 460 ($Yb(C_5Me_5)(S\text{-CH}_2C_6H_5)^+$), 444 ($Yb(C_5Me_5)_2^+$), 324 ($Yb(S\text{-CH}_2C_6H_5)^+$), 309 ($Yb(C_5Me_5)^+$). Anal. Calcd for $C_{31}H_{47}OSYb$: C, 58.1; H, 7.40; S, 5.01 %. Found: C, 55.6; H, 6.81; S, 4.09 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Se}-\text{C}_6\text{H}_5)(\text{OEt}_2)$; 6

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.68 g, 1.3 mmol) and diphenyl disulphide (0.20 g, 0.64 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 100 mL of hexane. The purple solution was stirred for 1 h, filtered and the filtrate was concentrated to 25 mL. Cooling at $-25\text{ }^\circ\text{C}$ produced purple crystals. Yield: 0.67 g (76 %). m.p. $156 - 160\text{ }^\circ\text{C}$. IR (Nujol, CsI): 3066 (w), 2723 (w), 1576 (s), 1469 (vs), 1460 (sh w), 1151 (w), 1093 (w), 1072 (s), 1021 (s), 802 (br w-m), 728 (vs), 690 (s), 668 (m), 580 (br w), 462 (br m), 384 (br m-s), 304 (vs), 281 (m-s) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , $32\text{ }^\circ\text{C}$): δ 62.7 ppm (2H, $\nu_{1/2} = 167\text{ Hz}$), 37.9 (1H, $\nu_{1/2} = 66\text{ Hz}$), 9.7 (32H, $\nu_{1/2} = 300\text{ Hz}$). M.S. (E.I.): $m/e = 601\text{ amu}$ ($\text{M}^+ - \text{Et}_2\text{O}$), 464 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{Se}-\text{C}_6\text{H}_5)^+$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 331 ($\text{Yb}(\text{Se}-\text{C}_6\text{H}_5)^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 158 ($\text{Se}-\text{C}_6\text{H}_5^+$). Anal. Calcd for $\text{C}_{30}\text{H}_{45}\text{OSeYb}$: C, 53.5; H, 6.73 %. Found: C, 49.6; H, 5.75 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Te}-\text{C}_6\text{H}_5)(\text{OEt}_2)$; 7

Diphenyl ditelluride was prepared from phenyllithium and tellurium metal ⁵⁰. $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.62 g, 1.2 mmol) and diphenyl ditelluride (0.24 g, 0.59 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 100 mL of hexane. The dark blue-green solution was stirred for 3 h, filtered and the filtrate was concentrated to 20 mL. Cooling at $-78\text{ }^\circ\text{C}$ produced olive green crystals. Yield: 0.25 g (29 %). m.p. $142 - 145\text{ }^\circ\text{C}$. IR (Nujol, CsI): 3064 (w), 2725 (w), 1570 (s), 1434 (s), 1325 (vw), 1298 (vw), 1261 (w), 1155 (vw), 1093 (br w), 1059 (w), 1016 (m-s), 1000 (w), 904 (vw), 802 (br m), 727 (vs), 696 (s), 653 (m), 460

(w), 386 (m), 306 (vs) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 21 $^\circ\text{C}$): δ 46.2 ppm (2H, $\nu_{1/2} = 300$ Hz), 16.4 (2H, $\nu_{1/2} = 100$ Hz), 11.9 (1H, $\nu_{1/2} = 80$ Hz), 8.5 (30H, $\nu_{1/2} = 145$ Hz). Anal. Calcd for $\text{C}_{30}\text{H}_{45}\text{OTeYb}$: C, 49.9; H, 6.28 %. Found: C, 43.6; H, 5.12 %.

$[\text{Yb}(\text{C}_5\text{Me}_5)(\text{S}-\text{CH}_2\text{C}_6\text{H}_5)_2]_2$; 8

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.47 g, 0.91 mmol) and dibenzyl disulphide (0.11 g, 0.45 mmol) were weighed into a Schlenk tube under nitrogen. A solution of benzylthiol (0.11 mL, 1.0 mmol) in 100 mL of toluene was added to the solids with stirring. The solution initially turned purple but changed colour to deep turquoise after a few minutes. Stirring was maintained 2 h, then the solution was filtered and the filtrate was concentrated to 20 mL. Cooling at -78 $^\circ\text{C}$ for several days produced fine turquoise needles. Hydrolysis failed to disclose the presence of any diethyl ether by proton NMR. Yield: 0.27 g (53 %). m.p. dec. 230 $^\circ\text{C}$. IR (Nujol, CsI): 3061 (w), 3025 (vw), 2720 (w), 1946 (vw), 1883 (vw), 1809 (vw), 1601 (s), 1583 (w), 1493 (m-s), 1451 (s), 1366 (w), 1317 (w), 1259 (vw), 1230 (m-s), 1196 (vw), 1182 (w), 1153 (w), 1099 (vw), 1070 (m), 1029 (m), 918 (w), 854 (w), 816 (vw), 803 (w), 754 (w-m), 738 (w), 703 (vs), 618 (vw), 589 (vw), 563 (w), 463 (w), 388 (br w), 350 (br vw), 317 (sh w), 309 (s), 249 (m-s) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 $^\circ\text{C}$): δ 68.9 ppm (4H, $\nu_{1/2} = 95$ Hz), 37.0 (4H, $\nu_{1/2} = 29$ Hz), 18.4 (4H, $\nu_{1/2} = 22$ Hz), 14.8 (2H, $\nu_{1/2} = 22$ Hz), -0.7 (15H, $\nu_{1/2} = 40$ Hz). Anal. Calcd for $\text{C}_{24}\text{H}_{29}\text{S}_2\text{Yb}$: C, 52.0; H, 5.27 %. Found: C, 52.6; H, 5.26 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}-\text{C}_6\text{H}_5)(\text{NH}_3)$; 9

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (0.57 g, 1.2 mmol) and diphenyl disulphide (0.13 g, 0.60 mmol) were weighed into a Schlenk tube under nitrogen and suspended in 60 mL of toluene. After stirring 2 h, the dark red solution was filtered, then the filtrate was concentrated to 25 mL and cooled to $-20\text{ }^\circ\text{C}$. Fine red crystals were isolated from the mother liquors by canula filtration. The crystals rapidly turned magenta in colour upon exposure to vacuum. Yield: 0.53 g (78 %). m.p. 206 - 208 $^\circ\text{C}$. IR (Nujol mull, CsI): 3350 (w-m), 3266 (w), 3058 (w), 2723 (w), 1596 (sh w), 1577 (m-s), 1560 (w), 1220 (vs), 1188 (vw), 1130 (vw), 1085 (s), 1062 (w), 1023 (m), 893 (w), 800 (vw), 740 (vs), 735 (sh w), 700 (s), 693 (s), 596 (vw), 507 (br m), 484 (m), 429 (w), 382 (w), 302 (vs), 280 (sh w) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , $32\text{ }^\circ\text{C}$): δ 40.0 ppm (2H, $\nu_{1/2}$ = 95 Hz), 12.8 (2H, $\nu_{1/2}$ = 25 Hz), 8.7 (1H, $\nu_{1/2}$ = 20 Hz), 3.8 (30H, $\nu_{1/2}$ = 55 Hz). Anal. Calcd for $\text{C}_{26}\text{H}_{38}\text{NSYb}$: C, 54.8; H, 6.72; N, 2.46 %. Found: C, 54.7; H, 6.84; N, 2.34 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}-p\text{-C}_7\text{H}_7)(\text{NH}_3)$; 10

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (0.73 g, 1.5 mmol) and di-p-tolyl disulphide (0.19 g, 0.77 mmol) were weighed into a Schlenk tube and suspended in 120 mL of toluene. The solution immediately turned dark red with dissolution of the solids. After 1 h the solution was filtered and the filtrate was concentrated to 40 mL. Cooling at $-20\text{ }^\circ\text{C}$ overnight yielded fine red crystals which turned magenta in colour on vacuum drying. Yield: 0.78 g (88 %). m.p. 208 - 211 $^\circ\text{C}$. IR (Nujol, CsI): 3360 (m), 3275 (w-m), 3090 (vw), 3060 (w), 2730 (m) 1890 (vw), 1790 (vw), 1642

(vw), 1595 (br s), 1481 (s), 1212 (vs), 1100 (w), 1087 (s), 1012 (br s), 808 (vs), 792 (sh w), 720 (w), 630 (m), 595 (w), 510 (sh w), 495 (s), 395 (br m), 370 (br m), 295 (s), 275 (sh w) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 $^\circ\text{C}$): δ 38.8 ppm (2H, $\nu_{1/2}$ = 110 Hz), 12.7 (2H, $\nu_{1/2}$ = 22 Hz), 3.8 (33H, $\nu_{1/2}$ = 63 Hz). Anal. Calcd for $\text{C}_{27}\text{H}_{40}\text{NSYb}$: C, 55.6; H, 6.91; N, 2.40 %. Found: C, 55.4; H, 6.72; N, 2.24 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S-}m\text{-C}_7\text{H}_7)(\text{NH}_3)$; 11

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (0.62 g, 1.3 mmol) and di-*m*-tolyl disulphide (0.17 g, 0.65 mmol) were weighed into a Schlenk tube and suspended in 100 mL of toluene. The wine red solution was stirred for 2 h, filtered and the filtrate concentrated to 40 mL. Cooling at -25 $^\circ\text{C}$ yielded red needles which rapidly turned magenta in colour on vacuum drying. Yield: 0.59 g (78 %). m.p. 206 - 207 $^\circ\text{C}$. IR (Nujol, CsI): 3356 (w), 3267 (vw), 2724 (w), 1599 (sh w), 1585 (s), 1566 (m), 1217 (vs), 1161 (vw), 1097 (w), 1075 (w), 1021 (br w), 893 (vw), 854 (br m), 809 (br w), 774 (vs), 729 (br w), 696 (m-s), 679 (w-m), 510 (br m-s), 438 (w-m), 381 (w), 300 (s), 279 (w), 255 (w) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 $^\circ\text{C}$): δ 51.6 ppm (1H, $\nu_{1/2}$ = 120 Hz), 41.7 (1H, $\nu_{1/2}$ = 100 Hz), 14.0 (1H, $\nu_{1/2}$ = 20 Hz), 9.8 (4H, $\nu_{1/2}$ = 12 Hz), 3.8 (30H, $\nu_{1/2}$ = 57 Hz); (75 $^\circ\text{C}$): δ 40.2 ppm (1H, $\nu_{1/2}$ = 100 Hz), 33.5 (1H, $\nu_{1/2}$ = 100 Hz), 12.3 (1H, $\nu_{1/2}$ = 20 Hz), 8.9 (1H, $\nu_{1/2}$ = 22 Hz), 7.8 (3H, $\nu_{1/2}$ = 10 Hz), 3.4 (30H, $\nu_{1/2}$ = 50 Hz). Anal. Calcd for $\text{C}_{27}\text{H}_{40}\text{NSYb}$: C, 55.6; H, 6.91; N, 2.40 %. Found: C, 55.3; H, 6.90; N, 2.28 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}-\text{CH}_2\text{C}_6\text{H}_5)(\text{NH}_3)$; 12

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (0.80 g, 1.7 mmol) and dibenzyl disulphide (0.22 g, 0.88 mmol) were weighed out under nitrogen and dissolved in 60 mL of toluene with stirring. The dark red solution was stirred for 2 h, filtered, and the filtrate concentrated to 20 mL and cooled to -10°C for several days. Dark red crystals were isolated by filtration of the mother liquor and subsequently recrystallized from toluene / hexane at -10°C . Yield: 0.65g (66%). m.p. 221 - 223 $^\circ\text{C}$. IR (Nujol, CsI): 3362 (w), 3318 (w), 3201 (w), 3119 (w-m), 2725 (w-m), 1597 (m), 1492 (m), 1260 (vs), 1221 (w), 1156 (w), 1065 (m), 1023 (m), 1000 (w), 920 (w), 803 (w-m), 775 (m), 725 (vw), 704 (vs), 691 (w), 562 (w), 516 (br m), 375 (br w), 313 (m), 303 (vs), 282 (sh w) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 20°C): δ 11.2 ppm (1H, $\nu_{1/2} = 46$ Hz), 9.1 (2H, $\nu_{1/2} = 30$ Hz), 4.0 (30H, $\nu_{1/2} = 70$ Hz), -2.4 (2H, $\nu_{1/2} = 49$ Hz), -16.1 (2H, $\nu_{1/2} = 78$ Hz). Anal. Calcd for $\text{C}_{27}\text{H}_{40}\text{NSYb}$: C, 55.6; H, 6.91; N, 2.40; S, 5.49 %. Found: C, 55.7; H, 7.09; N, 2.36; S, 5.46 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}-\text{CH}_3)(\text{NH}_3)$; 13

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (0.65 g, 1.4 mmol) was weighed into a Schlenk tube under nitrogen and suspended in 50 mL of toluene. Distilled dimethyl disulphide (0.14 mL, 1.5 mmol) was added to the stirred suspension by syringe. The cherry red solution was allowed to stir for 2 h, filtered and the filtrate concentrated to 20 mL. Cooling at -20°C overnight produced red crystals which did not change colour on vacuum drying. Yield: 0.35g (49%). m.p. 174 - 176 $^\circ\text{C}$. IR (Nujol, CsI): 3374 (m), 3320 (m), 3203 (w), 3115 (m), 2722 (w-m), 1773 (br w), 1595 (s),

1309 (m), 1259 (sh w), 1227 (vs), 1166 (vw), 1152 (vw), 1090 (w), 1060 (w), 1022 (m-s), 944 (br w), 802 (br m), 726 (w-m), 702 (w-m), 656 (w), 542 (br s), 386 (br m), 375 (m), 305 (vs), 282 (sh w) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 21 °C): δ 4.1 ppm (30H, $\nu_{1/2}$ = 65 Hz), -5.9 (3H, $\nu_{1/2}$ = 67 Hz).

M.S. (E.I.): m/e = 491 amu ($\text{M}^+ - \text{NH}_3$), 476 ($\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S})^+$), 444

($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 221 ($\text{Yb}(\text{S}-\text{CH}_3)^+$), 206 (YbS^+). Anal.

Calcd for $\text{C}_{21}\text{H}_{36}\text{NSYb}$: C, 49.7; H, 7.13; N, 2.75; S, 6.32 %. Found: C, 49.8; H, 7.28; N, 2.95; S, 6.02 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Se}-\text{C}_6\text{H}_5)(\text{NH}_3)$; 14

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (0.68 g, 1.4 mmol) and diphenyl diselenide (0.22 g, 0.71 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 100 mL of toluene with stirring. After 2 h, the solution was canula filtered, the filtrate was concentrated to 40 mL, and cooled at -20 °C overnight. Dark red crystals were isolated from the mother liquors by canula filtration. A rapid colour change to magenta was observed when the crystals were exposed to vacuum. Yield: 0.76g (87%).

m.p. 195 - 198 °C. IR (Nujol, CsI): 3355 (w), 3314 (vw), 3264 (w), 3056 (w-m), 2726 (w), 1594 (br w), 1574 (s), 1221 (vs), 1067 (m-s), 1021 (m-s), 734 (vs), 694 (s), 675 (m), 525 (br m), 470 (m), 384 (br m), 301 (vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 °C): δ 25.1 ppm (2H, $\nu_{1/2}$ = 60 Hz), 9.6 (2H, $\nu_{1/2}$ = 30 Hz), 7.4 (1H, $\nu_{1/2}$ = 35 Hz), 4.3 (30H, $\nu_{1/2}$ = 43 Hz). Anal.

Calcd for $\text{C}_{26}\text{H}_{38}\text{NSeYb}$: C, 50.6; H, 6.21; N, 2.27 %. Found: C, 50.2; H, 6.21; N, 2.07 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{Te}-\text{C}_6\text{H}_5)(\text{NH}_3)$; 15

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (0.86 g, 1.8 mmol) and diphenyl ditelluride (0.37 g, 0.90 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 80 mL of toluene with stirring. The red-brown solution was stirred for 3 h, filtered and the filtrate concentrated to 20 mL. Cooling at $-20\text{ }^\circ\text{C}$ for several days yielded dark purple needles. A second crop was obtained by further cooling of the mother liquor to $-78\text{ }^\circ\text{C}$. Yield: 0.65g (54%). m.p. 190 - 191 $^\circ\text{C}$. IR (Nujol, CsI): 3353 (w), 3254 (w), 3063 (vw), 3047 (vw), 2724 (w), 1955 (vw), 1941 (vw), 1882 (vw), 1867 (vw), 1811 (vw), 1753 (vw), 1570 (m-s), 1487 (m), 1430 (m), 1298 (vw), 1226 (vs), 1155 (vw), 1059 (w), 1018 (m), 999 (vw), 803 (br w), 730 (vs), 696 (m-s), 650 (w), 597 (vw), 517 (br m), 491 (br m), 458 (m), 388 (br w-m), 308 (vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 $^\circ\text{C}$): δ 142.9 ppm (3H, $\nu_{1/2}$ = 750 Hz), 16.5 (2H, $\nu_{1/2}$ = 280 Hz), 6.7 (2H, $\nu_{1/2}$ = 34 Hz), 6.0 (1H, $\nu_{1/2}$ = 44 Hz), 4.2 (30H, $\nu_{1/2}$ = 45 Hz). M.S. (E.I.) m/e = 649 amu ($\text{M}^+ - \text{NH}_3$), 461 ($\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)^+$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 410 ($\text{C}_6\text{H}_5\text{TeTeC}_6\text{H}_5^+$), 333 ($\text{C}_6\text{H}_5\text{TeTe}^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 284 ($\text{C}_6\text{H}_5\text{TeC}_6\text{H}_5^+$), 207 ($\text{C}_6\text{H}_5\text{Te}^+$). Anal. Calcd for $\text{C}_{26}\text{H}_{38}\text{NTeYb}$: C, 46.9; H, 5.76; N, 2.10 %. Found: C, 46.9; H, 5.75; N, 2.08 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OCMe}_3)(\text{NH}_3)$; 16

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (0.49 g, 1.0 mmol) was weighed into a Schlenk tube under nitrogen and suspended in 50 mL of toluene. Bis(tert-butyl)peroxide (0.30 mL, 1.6 mmol) was added to the stirred suspension by syringe. The colour of the reaction mixture changed to deep orange

after 1/2 h. Stirring was continued at room temperature for 2 h, then the solvent was removed under reduced pressure. The orange solid was redissolved in hexane and filtered. Concentration of the filtrate to 40 mL and cooling at -10 °C gave orange - red crystals. Several subsequent crops were isolated. Yield: 0.35 g (64 %). m.p. 184 - 186 °C. IR (Nujol, CsI): 3368 (w), 3264 (w), 2720 (w), 1592 (vw), 1349 (m), 1310 (vw), 1196 (vs), 1096 (vw), 1060 (vw), 1000 (vs), 893 (vw), 803 (vw), 789 (w), 727 (w-m), 501 (m), 483 (m), 378 (w), 350 (vw), 285 (br s) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 °C): δ 6.1 ppm (30H, $\nu_{1/2} = 260$ Hz), -57.5 (9H, $\nu_{1/2} = 124$ Hz). M.S. (E.I.): $m/e = 517$ amu ($\text{M}^+ - \text{NH}_3$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 382 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{OCMe}_3)^+$), 367 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{OCMe}_2)^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$). Anal. Calcd for $\text{C}_{24}\text{H}_{42}\text{NOYb}$: C, 54.0; H, 7.93; N, 2.62 %. Found: C, 53.0; H, 7.91; N, 2.49 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OSiMe}_3)(\text{NH}_3)$; 17

Bis(trimethylsilyl)peroxide was prepared from $\text{DABCO} \cdot 2\text{H}_2\text{O}_2$ (DABCO = 1,4-diaza-[2.2.2]-bicyclooctane) and trimethylsilyl chloride ⁵¹. $\text{DABCO} \cdot 2\text{H}_2\text{O}_2$ was prepared in air according to a literature procedure ⁵². $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (1.00 g, 2.09 mmol) was weighed into a Schlenk tube under nitrogen and suspended in 100 mL of toluene. Bis(trimethylsilyl)peroxide (0.31 mL, = 1.1 mmol) was added to the stirred suspension by syringe. An immediate colour change to red-orange was observed. After stirring overnight, the solution was filtered, and the filtrate concentrated to 20 mL and cooled at -25 °C. Dark orange crystals were isolated from the mother liquor by filtration and recrystallized from hexane to give orange plates. Yield: 0.55 g (48 %). m.p. 221 - 222 °C.

IR (Nujol, CsI): 3374 (w), 3289 (w), 2724 (w), 1597 (w), 1253 (m-s), 1240 (vs), 1200 (vs), 980 (br vs), 865 (sh w), 827 (br vs), 803 (sh vw), 746 (s), 669 (m-s), 495 (br s), 385 (br w), 309 (s), 295 (s), 279 (vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32 °C): δ 4.8 ppm (30H, $\nu_{1/2}$ = 210 Hz), -37.4 (9H, $\nu_{1/2}$ = 67 Hz). M.S. (E.I.): m/e = 533 amu ($\text{M}^+ - \text{NH}_3$), 518

($\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OSiMe}_2)^+$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 398 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{OSiMe}_3)^+$), 383 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{OSiMe}_2)^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 263 ($\text{Yb}(\text{OSiMe}_3)^+$), 247 ($\text{Yb}(\text{OSiMe}_2)^+$), 190 (YbO^+). Anal. Calcd for $\text{C}_{23}\text{H}_{42}\text{NOSiYb}$: C, 50.3; H, 7.70; N, 2.55 %. Found: C, 47.1; H, 7.85; N, 2.03 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{CNET}_2)$; 18

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.62 g, 1.2 mmol) and tetraethylthiuram disulphide (0.18 g, 0.61 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 50 mL of pentane with stirring. The solution slowly changed colour from green to dark purple over a period of 2 h. The reaction mixture was filtered, the filtrate was concentrated to 20 mL and cooled to -10 °C overnight. Large purple crystals were isolated from the concentrated mother liquor by canula filtration. Yield: 0.45 g (63 %). m.p. 227 - 228 °C. IR (Nujol, CsI): 2724 (w), 1486 (s), 1423 (s), 1357 (m), 1303 (w), 1275 (s), 1206 (s), 1140 (m), 1088 (m), 1024 (w), 986 (m), 910 (m), 839 (w-m), 800 (w), 778 (w), 608 (br w), 593 (w), 564 (m), 473 (vw), 389 (m), 359 (m), 311 (vs) cm^{-1} .

The melting point and infrared spectrum of this compound were identical with those of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{CNET}_2)$ previously prepared ²⁵ from $[\text{Na}(\text{OEt}_2)_2][\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Cl}_2]$ and $\text{NaS}_2\text{CNET}_2$ in diethyl ether.

$[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{O}_2\text{CC}_6\text{H}_5)]_2$; 19

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.51 g, 0.99 mmol) was dissolved in 100 mL of diethyl ether under nitrogen and precooled to $-78\text{ }^\circ\text{C}$. To this, a solution of benzoylperoxide (0.12 g, 0.50 mmol) in 100 mL of diethyl ether was added dropwise with vigorous stirring. The maroon solution was allowed to warm to room temperature with stirring over a 3 h period, filtered and the filtrate was concentrated to 50 mL. Slow cooling at $-10\text{ }^\circ\text{C}$ produced red prisms. Yield: 0.45 g (80 %). m.p. 248 - 252 $^\circ\text{C}$. IR (Nujol, CsI): 2720 (w), 1623 (sh w), 1601 (vs), 1560 (vs), 1491 (vw), 1447 (w), 1418 (s), 1406 (vw), 1314 (w), 1307 (w), 1275 (w), 1176 (vw), 1120 (vw), 1071 (w), 1024 (m), 847 (w), 816 (sh vw), 803 (w), 718 (vs), 689 (w), 666 (s), 572 (m), 412 (br m), 390 (br w), 307 (vs), 281 (w) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 21 $^\circ\text{C}$): The solution appears to contain three species (A, B, C) in the ratio 1:2:1. Species A: δ 175 ppm (2H, $\nu_{1/2}$ = 85 Hz), 11.1 (30H, $\nu_{1/2}$ = 260 Hz), -5.9 (2H, $\nu_{1/2}$ = 40 Hz), -8.2 (1H ?, $\nu_{1/2}$ = 35 Hz). Species B: δ 54.2 ppm (2H, $\nu_{1/2}$ = 25 Hz), 26.0 (2H, $\nu_{1/2}$ = 45 Hz), 2.1 (1H ?, $\nu_{1/2}$ = 18 Hz), -1.9 (30H, $\nu_{1/2}$ = 65 Hz). Species C: δ 38.1 ppm (2H, $\nu_{1/2}$ = 16 Hz), 18.7 (2H, $\nu_{1/2}$ = 17 Hz), 3.5 (1H, $\nu_{1/2}$ = 15 Hz), 2.3 (30H, $\nu_{1/2}$ = 55 Hz). Anal. Calcd for $\text{C}_{54}\text{H}_{70}\text{O}_4\text{Yb}_2$: C, 57.4; H, 6.25 %. Found: C, 56.8; H, 6.23 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{PMe}_2)$; 20

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.54 g, 1.0 mmol) and tetramethyldiphosphine disulphide (0.20 g, 1.1 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 60 mL of toluene under nitrogen with

stirring. The blue-violet solution was stirred for 2 h, concentrated to 30 mL and cooled at -10 °C overnight. Filtration of the reaction mixture afforded dark violet crystals. Yield: 0.48 g (81 %). m.p. 78 - 82 °C. IR (Nujol, CsI): 2920 (s), 2720 (w), 1290 (w), 1280 (m), 1260 (w), 1015 (w), 945 (s), 910 (m), 845 (w), 795 (vw), 730 (sh w), 720 (s), 622 (w), 590 (s), 495 (s), 375 (br w), 298 (s) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 21 °C): δ 7.5 ppm (30H, $\nu_{1/2}$ = 70 Hz), -23.1 (6H, $\nu_{1/2}$ = 30 Hz). $^{31}\text{P} \{^1\text{H}\}$ NMR: δ - 28.2 ppm. M.S.(E.I.): m/e = 569 amu (M^+), 434 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{S}_2\text{PMe}_2)^+$), 299 ($\text{Yb}(\text{S}_2\text{PMe}_2)^+$), 207 (YbS^+). Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{PS}_2\text{Yb}$: C, 46.5; H, 6.38; S, 11.3 %. Found: C, 46.3; H, 6.37; S, 10.9 %.

The reaction was repeated using about 40 mg $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ and 15 mg tetramethyldiphosphine disulphide in 2 mL of C_6D_6 . The reaction mixture was stirred for 15 minutes, cannulaed directly into an NMR tube and the $^{31}\text{P} \{^1\text{H}\}$ NMR recorded. In addition to the product resonance, two other phosphorus containing products were identified by comparison of their chemical shift and coupling constant (where appropriate) with literature values: Me_2PPMe_2 , singlet δ -58.4 ppm (literature ⁵³: singlet, - 58.7); $\text{Me}_2\text{P}(=\text{S})\text{PMe}_2$, doublets at 36.2 and -59.1 ppm, $J_{\text{PP}'}$ = 220 Hz (literature ⁵⁴: doublets at 35.6 and -58.7, $J_{\text{PP}'}$ = 224 ± 5 Hz). The total integrated intensity of all trivalent phosphorus (those upfield of 85% H_3PO_4 in this case) resonances was approximately equal to that of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{PMe}_2)$. No unreacted tetramethyldiphosphine disulphide was discernible in the reaction mixture.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{PEt}_2)$; 21

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.36 g, 0.70 mmol) and tetraethyldiphosphine disulphide (0.17 g, 0.70 mmol) were weighed into a Schlenk tube under nitrogen and dissolved in 40 mL of toluene with stirring. The purple solution was stirred for 2 h, concentrated to 10 mL and cooled at -78°C over several days. Large purple prisms were isolated from the concentrated mother liquor by filtration. Yield: 0.40 g (96 %). m.p. $75 - 77^\circ\text{C}$. IR (Nujol, CsI): 2724 (w), 1407 (w), 1260 (w), 1227 (vw), 1157 (vw), 1097 (w), 1039 (s), 1028 (s), 977 (w), 802 (m), 767 (s), 744 (m), 738 (m), 712 (m), 671 (s), 623 (sh w), 616 (vs), 507 (s), 386 (br m), 307 (br vs) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32°C): δ 7.4 ppm (30H, $\nu_{1/2} = 71$ Hz), -7.5 (6H, $\nu_{1/2} = 31$ Hz), -27.9 (4H, $\nu_{1/2} = 32$ Hz). $^{31}\text{P} \{^1\text{H}\}$ NMR: δ -5.1 ppm. M.S. (E.I.): $m/e = 597$ amu (M^+), 462 ($\text{Yb}(\text{C}_5\text{Me}_5)(\text{S}_2\text{PMe}_2)^+$), 327 ($\text{Yb}(\text{S}_2\text{PMe}_2)^+$). Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{PS}_2\text{Yb}$: C, 48.3; H, 6.76; S, 10.7 %. Found: C, 48.5; H, 6.92; S, 10.6 %.

The reaction was repeated using about 50 mg $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ and 30 mg tetraethyldiphosphine disulphide in 1.5 mL of C_6D_6 . The reaction mixture was cannulaed directly into an NMR tube and the $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum recorded. In addition to the ytterbium complex, three phosphorous compounds were identified: Et_2PPEt_2 , singlet, δ -32.0 ppm (literature 53 : singlet, -32.7); $\text{Et}_2\text{P}(=\text{S})\text{P}(=\text{S})\text{Et}_2$, singlet, 50.7 (literature 53 : singlet, 51.3); $\text{Et}_2\text{P}(=\text{S})\text{PEt}_2$, doublets at 54.8 and -34.2, $J_{\text{PP}} = 244$ Hz (literature 55 : doublets at 55.3 and -37.1, $J_{\text{PP}} = 243$ Hz). The total integrated intensity for all trivalent phosphorous resonances was approximately equal to that of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{PEt}_2)$.

Yb(C₅Me₅)₂I(thf); 22

Yb(C₅Me₅)₂(OEt₂) (1.15 g, 2.22 mmol) was weighed into a Schlenk flask under nitrogen and dissolved in 40 mL of toluene. A solution of iodine (0.30 g, 1.2 mmol) in 20 mL of toluene was added with vigorous stirring. The solution changed colour to deep blue-green with precipitation of a bright green solid. After stirring 1 h, the solvent was removed and the insoluble residue was washed thoroughly with hexane. The powder was redissolved in tetrahydrofuran to give a brilliant blue solution. On slight warming the solution changed colour irreversibly to deep gold. Concentration and cooling produced a small quantity of pink-red crystals. Yield: 0.21 g (14 %). m.p. dec. 160 °C. IR (Nujol, CsI): 2724 (vw), 2683 (vw), 1614 (m), 1344 (w-m), 1295 (vw), 1262 (vw), 1240 (w), 1175 (w-m), 1098 (vw), 1039 (m), 999 (vs), 954 (w), 923 (m), 915 (m), 849 (vs), 835 (vs), 724 (w), 669 (m), 572 (w), 460 (br w), 310 (s) cm⁻¹. The melting point and infrared spectrum are the same as the product characterized by Tilley ²⁵.

Attempted reaction with Tetraphenyldiphosphine

Attempts to react Yb(C₅Me₅)₂(OEt₂) with tetraphenyldiphosphine in hexane at room temperature and in toluene at reflux were unsuccessful. Similarly no reaction was observed between base-free Yb(C₅Me₅)₂ and a five-fold excess of the diphosphine in hexane. In all cases starting materials were recovered unchanged.

[Yb(C₅Me₅)₂]₂ [μ-S]; 23

(a) From Ph₃P=S The Yb(C₅Me₅)₂(OEt₂) (0.81 g, 1.6 mmol) and Ph₃P=S (0.23 g, 0.78 mmol) were weighed in a Schlenk tube under nitrogen and dissolved in 60 mL of toluene. The solution was heated to reflux with stirring for 5h. After cooling to room temperature the red solution was concentrated to ca. 20 mL and cooled to -20 °C. The sulphide was isolated as deep red needles by filtration Yield: 0.35 g (49 %). m.p. 278 - 282 °C: IR (Nujol, CsI): 2725 (m), 1492 (w-m), 1256 (w-m), 1212 (w-m), 1152 (w), 1095 (m), 1064 (w-m), 1022 (m), 800 (w), 728 (s), 694 (w-m), 666 (m), 638 (w), 588 (w), 517 (vw), 482 (w), 462 (w), 381 (vs), 310 (vs) cm⁻¹. ¹H NMR (C₇D₈, 32 °C): δ 13.4 ppm (60H, ν_{1/2} = 640 Hz). M.S. (E.I.) m/e = 920 amu (M⁺), 784 (M⁺ - C₅Me₅), 648 (M⁺ - 2 C₅Me₅), 512 (M⁺ - 3 C₅Me₅), 444 (Yb(C₅Me₅)₂⁺), 379 (M⁺ - 4 C₅Me₅), 309 (Yb(C₅Me₅)⁺). Anal. Calcd for C₄₀H₆₀SYb₂: C, 52.3; H, 6.58; S, 3.49 %. Found: C, 53.6; H, 6.71; S, 3.44 %.

(b) From As₂S₃ The Yb(C₅Me₅)₂(OEt₂) (0.60 g, 1.2 mmol) and arsenic(III) sulphide (0.15 g, 0.62 mmol) were weighed in a Schlenk tube under nitrogen. Hexane (120 mL) was added and the yellow-green suspension was stirred at room temperature overnight. Excess yellow arsenic(III) sulphide was allowed to settle, the red-orange supernatant was filtered and the filtrate concentrated to ca. 20 mL. Fine red crystals of the bridging sulphide deposited on cooling to -20 °C (0.29 g, 51 %). The infrared spectrum of this material was identical with that obtained in (a).

(c) From COS The $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.81 g, 1.6 mmol) was dissolved in 80 mL of ether under nitrogen with stirring. Carbonyl sulphide (25 mL of gas, 1.2 mmol) was added by syringe. The red solution was stirred for 1 h, filtered and the filtrate was concentrated to ca. 10 mL. Cooling to -20°C yielded a muddy red solid which was recrystallized from hexane to give fine red crystals (0.12 g, 17 %). The infrared spectrum and melting point of this material were identical with those in (a).

$[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2 [\mu\text{-Se}]$; 24

(a) From $\text{Ph}_3\text{P=Se}$ $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.67 g, 1.3 mmol) and $\text{Ph}_3\text{P=Se}^{56}$ (0.22 g, 0.65 mmol) were dissolved in hexane (70 mL) with stirring. The purple solution was stirred for 1 h, filtered and the filtrate was concentrated to ca. 15 mL. Cooling at -25°C for 2 days yielded purple crystals of the bridging selenide. Yield: 0.40 g (64 %). m.p. $265 - 270^\circ\text{C}$. IR (Nujol, CsI): 2725 (m), 1172 (m-s), 1163 (sh w), 1153 (s), 1095 (m-s), 1064 (m-s), 1023 (s), 956 (w), 940 (vw), 928 (w), 802 (m), 722 (m), 667 (w-m), 639 (vw), 621 (w), 588 (m), 384 (vs), 311 (vs), 247 (vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32°C): δ 12.1 ppm (60H, $\nu_{1/2} = 500$ Hz). M.S. (E.I.) $m/e = 966$ amu (M^+), 831 ($\text{M}^+ - \text{C}_5\text{Me}_5$), 696 ($\text{M}^+ - 2 \text{C}_5\text{Me}_5$), 560 ($\text{M}^+ - 3 \text{C}_5\text{Me}_5$), 444 ($\text{Yb}(\text{C}_5\text{Me}_5)_2^+$), 426 ($\text{M}^+ - 4 \text{C}_5\text{Me}_5$), 387 ($\text{Yb}(\text{C}_5\text{Me}_5)\text{Se}^+$), 309 ($\text{Yb}(\text{C}_5\text{Me}_5)^+$), 253 (YbSe^+). Anal. Calcd for $\text{C}_{40}\text{H}_{60}\text{SeYb}_2$: C, 49.7; H, 6.26 %. Found: C, 49.9; H, 6.49 %.

(b) From Se metal $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (0.61 g, 1.2 mmol) was weighed in a Schlenk tube under nitrogen and dissolved in 100 mL of hexane and powdered selenium metal (0.10 g, 1.2 mmol) was added. The solution slowly changed colour to a deep purple on stirring overnight. The supernatant was separated from excess selenium by filtration, the filtrate was concentrated to ca. 15 mL, and cooled to -20°C overnight. Purple crystals were isolated from the mother liquor that had the same infrared spectrum and melting point as those obtained in (a). Yield: 0.38 g (66%).

$[\text{Yb}(\text{C}_5\text{Me}_5)_2]_2 [\mu\text{-Te}]$; 25

(a) From n-Bu₃P=Te $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (1.15 g, 2.22 mmol) was weighed in a Schlenk tube under nitrogen and dissolved in 80 mL of hexane. In a separate Schlenk tube, n-Bu₃P=Te⁵⁷ (0.37 g, 1.1 mmol) was dissolved in hexane (45 mL) precooled to -30°C . The phosphine telluride solution was added to the green $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ solution by canula with vigorous stirring. An immediate colour change to a very dark blue - green was observed. After stirring for 1 h, the solution was filtered, the filtrate was concentrated to 20 mL and cooled to -20°C for several days. Green-black crystals of the bridging telluride were isolated by filtration. Yield: 0.47 g (41 %). m.p. 235 - 238 °C. IR (Nujol, CsI): 2720 (m), 1260 (m), 1160 (m), 1100 (br s), 1022 (s), 798 (m-s), 720 (w), 460 (br w), 382 (s), 312 (vs), 260 (br w) cm^{-1} . ¹H NMR (C₆D₆, 32 °C): δ 12.6 ppm (60 H; $\nu_{1/2} = 290$ Hz). M.S. (E.I.) m/e = 1015 amu (M⁺), 880 (M⁺ - C₅Me₅), 745 (M⁺ - 2 C₅Me₅), 609 (M⁺ - 3

C_5Me_5), 573 ($Yb(C_5Me_5)_2Te^+$), 444 ($Yb(C_5Me_5)_2^+$), 309 ($Yb(C_5Me_5)^+$). Anal.
Calcd for $C_{40}H_{60}TeYb_2$: C, 47.4; H, 5.96 %. Found: C, 48.4; H, 6.37 %.

(b) From Te metal $Yb(C_5Me_5)_2(OEt_2)$ (0.57 g, 1.1 mmol) was weighed into a Schlenk under nitrogen and dissolved in 100 mL of hexane. A large excess of crushed tellurium metal was added to the solution, and the mixture was allowed to stir for 3 days. At the end of this period the solution was deep green-blue. Filtration of the supernatant from the excess tellurium followed by concentration of the filtrate to ca. 10 mL and cooling produced green-black blocks (0.30 g, 54 %). The solid was identified as the bridging telluride by its infrared spectrum. Yield: 0.30 g, 54 %.

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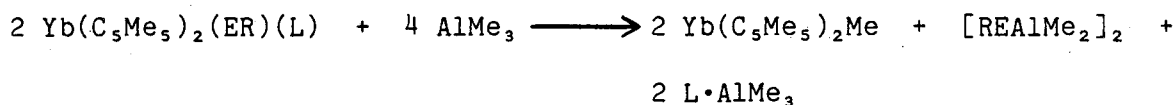
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Chapter 3: Reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ and $\text{Yb}(\text{C}_5\text{Me}_5)_2$
with Metal Alkyls.

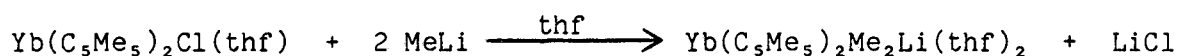
Reactions with Trimethylaluminum.

The reactivity of the chalcogenide complexes described in the previous chapter with trimethylaluminum was investigated in order to establish the availability of the chalcogenide lone pair for adduct formation with a Lewis acid. In addition, the strength of the Al-O bond (103 kcal/mol in $[\text{Et}_2\text{AlOEt}]_2$)¹ suggested that methylation of ytterbium might occur with formation of a stable aluminum-chalcogenide species (Equation 1). This was of considerable interest because the only known route to base-free $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Me}$ is extremely labourious and the full details of this procedure have yet to be published². Traditional metathetical reactions, involving chloride complexes such as $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{thf})$ and alkyl lithium reagents, invariably yield anionic complexes (Equation 2), which are not readily converted into the neutral species³⁻⁵. Only very large alkyl lithium reagents, such as $\text{LiCH}(\text{SiMe}_3)_2$, allow isolation of base-free alkyl complexes (Equation 3)⁶⁻⁷. Better synthetic routes must be developed before the reactivity of bis(pentamethylcyclopentadienyl)lanthanide alkyl complexes can be probed.

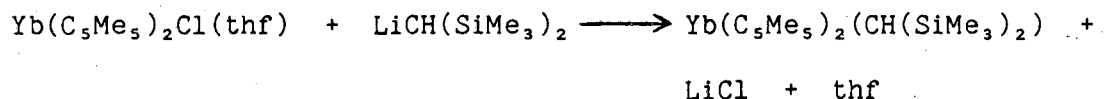
Equation 1



Equation 2

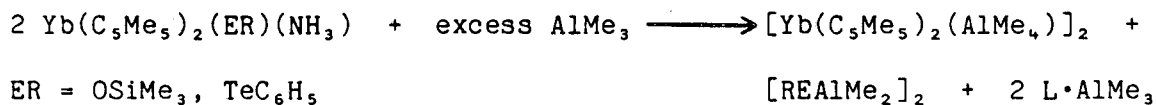


Equation 3



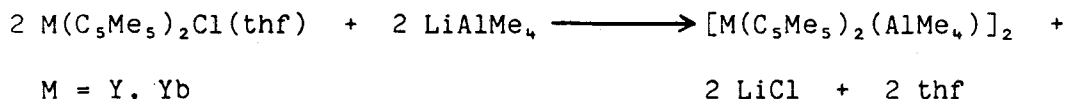
The reaction of AlMe_3 with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ proceeds rapidly on mixing in toluene to give a deep blue solution yielding blue crystals on concentration and cooling. The type of product obtained depends on the identity of the organic chalcogenide (RE^-). When RE^- is Me_3SiO^- or $\text{C}_6\text{H}_5\text{Te}^-$, this reaction produces the tetramethylaluminate complex, 1, as deep blue crystals, which rapidly turn opaque on exposure to vacuum (Equation 4). Complex 1 can be recrystallized from hot hexane but the crystals obtained once again become opaque on exposure to vacuum. This has made it difficult to obtain crystals suitable for X-ray crystallography, however the identity of the complex is well established by spectroscopic techniques.

Equation 4



The infrared spectrum of 1 contains strong bands due to the characteristic Al-C stretching modes of the AlMe_4^- anion, at 563 and 543 cm^{-1} . Table 1 shows the corresponding stretching frequencies for a number of AlMe_4^- complexes. Complex 1 and the Lu analogue are reportedly produced in the reaction between $\text{M}(\text{C}_5\text{Me}_5)_2\text{Me}_2\text{Li}$ ($\text{M} = \text{Yb, Lu}$) and AlMe_3 in pentane⁴. No physical properties have been reported for these compounds. The analogous yttrium complex I has been prepared according to Equation 5¹⁰. As expected, $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{thf})$ also reacts with LiAlMe_4 to produce 1 in good yield. The infrared spectra of the yttrium and ytterbium complexes are superimposable, further confirming the identity of 1.

Equation 5



The physical properties of 1 are given in Table 2. The complex appears to decompose when heated under high vacuum and as a result only the fragment ion, $\text{Yb}(\text{C}_5\text{Me}_5)_2^+$, is observed in the mass spectrum. The proton NMR spectrum of 1 is complex. A major set of three resonances (Species A) is observed at 247, 5.1 and -26.5 ppm in the ratio 6:30:6 at 32 °C. A minor set of two resonances (Species B) is also observed at 31.5 and 4.1 ppm in a relative ratio of 6:30. Assuming that the largest peak of each set represents the C_5Me_5 resonance of a different species, then the ratio of A:B is ca. 4:1 at 32 °C, but the ratio increases with increasing temperature to ca. 8:1 at 79 °C. On cooling the ratio again

Table 1: Characteristic Infrared Frequencies^(a)
of Some AlMe₄⁻ Metal Complexes

<u>1</u>	<u>LiAlMe₄</u> ^(b)	<u>KAlMe₄</u> ^(c)	<u>[Y(C₅Me₅)₂(μ-Me₂)AlMe₂]₂</u> ^(d)
1178 m	1204 vs 1111 m	1150 s	1175 s
1097 w	1100 vs		1090 w
877 br vs			870 s
783 m	766 s		780 m
743 s	739 vs	725 vs	740 s
677 s			675 s
623 s	632 vs		620 s
568 s	567 vs	565 s	565 s
543 s		548 s	545 s

(a) Recorded as nujol mulls between CsI or KBr plates. Frequencies expressed in cm⁻¹, followed by reported intensity. (b) Reference 8.

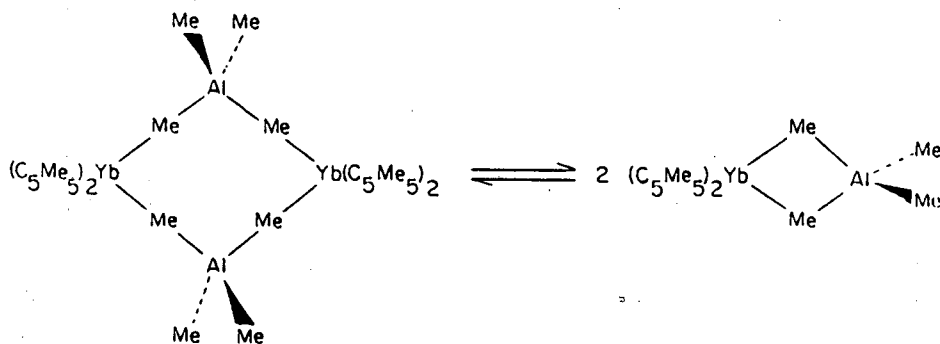
(c) Reference 9. Only selected bands were reported. (d) Reference 10.

Table 2: Physical Properties of Complexes 1 - 6.

	<u>Colour</u>	<u>m.p. (°C)</u>
<u>1</u>	blue-violet	220 - 222
<u>2</u>	blue	213 - 215
<u>3</u>	blue	200 - 202
<u>4</u>	lavender	230 - 232
<u>5</u>	purple	180 - 182
<u>6</u>	blue	238 - 240

decreases to 4:1 at 32 °C. A similar observation was reported for the diamagnetic yttrium compound I, except in this case, a ratio of ca. 5:1 was observed at room temperature which decreased with increasing temperature ¹⁰. For Y, the resonances due to A and B were attributed to a monomer-dimer equilibrium in which the dimer predominates in solution (Equation 6). On the basis of these results, it is possible that a monomer-dimer equilibrium is also operative in the ytterbium system, although the change in the ratio of the two species with temperature requires that the monomer predominate at 32 °C. The concentration of the monomer must increase with increasing temperature because the entropy term (TΔS), which favours two monomers over one dimer, increases with temperature. Thus in the case of 1, Species A must be the monomer, while Species B represents the dimer.

Equation 6



The observation of inequivalent methyl resonances in both the yttrium and ytterbium complexes clearly indicates that bridge-terminal methyl exchange is not occurring for either the monomer or dimer at room temperature. The barrier to bridge-terminal exchange has been reported as 15.9 kcal/mol¹¹ in $Y(C_5H_5)_2(\mu-Me_2)AlMe_2$, II. Given the large increase in steric bulk going from C_5H_5 to C_5Me_5 , it is not surprising that exchange does not occur in the pentamethylcyclopentadienyl compounds. It is informative to note that $Sc(C_5H_5)_2(\mu-Me_2)AlMe_2$, III, does not undergo bridge-terminal exchange until > 100 °C, while the yttrium analogue does so at 40 °C¹². Presumably the much smaller ionic radius of Sc(III) compared to Y(III) (0.870 versus 1.019 Å in 8 coordination)¹³ also prevents bridge-terminal methyl exchange for steric reasons. Complexes II and III exist as monomers in solution and in the solid state^{11 12 14}, indicating that steric crowding may be responsible for dimer formation in the C_5Me_5 complexes. Dimer formation decreases the interaction between the terminal methyl groups on aluminum and the methyl groups of the C_5Me_5 rings, while maintaining a coordination number of 8 at the metal center.

The proton NMR spectrum of 1 is tentatively assigned in Table 3. The bridging methyl resonance of the monomer is assigned as the furthest downfield resonance because of the close proximity of these protons to the paramagnetic center. The bridging methyl protons of the dimer are not observed, presumably because of extreme line broadening and a very large chemical shift. It seems rather surprising that the bridging methyl resonance is only observed for the monomer. Without the benefit of the metal-methyl proton coupling observed in the Y system,

Table 3: Proton NMR^(a) Assignments for Complex 1.

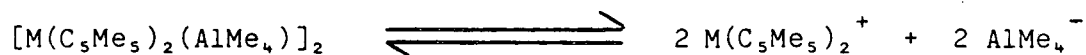
<u>Species A: Monomer</u>	Al-Me(bridge)	247	(6H, 544 Hz).
	Al-Me(terminal)	-26.5	(6H, 30 Hz).
	C ₅ Me ₅	5.2	(30H, 45 Hz).
<u>Species B: Dimer</u>	Al-Me(bridge)		not observed.
	Al-Me(terminal)	31.5	(6H, 40 Hz).
	C ₅ Me ₅	4.0	(30H, 28 Hz).

(a) Recorded in C₇D₈ at 32 °C. Chemical shifts in ppm downfield of external tetramethylsilane. Relative integrated intensities and width at half peak height are given in brackets.

it is not possible to state unequivocally that the resonance at 247 ppm is due to the bridging methyl protons of the monomer. It is possible that the solution contains other species in equilibrium with the monomer and dimer of 1. It must therefore be stressed that the monomer-dimer equilibrium is merely the minimum postulate which can account for the experimental observations.

The methyl resonances of the yttrium complex I are replaced by a single resonance at ca. 90 °C. This has been attributed to a dissociative process ¹⁰ and not to bridge-terminal exchange, because no ⁸⁹Y (I=1/2) coupling is observed for the new methyl signal. Although this was attributed to ionic dissociation (Equation 7) on the basis of a strong solvent polarity effect, the evidence presented in the literature does not convincingly rule out simple AlMe₃ dissociation (Equation 8). The methyl signals of 1 also disappear at ca. 140 °C, although in this case no new resonances are observed to the limiting temperature of 175 °C. It is not possible to completely rule out bridge-terminal methyl exchange at 140 °C for 1 because no coupling information is available with ytterbium(III), however the similarity in behaviour between the Y and Yb complexes strongly implies that a dissociative mechanism is operative here as well. In both complexes, the original spectra reappear on cooling.

Equation 7



M = Y or Yb

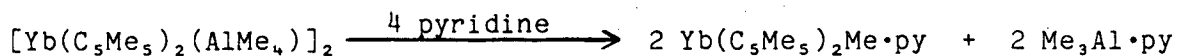
Equation 8



M = Y or Yb

The addition of one or more molar equivalents of pyridine to a solution of 1 in C₆D₆ produces a deep orange solution. The proton NMR spectrum of this solution shows the presence of one equivalent of Me₃Al·py for each Yb(C₅Me₅)₂Me·py (Equation 9). The methyl resonance of Yb(C₅Me₅)₂Me·py is not observed because the close proximity of these protons to the metal center results in extreme line broadening.

Equation 9



Diethyl ether and tetrahydrofuran also disssolve 1 to produce an orange solution. However, removal of the solvent results in reformation of 1. Tetrahydrofuran appears to produce some orange Yb(C₅Me₅)₂Me(thf) but complete conversion cannot be achieved. Diethyl ether produces none of the corresponding methyl-diethyl etherate. These observations contradict literature ³ ⁴ claims that 1 is readily cleaved by diethyl ether at -40 °C and that the addition of excess AlMe₃ to Yb(C₅Me₅)₂Me(thf) does not produce 1. The differences in behaviour observed here suggest that the compound reported in the literature is not the tetramethylaluminate complex 1. Unfortunately, since no physical properties were reported, it is not possible to resolve this question at this time. The results obtained in this work suggest that the base strength towards ytterbium decreases in the order: pyridine >

tetrahydrofuran > diethyl ether. This observation is in agreement with established trends for $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$ complexes ¹⁵. It is interesting to note that while $\text{Yb}(\text{C}_5\text{H}_5)_2(\mu\text{-Me}_2)\text{AlMe}_2$ can be converted to $[\text{Yb}(\text{C}_5\text{H}_5)_2(\mu\text{-Me})]_2$ according to Equation 10 ¹⁶, complex 1 cannot. In this regard 1 behaves more like the scandium complex III ¹⁶: the metal center in 1 is a stronger Lewis acid than Me_3Al .

Equation 10



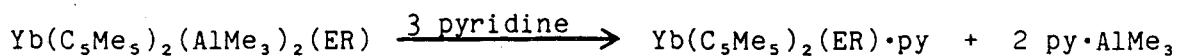
Unfortunately the strong interaction between pyridine and Yb(III) which allows formation of $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Me} \cdot \text{py}$ also makes it impossible to produce the base-free methyl complex by removal of pyridine. It has been shown ^{6 17} that diethyl ether is the strongest Lewis base which can be removed from ytterbium(II) and this base is not strong enough to allow isolation of the methyl-diethyl etherate. It may also prove more difficult to remove diethyl ether from Yb(III) than Yb(II) because the trivalent metal should exhibit enhanced Lewis acidity by virtue of its smaller size and higher oxidation state.

The reaction of AlMe_3 with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ when RE^- is $\text{C}_6\text{H}_5\text{S}^-$, $p\text{-C}_6\text{H}_4\text{S}^-$, $\text{C}_6\text{H}_5\text{Se}^-$ or Me_3CO^- , produces dark blue or blue-violet crystals. The infrared spectra of these complexes clearly show that the RE^- group is present in the product. For example, the phenylthiolate 2 and phenylselenolate 3 products show the C-H out-of-plane bending modes characteristic of monosubstituted aryl rings ¹⁸ at ca. 690 (696 and 694 cm^{-1} , respectively) and between 700 and 750 cm^{-1} (745 and 737 cm^{-1}).

Similarly, the p-tolylthiolate product 4 displays the single strong C-H out-of-plane bending vibration typically found for para-disubstituted aryl rings in the 800 to 850 cm^{-1} range ¹⁸, at 813 cm^{-1} . The t-butoxide product, 5, shows the C-O stretching frequency characteristic of alkoxides ¹⁹ at 914 cm^{-1} .

Addition of pyridine to a solution of complexes 2 - 5 in C_6D_6 produces an orange solution as observed for 1. The proton NMR spectrum of this solution shows the presence of two equivalents of $\text{Me}_3\text{Al}\cdot\text{py}$ for each equivalent of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})\cdot\text{py}$ (Equation 11). The chalcogenide-pyridine complexes were identified by comparison with authentic samples prepared by the displacement of diethyl ether from $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{OEt}_2)$ with pyridine. Elemental analysis also suggests the presence of two equivalents of AlMe_3 . The melting points of these complexes (Table 2) are similar to 1 and vary between 180 and 240 $^\circ\text{C}$. None of these compounds sublime under high vacuum, so it is not possible to obtain any mass spectral information.

Equation 11



The stoichiometry of 2 - 5 rules out simple adduct formation between the lone pair of the complexed chalcogenide atom and trimethylaluminum because it is only possible to bind one equivalent of trimethylaluminum in this manner. The proton NMR spectrum of these complexes are complicated and appear to contain more than one species. The crystal structure of the p-tolylthiolate-trimethylaluminum complex, 3, has been carried out by Zalkin ²⁰ in order to establish the solid

state structure and, hopefully, to provide some insight into the complicated solution behaviour of this class of compounds. An ORTEP plot of 3 is given in Figure 1. Some selected bond distances and angles are compiled in Table 4. The structure consists of an unusual 12-membered ring in which the p-tolylthiolate ligand is no longer coordinated to ytterbium. Instead each p-tolylthiolate unit is coordinated to two trimethylaluminum groups. The coordination about ytterbium is pseudotetrahedral, consisting of two C_5Me_5 rings and two bridging methyl groups. The two unique Yb-Me-Al angles are nearly linear at $171.1(4)^\circ$ and $175.4(4)^\circ$. The protons on the bridging methyl groups were located and refined isotropically. All three protons of each bridging methyl are directed towards the Yb along the Al-C vector. The wide Yb-Me-Al angle allows aluminum and sulphur to form strong bonds without significant distortion at either atom. Thus the coordination geometry about aluminum is only slightly distorted from tetrahedral, with the angles ranging from $100-113^\circ$ about the metal atom. The sum of the angles about sulphur is 335.5° indicating a pyramidal sulphur center with a well developed lone pair. The near linear Yb-Me-Al angles also help minimize steric interactions between the methyl groups on Al and the C_5Me_5 rings on Yb.

The Al-S distances of $2.381(3)$ and $2.369(3)$ Å are intermediate between the Al-S single bond distance of 2.348 Å found in the methylthiolate-bridged polymer, $[MeSAI Me_2]_x$ ²¹, and the dative Al+S bond length of 2.40 Å found in $H_2S \cdot AlBr_3$ ²². The average Yb- μ -Me distance of 2.67 Å is longer than the bridging methyl distances of $2.49(2)$ and $2.54(2)$ Å found in $[(C_5H_5)_2Yb(\mu-Me)]_2$ ¹⁶ or the ca. 2.58 Å

Figure 1 ORTEP Diagram for $[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)_2(\text{S-p-C}_7\text{H}_7)]_2 \cdot \text{C}_7\text{H}_8$; 3.

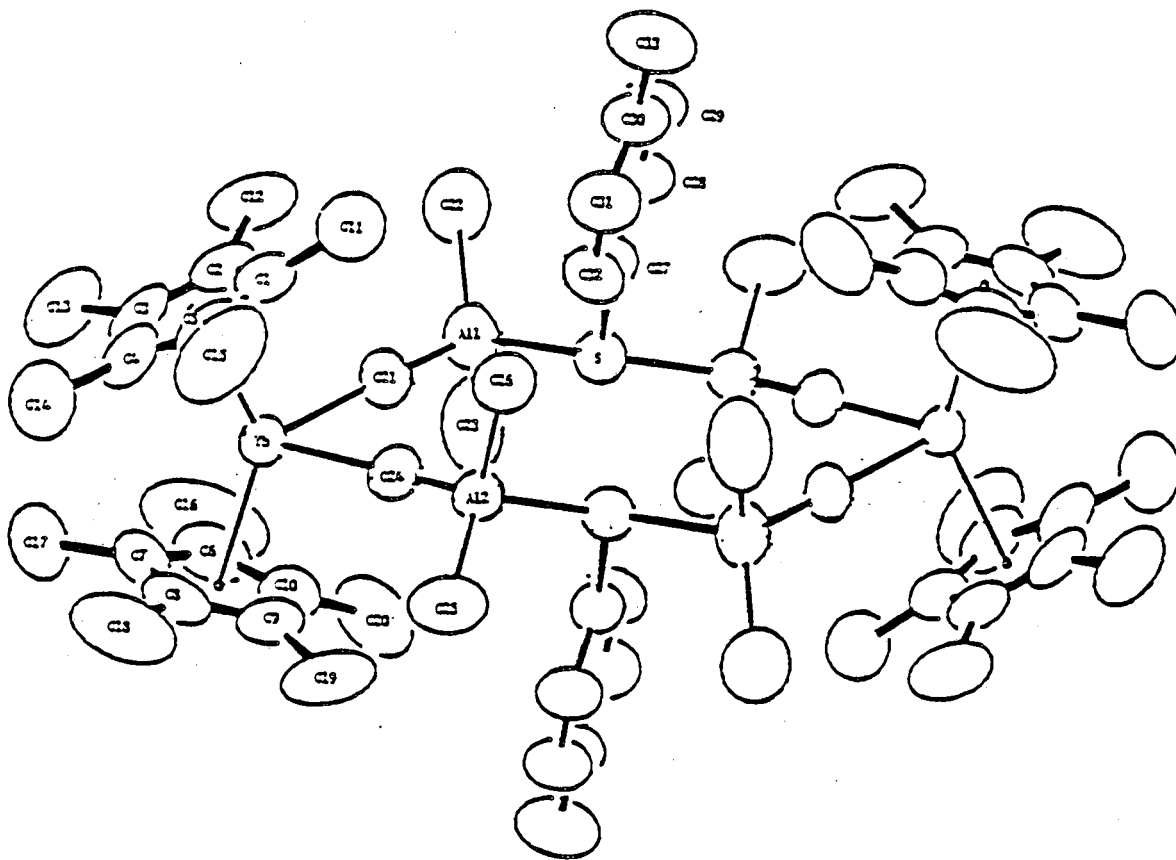


Table 4: Selected Distances (Å) and Angles (°) in

$[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)_2(\text{S-p-C}_7\text{H}_7)]_2 \cdot \text{C}_7\text{H}_8$; 3.

Yb - Cp(1) ^(a)	2.35
Yb - Cp(2)	2.35
<Yb - C(Cp)>	2.62(2)
<C(Cp) - C(Cp)>	1.41(2)
<C(Cp) - C(Me)>	1.54(1)
Yb - C(21) ^(b)	2.667(7)
Yb - C(24)	2.670(7)
Al(1) - C(21)	2.013(7)
Al(1) - C(22)	1.984(8)
Al(1) - C(23)	1.986(8)
Al(1) - S	2.381(3)
Al(2) - C(24)	2.017(7)
Al(2) - C(25)	2.00(1)
Al(2) - C(26)	1.99(1)
Al(2) - S	2.369(3)
S - C(aryl)	1.770(7)

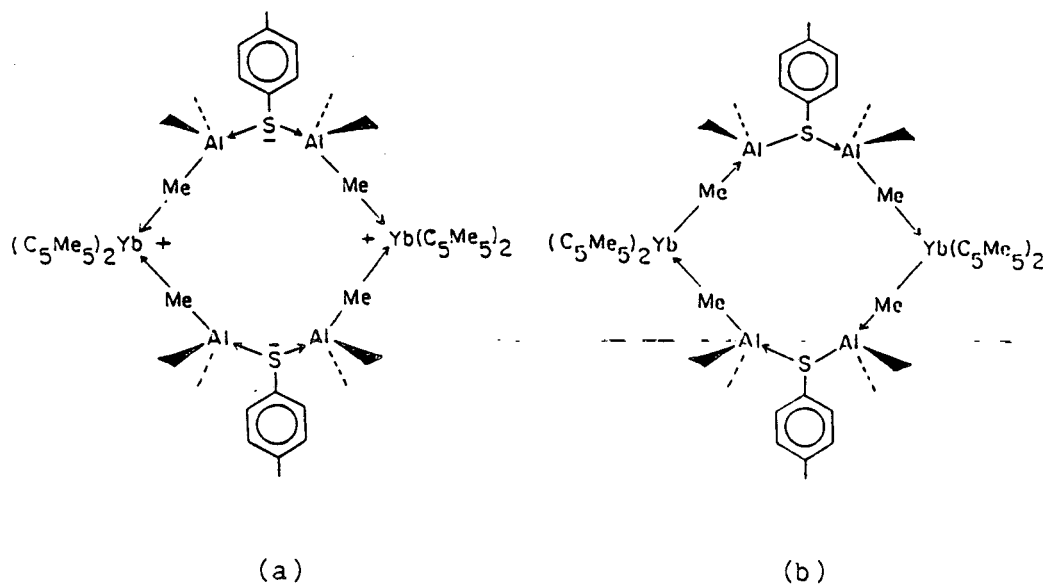
Table 4 continued.

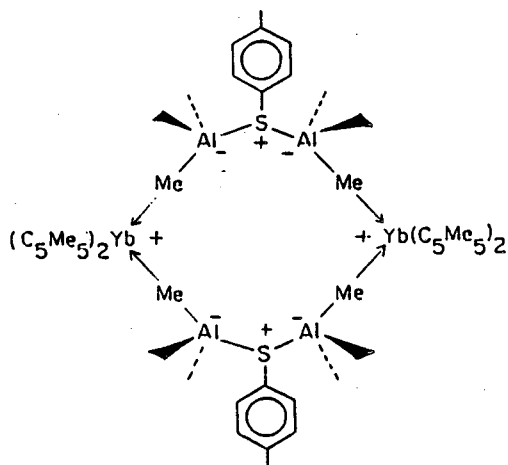
Cp(1) - Yb - Cp(2)	147.6
Cp(1) - Yb - C(21)	97.8
Cp(1) - Yb - C(24)	103.9
Cp(2) - Yb - C(21)	106.3
Cp(2) - Yb - C(24)	98.5
C(21) - Yb - C(24)	87.7(3)
Yb - C(21) - Al(1)	171.1(4)
Yb - C(24) - Al(2)	175.4(4)
C(21) - Al(1) - C(22)	112.8(4)
C(21) - Al(1) - C(23)	111.7(4)
C(21) - Al(1) - S	100.2(3)
C(24) - Al(2) - C(25)	110.7(4)
C(24) - Al(2) - C(26)	112.7(4)
C(24) - Al(2) - S	99.8(3)
Al(1) - S - C(aryl)	110.1(3)
Al(2) - S - C(aryl)	105.6(3)
Al(1) - S - Al(2)	119.8(1)

(a) Cp(1) and Cp(2) denote the ring centroids of C(1)-C(5) and C(6)-C(10), respectively. (b) C(21) and C(24) are the bridging methyl groups of Al(1) and Al(2), respectively. The corresponding terminal methyl groups are C(22), C(23) and C(25), C(26) for Al(1) and Al(2)

found in $(C_5H_5)_2Yb(\mu-Me)_2AlMe_2$ ^{11 14}. In both of these compounds the angle between the bridging methyl group and the metal centers is less than 90° , so comparison with complex 3, where the bridging angle is ca. 173° , may not be meaningful. The asymmetric methyl lutetium dimer² $(C_5Me_5)_2Lu(\mu-Me)Lu(C_5Me_5)_2Me$, IV, has a bridge angle of 170° . The longer Lu- μ -Me distance of 2.756(9) Å is somewhat greater than that observed in 3. As might be expected, the Yb- μ -Me distances in 3 are considerably longer than the terminal Yb-Me distance of 2.36(1) Å found in $Yb(C_5H_5)_2Me \cdot (thf)$ ²³. The terminal Al-Me bond lengths in 3 are ca. 0.03 Å shorter than the Al- μ -Me distances. Given the Al-S bond lengths, and to a lesser extent the Yb- μ -Me and terminal Al-Me distances, it is probably reasonable to view the solid state structure of 3 as a trimethylaluminum-separated ion pair (Figure 2a) with small contributions from the resonance forms shown in Figures 2b and 2c.

Figure 2





(c)

Complexes 2, 4, and 5 probably have solid state structures similar to 3 because all of these complexes have the same stoichiometry and similar physical properties. Complex 6 has not been investigated in detail, although the stoichiometry of this complex also suggests a structure similar to 3. The formation of a dichlorodimethylaluminate complex such as $\text{Yb}(\text{C}_5\text{Me}_5)_2(\mu\text{-Cl})_2\text{AlMe}_2$, similar to the known complexes $\text{Y}(\text{C}_5\text{H}_5)_2(\mu\text{-Cl})_2\text{AlMe}_2$ ¹⁶ and $\text{Y}(\text{C}_5\text{Me}_5)_2(\mu\text{-Cl})_2\text{AlEt}_2$ ²⁴, can probably be ruled out on the basis of elemental analysis and proton NMR spectroscopy. The proton NMR spectrum (Table 5) shows two resonances in a 30:18 ratio consistent with a 2:1 adduct, providing an average structure is observed on the NMR timescale.

The solid state structures of complexes 2 to 4 are not maintained in solution. As already mentioned, the proton NMR spectra of these complexes are extremely complex, although resonances attributable to the tetramethylaluminate complex 1 are observable in each. The relative

Scheme 1

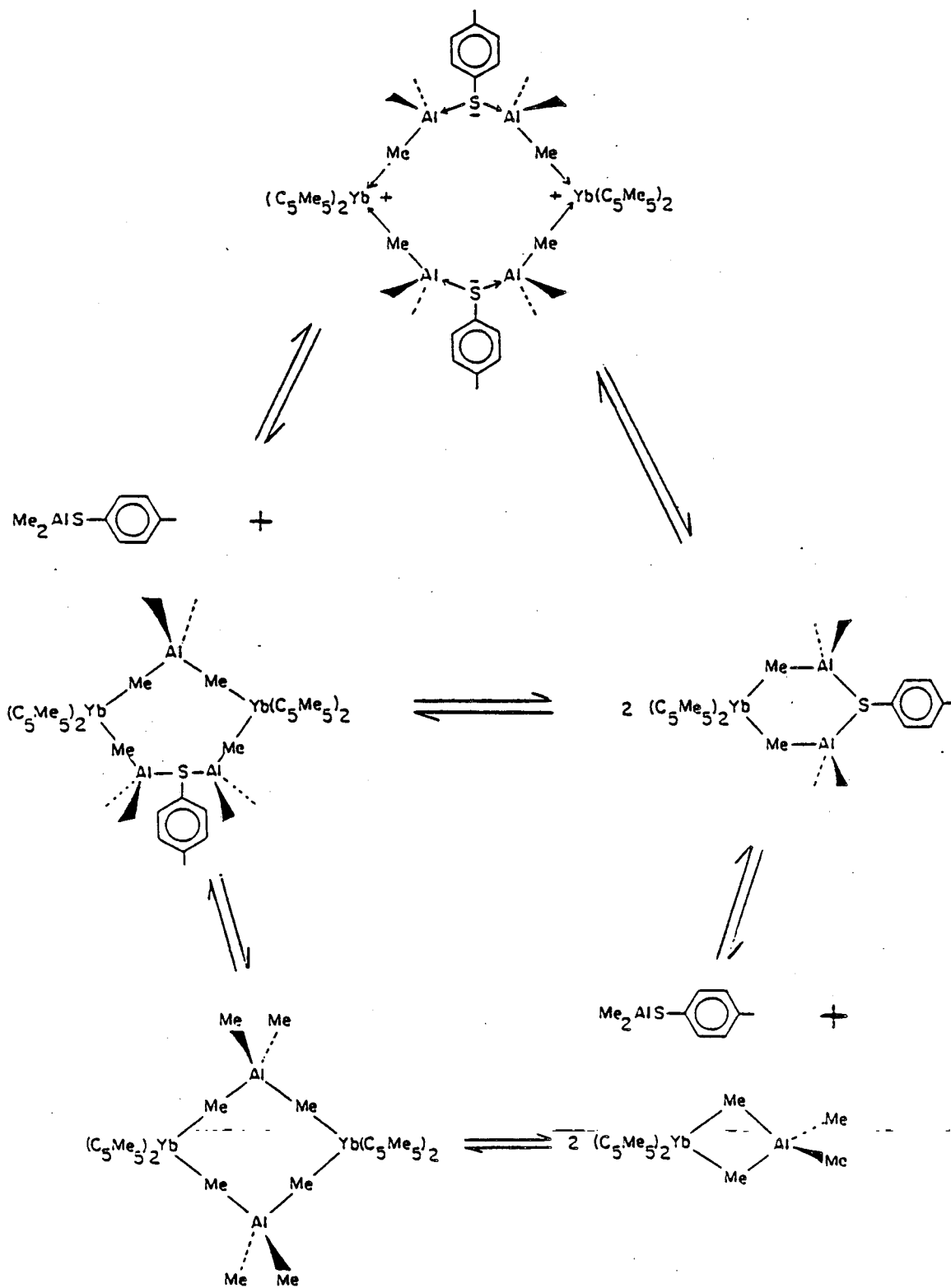


Table 5: Proton NMR^(a) Spectra for Complexes 2 - 6.

2 247 * (6H, > 500 Hz), 80.1 (4H, 350 Hz), 31.6 * (2H, 33 Hz),
29.0 (1H, 125 Hz), 20.5 (16H, 175 Hz), 14.2 (4H, 95 Hz),
6.2 (78H, 65 Hz), 5.3 * (30H, 60 Hz), 4.1 * (7H, 35 Hz),
-0.4 (2H, 5 Hz), -2.6 (2H, 35 Hz), -13.0 (3H, 37 Hz),
-27.0 * (6H, 30 Hz).

3 247 * (6H, > 500 Hz), 78.4 (4H, 285 Hz), 27.0 (3H, 89 Hz),
12.0 (5H, 37 Hz), 6.2 (53H, 72 Hz), 5.1 * (30H, 55 Hz),
-0.2 (1H, 12 Hz), -13.2 (4H, 42 Hz), -26.8 * (6H, 35 Hz).

4 247 * (6H, > 350 Hz), 6.0 (21H, 80 Hz), 5.1 * (30H, 50 Hz),
3.9 * (2H, 35 Hz), -0.5 (4H, 30 Hz), -10.0 (3H, 54 Hz),
-27.0 * (6H, 21 Hz).

Table 5 continued.

5 41.6 (9H, 313 Hz), 4.5 (30H, 150 Hz), -26.0 (9H, 43 Hz).

6 12.5 (18H, 242 Hz), 5.8 (30H, 51 Hz).

(a) Recorded in C₂D₆ at 32 °C. Chemical shifts are expressed in ppm downfield of external tetramethylsilane. Relative integrated intensity and width at half peak height are given in brackets. The asterisk * denotes peaks also found in the proton NMR spectrum of 1 (see text and Table 3).

integrated intensities of the resonances also vary with temperature, suggesting that equilibria similar to those in Scheme 1 are occurring in solution. Since it is not possible to positively identify the various resonances in these complexes, the NMR data is presented without assignment in Table 5.

In order to further establish the presence of equilibria in solution, an excess of independently prepared $C_6H_5SAlMe_2$ was added to a solution of complex 2 in C_6D_6 . The proton NMR spectrum of this solution does not show any resonances due to complex 1. Similarly the addition of ca. one equivalent of $C_6H_5SAlMe_2$ to a solution of 1 in C_6D_6 produces the proton NMR spectrum of 2. These observations are consistent with the equilibria shown in Scheme 1, however it is not possible to establish which species, other than the monomer and dimer of 1, are present in solution because the chemical shifts of the various species shown in Scheme 1 are unknown and cannot be predicted with any certainty. In addition, the possibility that some resonances are not observed due to a large paramagnetic chemical shift or extreme line broadening, rather than chemical exchange phenomena, further complicates any attempt to study this system of equilibria. The chemical shifts of the resonances do not follow the Curie-Weiss law in variable temperature experiments confirming the fact that chemical exchange processes are occurring in solution.

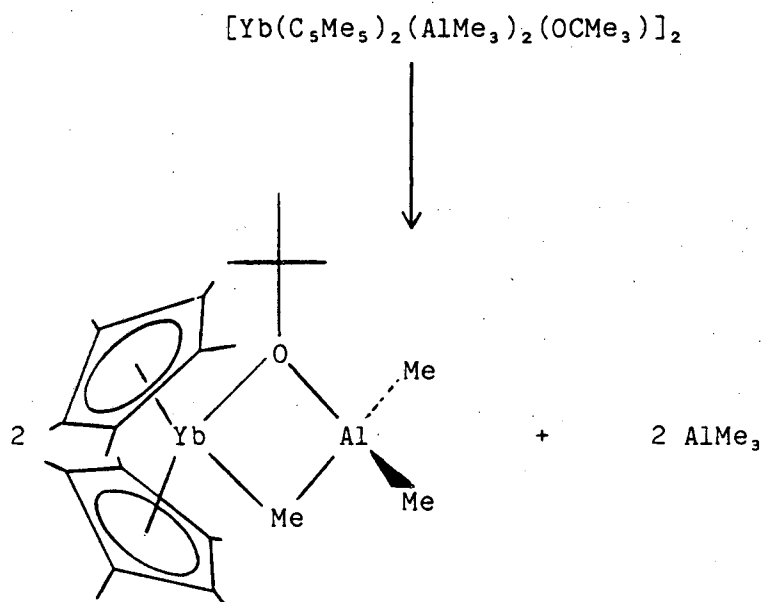
The fact that several species exist in equilibrium in solution suggests that the compound isolated from the reaction mixture represents the thermodynamic product. It follows then that the difference in reactivity between the phenyltelluroolate and trimethylsiloxide on one hand, and the t-butoxide, arylthiolate and

phenylselenolate on the other, depends on the bond strengths of the products. If, for the sake of simplicity, the two structural types encountered are viewed as shown in Figure 2, then it is easy to see that the principle difference between the two structures is the presence of a dative E+Al bond in Figure 2b which is not found in Figure 2a. From this it seems logical that a strong donor bond should favour the structure shown in Figure 2b. The strength of the Al+E bond has been shown to decrease in the order: O > S > Se >>Te²⁵. Thus, as predicted, the stronger Lewis bases, O, S, and Se form the 12-membered ring structure (Figure 2a) while the weakly basic Te does not. It should be noted that formation of 1 also produces REAlMe₂ as a byproduct (Equation 4). Since most compounds of this type are dimeric or polymeric and contain bridging RE groups^{21 26}, strong E+Al bonds might reasonably be expected to favour formation of complex 1. Nevertheless strong donor bonds should still favour structure 2b because coordination of AlMe₃ to ytterbium through a bridging methyl group should enhance the Lewis acidity of the aluminum center compared to free AlMe₃. Siloxanes are known to be poorer Lewis bases than ethers²⁷ so this might explain the formation of 1 in the reaction of Yb(C₅Me₅)₂(OSiMe₃)(NH₃) with AlMe₃.

The proton NMR spectrum of 5 is surprisingly simple. The addition of independently prepared t-BuOAlMe₂ to a solution of 5 in C₆D₆ does not result in the disappearance of any resonances. Similarly, addition of t-BuOAlMe₂ to a solution of 1 in C₆D₆ does not generate the proton NMR spectrum of 5. These observations seem to imply that 5 is not dissociated in benzene. However if this is the case, four resonances should be observed in the ratio 30:12:6:9 for the C₅Me₅, terminal Me,

bridging Me and t-butyl protons respectively, assuming stopped exchange (30:18:9 if fluxional). In fact, only three resonances are observed in a 30:9:9 ratio. Analytical data and pyridine cleavage experiments indicate a 2:1 AlMe₃ adduct in the solid state, so it appears that dissociation occurs in solution; the observed ratios in the proton NMR are consistent with a 1:1 adduct similar to that depicted in Equation 12.

Equation 12



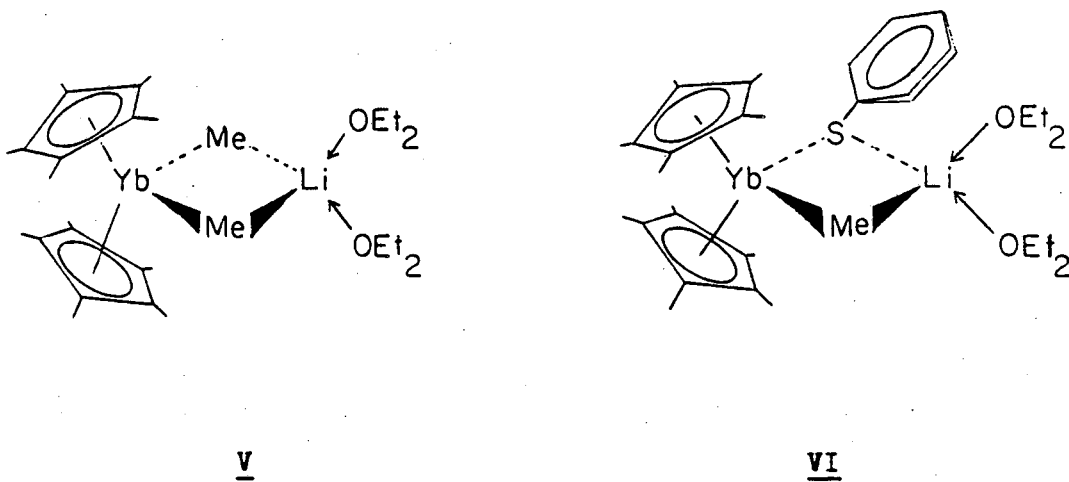
The previous results clearly show that subtle changes in the steric and electronic properties of the organic chalcogenide complex can result in dramatic changes in the type of product isolated. This observation and the equilibria observed in the proton NMR spectra of complexes 1 - 6, suggest that there is little difference, thermodynamically, between a wide variety of products. As a result, isolation of a specific product is often governed by how well the compound packs into the crystal lattice. Obviously NMR is of limited

use as a diagnostic tool in chemistry of this type, except as a means of determining stoichiometry by hydrolysis and pyridine cleavage reactions.

Reactions with Lithium Alkyls

The reaction of one or two equivalents of methyllithium with the thiolate complexes described in Chapter 2 proceeds rapidly in diethyl ether to produce an orange solution. Concentration and cooling the solution yields powdery white precipitates initially and eventually produces orange powders. Both solids contain lithium as shown by a positive lithium flame test. The white powder appears to be LiC_5Me_5 , from the infrared spectrum and colour. The orange powder is insoluble in hexane but gives powdery products from toluene and an oily orange solid from tetrahydrofuran. The presence of lithium suggests that this product is an anionic species, such as the dimethyl anion, V, or the methyl-thiolate anion, VI. Dimethyl anion complexes have been reported to form in the reaction of $\text{M}(\text{C}_5\text{Me}_5)_2\text{Cl}_2\text{Li}(\text{OEt}_2)_2$ ($\text{M} = \text{Yb, Lu}$) with methyllithium³⁴. However since no physical properties nor spectroscopic information has been published, it is not possible to compare the orange powder produced here with the literature compounds. Schumann²⁹ has had some success in isolating anionic lanthanide alkyls as crystalline complexes by addition of N,N,N',N'-tetramethylethylenediamine (tmed) as a lithium stabilizing agent. The addition of tmed during reaction or to a tetrahydrofuran solution of the orange precipitate produces oily orange solids in these reactions.

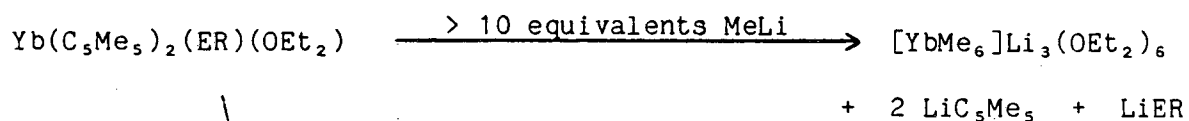
The observation of LiC_5Me_5 indicates that both ring loss and anion formation are occurring. Recently the mono-ring anion $\text{Yb}(\text{C}_5\text{Me}_5)\text{Me}_3\text{Li}(\text{tmed})$ has been prepared from the stoichiometric reaction of YbCl_3 with NaC_5Me_5 and MeLi in the presence of tmed , although the infrared spectrum and melting point have not been reported³⁰. The formation of a mono-ring anion would be consistent with the observed reaction products.



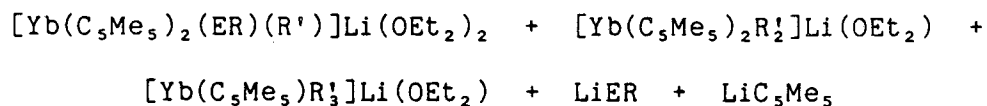
The addition of a large excess of MeLi to the thiolate complexes produces a yellow solution. Concentration of the solution produces a yellow powder and LiC_5Me_5 . It is noteworthy that the hexamethyl trianion, $[\text{YbMe}_6]\text{Li}_3(\text{tmed})_3$, reported in the literature³¹, is also yellow. This reaction has not been investigated in detail, but the results do seem to suggest that complete ring loss occurs on addition of a large excess of MeLi . The removal of C_5H_5^- as the lithium salt is well known in the reactions of alkyl lithium reagents with transition metal cyclopentadienyl compounds³².

The reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ with $t\text{-BuLi}$ are similar to those with MeLi except in this case a dark red, pyrophoric powder precipitates directly from hexane. The insoluble materials redissolve readily in tetrahydrofuran but cooling to -78°C again results in precipitation of white LiC_5Me_5 . A pink solid can be precipitated from the remaining tetrahydrofuran solution by slow addition of hexane. This product gives a positive lithium flame test. These results suggest that both ring loss and anion formation are occurring with $t\text{-BuLi}$ as well. No further attempts were made to isolate the pink solid as a crystalline material. The purported reaction products of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ with lithium alkyls are summarized in Scheme 2.

Scheme 2

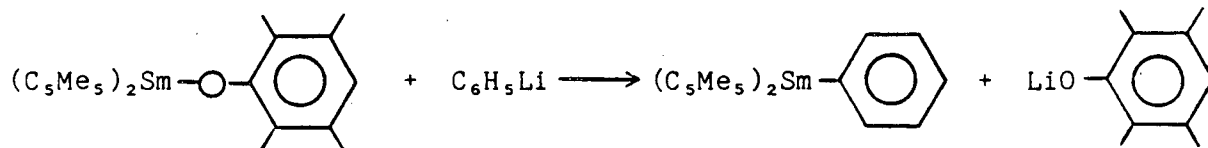


one or two
equivalents $\text{R}'\text{Li}$
 $\text{R}' = \text{Me}, t\text{-Bu}, \text{Ph}.$



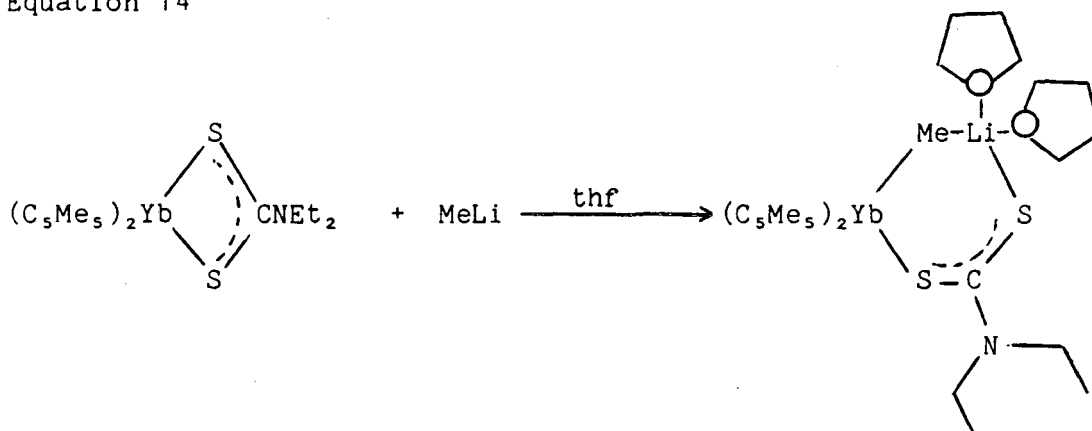
It is interesting to note that the identity of the organic chalcogenide group (RE) seems to have no effect on the products isolated. This would seem to imply that all of the reactions produce the same products; loss of the organic chalcogenide as LiER occurs rapidly. The reaction of $\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{O}-2,3,5,6-\text{C}_6\text{Me}_4\text{H})$ with phenyllithium has been reported to produce a small yield of $\text{Sm}(\text{C}_5\text{Me}_5)_2(\text{C}_6\text{H}_5)$ (Equation 13) ³³. A survey reaction shows that phenyllithium and $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ produce a brown oil regardless of the identity of the organic chalcogenide used. No reactions involving alkylolithium reagents and trivalent lanthanide complexes containing an organic chalcogenide ligand have been reported. The observation of ring loss and anion formation does not argue well for the preparation of lanthanide alkyl complexes by metathetical procedures with lithium reagents. As noted earlier, these reactions have only been successful when the alkyl group is so bulky (eg. $\text{CH}(\text{SiMe}_3)_2$) ^{6 7} that anion formation is prohibited for steric reasons.

Equation 13



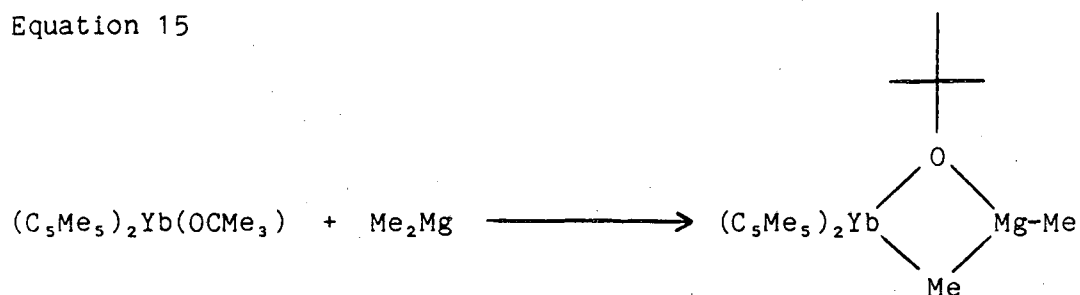
The reaction of MeLi with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{CNET}_2)$ was investigated with the hope that formation of a very insoluble lithium chelate salt ($\text{Et}_2\text{NCS}_2\text{Li}$) would allow preparation of the neutral methyl complex. Addition of MeLi to a purple solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{CNET}_2)$ in diethyl ether or toluene results in a rapid colour change to orange. However concentration and cooling produces purple crystals and a white powder. The purple product is readily identified as the starting dithiocarbamate complex by its melting point and infrared spectrum. Presumably the white powder is MeLi. Removal of the solvent produces the same products. These results suggest that adduct formation occurs in solution between one sulphur atom and lithium (Equation 14). Apparently sulphur chelate formation with ytterbium is more favourable than adduct formation with MeLi in the solid state.

Equation 14



The reaction of the orange t-butoxide complex, $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OCMe}_3)$, with Me_2Mg was also briefly investigated since magnesium alkoxides are generally insoluble in hydrocarbons¹⁹. The addition of a toluene solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OCMe}_3)$ to Me_2Mg slowly produces a cherry red solution. Since all of the Me_2Mg dissolves without precipitation of any solids, it would appear that adduct formation also occurs in this reaction (Equation 15). Removal of the solvent leaves a sticky red solid which produces a glassy red powder when washed with hexane. This seems to indicate that this adduct persists in the solid state. No further characterization of this complex was carried out.

Equation 15



Reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ with Copper Reagents

The failure of metathetical routes to yield neutral ytterbium(III) alkyls prompted an investigation of the reactions of divalent ytterbium with reducible transition metal alkyls. Copper reagents appeared to be a good choice because copper(I) is readily reduced to the metal ($\xi = 0.28$ V versus S.C.E.)¹⁸ and the reagents are comparatively safe to prepare in the base-free form. The reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ with methyl- and mesitylcopper have been investigated.

Methylcopper reacts rapidly with $\text{Yb}(\text{C}_5\text{Me}_5)_2$ in toluene at -10°C to form a deep red-orange solution with deposition of copper metal. Deep red-orange platelets of the base-free methyl complex, $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Me}$ 7, can be isolated from this solution (Equation 16). Complex 7 has an infrared spectrum almost identical to that of the bridging oxide $[(\text{C}_5\text{Me}_5)_2\text{Yb}]_2[\mu\text{-O}]^{34}$. The Yb-C stretching frequency occurs at 661 cm^{-1} in 7 compared with a Yb-O stretching frequency of 673 cm^{-1} in the bridging oxide. Since the mass of oxygen is nearly the same as that of a methyl group, this indicates that the Yb-O and Yb-C bond strengths are comparable. The Yb-O bond strength is believed to be very strong so it follows that the Yb-C bond is also very strong. The methyl complex is easily distinguishable from the bridging oxide on the basis of solubility because while the methyl complex dissolves in hexane, the bridging oxide is almost completely insoluble in this solvent.

The proton NMR spectrum of 7 (Table 6) consists of a single broad resonance at 7.4 ppm. The methyl resonance is not observed; this is not surprising for protons on an atom bonded directly to the paramagnetic ytterbium(III) center. As expected, hydrolysis only shows the presence of $\text{C}_5\text{Me}_5\text{H}$ because CH_4 gas escapes from the hydrolysate.

The possibility of a mixed valence complex, such as $(\text{C}_5\text{Me}_5)_2\text{Yb}(\mu\text{-Me})\text{Yb}(\text{C}_5\text{Me}_5)_2$, can be ruled out on the basis of magnetic susceptibility measurements. The observed moments of 5.9 and 6.7 B.M. per dimer at low (5-30 K) and high (100-280 K) temperature, respectively, are close to the theoretical values of 5.5 and 6.3 B.M. predicted for non-interacting ytterbium(III) centers and are considerably larger than the 3.8 and 4.5 B.M. expected for a simple mixed valence complex (see Chapter 1).

Table 6: Physical Properties of Complexes 7 and 8.

<u>Colour</u>	<u>m.p. (°C)</u>	<u>ν Yb-C₅Me₅ (a)</u>	<u>¹H NMR (b)</u>	<u>M⁺ (c)</u>
<u>7</u> red-orange	219 - 221	326	7.4 (310 Hz)	459
<u>8</u> red-orange	237 - 241	312	11.1 (6H, 22 Hz) 8.8 (30H, 65 Hz) -40.8 (1H, 23 Hz)	543

(a) Frequencies expressed in cm⁻¹. (b) Recorded in C₆D₁₂ (7) or C₆D₆.

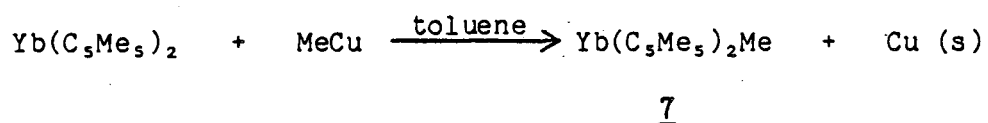
(8) Chemical shifts expressed in ppm downfield of external

tetramethylsilane. Relative integrated intensities and line width at

half peak height are given in brackets. (c) Parent ion observed in the

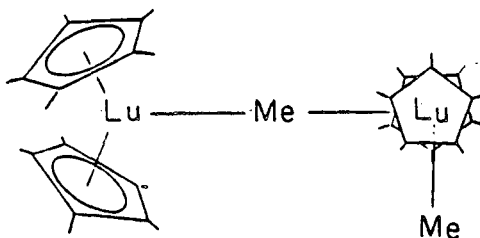
70 eV electron impact mass spectrum.

Equation 16



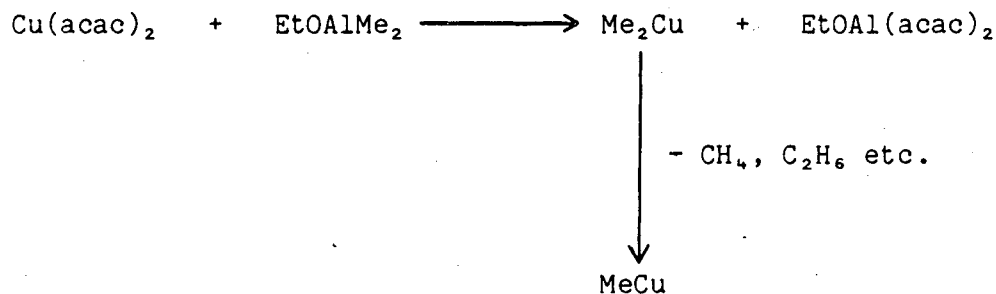
The analogous base-free lutetium complex, IV, has reportedly been prepared by removal of NEt_3 from $\text{Lu}(\text{C}_5\text{Me}_5)_2\text{Me}(\text{NEt}_3)$, VII, under vacuum². No synthetic details have been published for the preparation of VII. The crystal structure² of IV is shown schematically in Figure 5. Presumably asymmetric dimer formation occurs because steric interactions between the C_5Me_5 rings on the two ytterbium ions are too large to allow both methyl groups to bridge. Given the similar size of $\text{Yb}(\text{III})$ and $\text{Lu}(\text{III})$ ^{1,3} it seems reasonable to assume that 7 and IV are isostructural. Unfortunately, since the physical properties of IV have not been reported, no comparison can be made. The parent ion in the mass spectrum of 7 at 459 amu represents the monomeric species. However, it is doubtful that a methyl bridge of the type in Figure 5 would remain intact in the mass spectrometer.

Figure 5

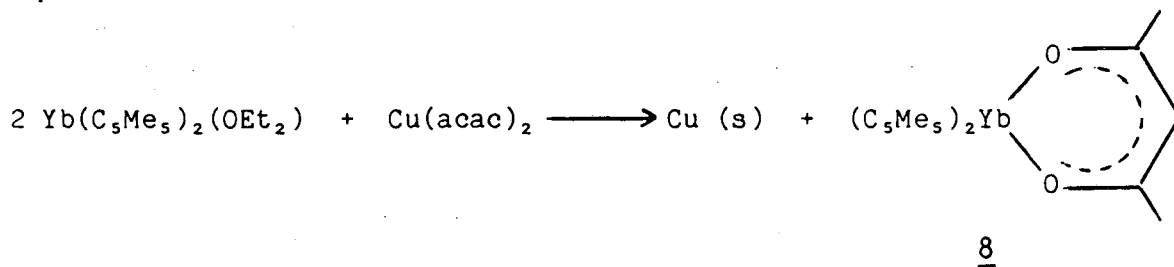


Another, more soluble, red-orange product is sometimes isolated in the reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ with MeCu . This product has been unequivocally identified as $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{acac})$ 8 (acac = acetylacetonate) by proton NMR, mass spectroscopy and elemental analysis (Table 6). The infrared spectrum is also very informative: 8 exhibits very strong bands at 1520, 1268, 1021, 667 and 541 cm^{-1} , characteristic of acetylacetonato metal complexes³⁵. Presumably 8 is formed by reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ with excess $\text{Cu}(\text{acac})_2$ used in the preparation of MeCu shown in Equation 17. Addition of excess Me_2AlOEt prevents the formation of 8, so it is clear that this compound does not arise from any reaction between $\text{Yb}(\text{C}_5\text{Me}_5)_2$ and $\text{EtOAl}(\text{acac})_2$. As expected, the stoichiometric reaction between $\text{Cu}(\text{acac})_2$ and $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ does indeed produce 8 in ca. 80% yield (Equation 18).

Equation 17



Equation 18



Mesitylcopper ³⁶ does not react with $\text{Yb}(\text{C}_5\text{Me}_5)_2$ at room temperature or at toluene reflux over several days. This is attributable to the steric bulk of the mesityl group because the reduction potential is not expected to change dramatically as a function of the organic group. The low air and moisture sensitivity of this compound is probably also due to the bulk of the mesityl ligand. The reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ with less bulky arylcopper or silver reagents would be worth investigating in detail.

Experimental

$[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)]_2$; 1

(a) From $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OSiMe}_3)(\text{NH}_3)$: Trimethylaluminum (1.8 mL of a 1.3 M pentane solution; 2.3 mmol) was added by syringe to a stirred solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OSiMe}_3)(\text{NH}_3)$ (0.43 g, 0.76 mmol) in 150 mL of hexane. An immediate colour change from deep orange to blue-violet occurred. Stirring was continued 2 h then the solution filtered and the filtrate concentrated to 80 mL. Cooling at -10°C overnight produced violet blocks which rapidly turned opaque on exposure to vacuum. Yield: 0.26 g (64 %). m.p. $220 - 222^\circ\text{C}$. IR (Nujol, CsI): 2720 (w), 1259 (w), 1178 (m), 1119 (vw), 1097 (w), 1061 (w), 1022 (m), 877 (br vs), 801 (br m), 783 (br m), 743 (s), 698 (sh vw), 677 (s), 623 (s), 592 (vw), 568 (s), 543 (s), 511 (vw), 495 (vw), 385 (m), 314 (vs), 309 (sh m) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32°C): Two species appear to present in solution in a ratio A:B of 4:1 at 32°C . Species A: δ 247.0 ppm (6H, $\nu_{1/2} = 600$ Hz), 5.2 (30H, $\nu_{1/2} = 45$ Hz), -26.5 (6H, $\nu_{1/2} = 30$ Hz); Species B: δ 31.5 ppm (6H, $\nu_{1/2} = 40$ Hz), 4.0 (30H, $\nu_{1/2} = 28$ Hz). 79°C : The ratio of A:B is ca. 8:1. Species A: δ 204 ppm (6H, $\nu_{1/2} = 544$ Hz), 4.5 (30H, $\nu_{1/2} = 65$ Hz), -21.2 (6H, $\nu_{1/2} = 56$ Hz). Species B: δ 27.2 ppm (6H, $\nu_{1/2} = 55$ Hz), 4.5 (30H overlaps resonance in A). Anal. Calcd for $\text{C}_{40}\text{H}_{84}\text{Al}_2\text{Yb}_2$: C, 54.3; H, 7.98 %. Found: C, 52.8; H, 8.14 %.

In order to establish the ratio of trimethylaluminum to pentamethylcyclopentadienyl rings, a small sample of the complex was dissolved in C_7D_8 and a few drops of pyridine were added by syringe.

The red-orange solution was examined by proton NMR: δ 3.8 ppm (30H, C_5Me_5 protons of $Yb(C_5Me_5)_2Me(py)$), -0.27 (9H, methyl protons of $Me_3Al \cdot py$). No resonance attributable to the ytterbium bonded methyl group was observed.

The solution behaviour of this compound was investigated by proton NMR. The addition of excess trimethylaluminum to a sample dissolved in C_7D_8 caused no change in the NMR spectrum, ruling out exchange with free trimethylaluminum. Above 140 °C the resonances corresponding to the peaks at 247 and -26.5 ppm in the 32 °C spectrum, broaden and disappear.

(b) From $Yb(C_5Me_5)_2(TePh)(NH_3)$: A pentane solution of trimethylaluminum (1.6 mmol) was added to a stirred solution of $Yb(C_5Me_5)_2(TePh)(NH_3)$ (0.36 g, 0.54 mmol) in 100 mL of toluene by syringe. The deep blue-violet solution was stirred 1 h, filtered and the filtrate was concentrated to 30 mL. Cooling at -10 °C produced large blue crystals which became opaque on exposure to vacuum. The melting point, infrared and NMR spectra of this product were identical with those in (a) above. Yield: 0.21 g (73 %).

(c) From $Yb(C_5Me_5)_2Cl(thf)$ and $LiAlMe_4$: $Yb(C_5Me_5)_2Cl(thf)$ and $LiAlMe_4$ were prepared according to published procedures^{15 37}. $Yb(C_5Me_5)_2Cl(thf)$ (1.80 g, 3.27 mmol) and $LiAlMe_4$ (0.38 g, 4.0 mmol) were weighed into a Schlenk and dissolved in 150 mL of toluene with vigorous stirring. The purple solution was stirred at room temperature overnight. After allowing the reaction mixture to settle, the blue-violet mother liquor was filtered and the filtrate was concentrated to ca. 100 mL. Cooling at -10 °C afforded blue crystals. Several subsequent crops of crystals were isolated for a total yield of 1.10 g

(64 %). The infrared spectrum and melting point of this compound this compound were identical with those in (a). Qualitative tests for chloride and lithium ions in an acidified hydrolysate were negative.

$[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)_2(\text{SPh})]_2$; 2

A solution of trimethylaluminum in pentane (1.4 mmol) was added to a stirred solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{SPh})(\text{NH}_3)$ (0.29 g, 0.46 mmol) in 50 mL of toluene, by syringe. The blue solution was stirred 1 h, filtered and the filtrate was cooled at -78°C for several days. Blue needles were isolated from the mother liquor by filtration. Yield: 0.25 g (75 %). m.p. $213 - 215^\circ\text{C}$. IR (Nujol, CsI): 2720 (vw), 1581 (w), 1260 (vw), 1188 (s), 1156 (sh vw), 1086 (m), 1070 (vw), 1024 (m-s), 941 (s), 920 (s), 797 (br vs), 745 (s), 729 (m), 696 (vs), 650 (vs), 586 (s), 528 (m), 484 (vw), 464 (vw), 429 (vw), 386 (w), 362 (m-s), 314 (vs) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32°C): δ 247 ppm (6H, $\nu_{1/2} > 500$ Hz), 80.1 (4H, $\nu_{1/2} = 350$ Hz), 31.6 (2H, $\nu_{1/2} = 33$ Hz), 29.0 (1H, $\nu_{1/2} = 125$ Hz), 20.5 (16H, $\nu_{1/2} = 175$ Hz), 14.2 (4H, $\nu_{1/2} = 95$ Hz), 6.2 (78H, $\nu_{1/2} = 65$ Hz), 5.3 (30H, $\nu_{1/2} = 60$ Hz), 4.1 (7H, $\nu_{1/2} = 35$ Hz), -0.4 (2H, $\nu_{1/2} = 5$ Hz), -2.6 (2H, $\nu_{1/2} = 35$ Hz), -13.0 (3H, $\nu_{1/2} = 37$ Hz), -27.0 (6H, $\nu_{1/2} = 30$ Hz) Relative integrated intensities vary with temperature. Anal. Calcd for $\text{C}_{64}\text{H}_{100}\text{Al}_4\text{S}_2\text{Yb}_2$: C, 55.2; H, 7.67; S, 4.60 %. Found: C, 53.3; H, 7.70; S, 4.28 %.

The ratio of trimethylaluminum (as $\text{Me}_3\text{Al}\cdot\text{py}$, $\delta -0.2$ ppm) to pentamethylcyclopentadienyl rings (as $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{SPh})(\text{py})$, $\delta 1.7$ ppm) was found to be 0.95:1 by proton NMR.

The addition of a large (> 5 equivalents) excess of $C_6H_5SAlMe_2$ to a solution of 2 in C_7D_8 produced a new proton NMR spectrum: δ 80.3 (2H, $\nu_{1/2} = 450$ Hz), 28.9 (1H, $\nu_{1/2} = 325$ Hz), 20.7 (2H, $\nu_{1/2} = 110$ Hz), 19.4 (2H, $\nu_{1/2} = 90$ Hz), 15.3 (4H, $\nu_{1/2} = 95$ Hz), 6.3 (30H, $\nu_{1/2} = 110$ Hz), -2.9 (3H, $\nu_{1/2} = 33$ Hz), -13.7 (4H, $\nu_{1/2} = 85$ Hz).

The addition of ca. one equivalent of $C_6H_5SAlMe_2$ to a solution of 1 in C_7D_8 produced a proton NMR spectrum similar to 2 above: δ 248 ppm (3H, $\nu_{1/2} > 500$ Hz), 80.0 (3H, $\nu_{1/2} = 380$ Hz), 27.6 (3H, $\nu_{1/2} = 155$ Hz), 20.3 (8H, $\nu_{1/2} = 192$ Hz), 14.2 (6H, $\nu_{1/2} = 175$ Hz), 6.2 (60H, $\nu_{1/2} = 120$ Hz), 5.2 (15H, $\nu_{1/2} = 65$ Hz), -0.1 (6H, $\nu_{1/2} = 10$ Hz), -2.8 (4H, $\nu_{1/2} = 40$ Hz), -12.3 (6H, $\nu_{1/2} = 58$ Hz), -27.3 (3H, $\nu_{1/2} = 34$ Hz).

Preparation of $C_6H_5SAlMe_2$: $AlMe_3$ (5.5 mmol) was diluted with 150 mL of pentane and the solution was precooled to -78 °C. Thiophenol (5.4 mmol) was added by syringe with vigorous stirring. After allowing the solution to slowly warm to room temperature, the solvent was removed under reduced pressure. The white residue was redissolved in hexane, filtered and the filtrate was slowly cooled to -10 °C. White crystals were isolated from the mother liquor by canula filtration. m.p. 130 - 132 °C. IR (Nujol, CsI): 2700 (vw), 1577 (m), 1478 (s), 1441 (s), 1367 (w), 1332 (vw), 1305 (w), 1202 (w), 1193 (s), 1158 (w), 1084 (w), 1069 (w), 1024 (m), 1000 (w), 964 (vw), 909 (w-m), 742 (vs), 717 (s), 690 (vs), 681 (sh s), 648 (s), 612 (s), 577 (s), 477 (s), 436 (m), 347 (vs), 334 (vs), 280 (w), 256 (s) cm^{-1} . 1H NMR (C_7D_8 , 21 °C): δ 7.47 ppm (2H, m), 6.90 (3H, m), -0.28 (6H, s).

$[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)_2(\text{S-p-C}_7\text{H}_7)]_2 \cdot \text{C}_7\text{H}_8$; 3

A solution of trimethylaluminum in pentane (4.7 mmol) was added to a stirred solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S-p-C}_7\text{H}_7)(\text{OEt}_2)$ (1.00 g, 1.56 mmol) in 100 mL of toluene by syringe. The blue solution was stirred 2 h, filtered and the filtrate was concentrated to 20 mL. Cooling at -10°C produced dark blue prisms. Yield: 0.98 g (78 %). m.p. 200 - 202 $^\circ\text{C}$. IR (Nujol, CsI): 2729 (w), 1491 (m-s), 1208 (w), 1187 (vs), 1089 (m), 1065 (w), 1018 (m-s), 933 (br s), 897 (br s), 813 (vs), 796 (br s), 695 (br vs), 652 (vs), 585 (vs), 527 (m-s), 497 (w), 385 (w), 378 (m), 360 (vw), 309 (vs), 290 (w-m), 281 (vw) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32°C): δ 247.0 ppm (6H, $\nu_{1/2} > 500$ Hz), 78.4 (4H, $\nu_{1/2} = 285$ Hz), 27.0 (3H, $\nu_{1/2} = 89$ Hz), 12.0 (5H, $\nu_{1/2} = 37$ Hz), 6.2 (53H, $\nu_{1/2} = 72$ Hz), 5.1 (30H, $\nu_{1/2} = 55$ Hz), -0.2 (1H, $\nu_{1/2} = 12$ Hz), -13.2 (4H, $\nu_{1/2} = 42$ Hz), -26.8 (6H, $\nu_{1/2} = 35$ Hz) Relative integrated intensities vary with temperature.

Anal. Calcd for $\text{C}_{73}\text{H}_{118}\text{Al}_4\text{S}_2\text{Yb}_2$: C, 57.9; H, 7.86; S, 4.24 %. Found: C, 55.2; H, 7.65; S, 4.78 %.

Addition of pyridine to a solution of this compound in C_6D_6 showed the presence of two trimethylaluminum units (as $\text{Me}_3\text{Al}\cdot\text{py}$, δ -0.2 ppm) per two pentamethylcyclopentadienyl rings (as $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S-p-C}_7\text{H}_7)(\text{py})$, δ 1.6 ppm) by proton NMR.

$[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)_2(\text{SePh})]_2$; 4

A solution of trimethylaluminum in pentane (2.9 mmol) was added to a stirred solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{SePh})(\text{NH}_3)$ (0.60 g, 0.97 mmol) in 50 mL of toluene by syringe. The mauve solution was stirred 3 h, filtered and the filtrate was concentrated to 25 mL. Cooling at -10°C for several days produced deep lavender crystals which became opaque on exposure to vacuum. Yield: 0.45 g (62 %). m.p. $230 - 232^\circ\text{C}$. IR (Nujol, CsI): 2720 (w), 1577 (m), 1189 (s), 1072 (vw), 1022 (m), 1000 (vw), 936 (br vs), 795 (sh w), 760 (sh m), 737 (vs), 694 (vs), 650 (vs), 586 (vs), 527 (br m), 486 (m), 390 (br w), 318 (vs), 303 (vw), 280 (m) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 32°C): δ 247 ppm (6H, $\nu_{1/2} > 350$ Hz), 6.0 (21H, $\nu_{1/2} = 80$ Hz), 5.1 (30H, $\nu_{1/2} = 50$ Hz), 3.9 (2H, $\nu_{1/2} = 35$ Hz), -0.5 (4H, $\nu_{1/2} = 30$ Hz), -10.0 (3H, $\nu_{1/2} = 54$ Hz), -27.0 (6H, $\nu_{1/2} = 21$ Hz) Relative integrated intensities varied with temperature. These were the only paramagnetic resonances observable. Anal. Calcd for $\text{C}_{64}\text{H}_{106}\text{Al}_4\text{Se}_2\text{Yb}_2$: C, 51.7; H, 7.18 %. Found: C, 51.3; H, 7.19 %.

Addition of pyridine to a C_7D_8 solution of this compound confirmed the presence of two trimethylaluminum units (as $\text{Me}_3\text{Al}\cdot\text{py}$) per two pentamethylcyclopentadienyl rings (as $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{SePh})(\text{py})$, δ 1.4 ppm) by proton NMR.

$[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)_2(\text{OCMe}_3)]_2$; 5

A solution of trimethylaluminum in pentane (1.2 mmol) was added to a deep orange solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OCMe}_3)(\text{NH}_3)$ (0.20 g, 0.37 mmol) in 200 mL of hexane by syringe. An immediate colour change to purple occurred. Stirring was continued for 6 h, the solution was filtered and

the filtrate was concentrated to 40 mL. Cooling at $-78\text{ }^{\circ}\text{C}$ produced purple plates. Yield: 0.10 g (46 %). m.p. 180 - 182 $^{\circ}\text{C}$. IR (Nujol, CsI): 2720 (w), 1365 (w), 1309 (vw), 1261 (vw), 1243 (w), 1180 (m-s), 1090 (vw), 1024 (w), 914 (s), 803 (w), 767 (w-m), 721 (sh vw), 693 (br vs), 628 (br s), 596 (vw), 499 (w-m), 472 (vw), 380 (br w), 297 (m) cm^{-1} . $^1\text{H NMR}$ (C_6D_6 , 32 $^{\circ}\text{C}$): δ 41.6 ppm (9H, $\nu_{1/2} = 313$ Hz), 4.5 (30H, $\nu_{1/2} = 150$ Hz), -26.0 (9H, $\nu_{1/2} = 43$ Hz). Anal. Calcd for $\text{C}_{60}\text{H}_{114}\text{Al}_4\text{O}_2\text{Yb}_2$: C, 54.5; H, 8.70 %. Found: C, 53.7; H, 8.49 %.

Addition of a small amount of pyridine to a solution of this compound in C_6D_6 indicated that the ratio of C_5Me_5 rings (as $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OCMe}_3)(\text{py})$, δ 9.2 ppm) to trimethylaluminum (as $\text{Me}_3\text{Al}\cdot\text{py}$, δ -0.27 ppm) was 0.95:1 by proton NMR.

The addition of $\text{Me}_3\text{COAlMe}_2$ to a solution of 5 in C_7D_8 did not cause any noticeable change in the proton NMR spectrum. Addition of a large excess of $\text{Me}_3\text{COAlMe}_2$ to a solution of 1 in C_7D_8 did not produce the proton NMR spectrum of 5. The spectrum obtained was identical with that of 1 and $\text{Me}_3\text{COAlMe}_2$ alone.

Preparation of $\text{Me}_3\text{COAlMe}_2$: AlMe_3 (10.0 mmol) was diluted with 200 mL of pentane and the solution was cooled to $-78\text{ }^{\circ}\text{C}$. A solution of Me_3COH (9.8 mmol) in 100 mL of diethyl ether was slowly added by canula with rapid stirring. The reaction mixture was allowed to warm slowly to room temperature, then the solvent was removed under reduced pressure. The sticky white residue was redissolved in a small amount of pentane and the solution cooled at $-78\text{ }^{\circ}\text{C}$. White microcrystals were isolated from the mother liquor by canula filtration. $^1\text{H NMR}$ (C_6D_6 , 32 $^{\circ}\text{C}$): δ 1.18 ppm (9H, s), -0.46 (6H, s).

$[\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{AlMe}_3)_2\text{Cl}]_2$; 6

$\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Cl}_2\text{Na}(\text{OEt}_2)_2$ was prepared from YbCl_3 and $\text{Na}(\text{C}_5\text{Me}_5)$ in diethyl ether. The use of diethyl ether as solvent rather than thf avoids the formation of $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Cl}(\text{thf})$ as a byproduct and provides the anion in a much higher yield (80 %) than in the literature preparation¹⁵.

A large excess of trimethylaluminum in pentane (1.0 mmol) was added to a solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2\text{Cl}_2\text{Na}(\text{OEt}_2)_2$ (0.23 g, 0.34 mmol) in 20 mL of toluene by syringe. The resulting blue solution was stirred 1 h, filtered and the filtrate concentrated to 10 mL. Cooling at $-10\text{ }^\circ\text{C}$ over several days produced dark blue chunks. Hydrolysis of a small sample of this compound in $\text{D}_2\text{O} / \text{C}_6\text{D}_6$ showed that diethyl ether was not present by proton NMR. Yield: 0.12 g (57 %). m.p. 238 - 240 $^\circ\text{C}$ (green liquid). IR (Nujol, CsI): 2720 (w), 1419 (vw), 1366 (vw), 1309 (vw), 1186 (m), 1063 (vw), 1022 (m), 982 (m), 956 (m), 902 (w), 876 (w), 826 (sh w), 780 (br m), 739 (w), 722 (vw), 702 (s), 680 (vw), 656 (s), 621 (w-m), 594 (m), 569 (w-m), 539 (m-s), 385 (br m), 352 (w), 315 (s), 248 (m) cm^{-1} . ^1H NMR (C_6D_6 , 32 $^\circ\text{C}$): δ 12.5 ppm (18H, $\nu_{1/2} = 242$ Hz), 5.8 (30H, $\nu_{1/2} = 51$ Hz). Anal. Calcd for $\text{C}_{52}\text{H}_{96}\text{Al}_4\text{Cl}_2\text{Yb}_2$: C, 50.1; H, 7.76; Cl, 5.69 %. Found: C, 49.9; H, 7.70; Cl, 4.90 %.

[Yb(C₅Me₅)₂Me]₂; 7

Methylcopper was prepared on a 1.25 mmol scale from Me₂AlOEt and Cu(acac)₂ according to a literature procedure ³⁸. Care was taken to keep the reaction mixture at -10 °C or colder at all times. The yellow methylcopper product was washed twice with 100 mL of precooled diethyl ether at -40 °C (Caution: the canula filters will detonate after warming to room temperature in air). The solid was then vacuum dried at -30 °C for 3 h.

A precooled solution of base-free Yb(C₅Me₅)₂ (0.55g, 1.2 mmol) in 100 mL of hexane was slowly added to the solid methyl copper at -50 °C with stirring. The solution was then allowed to warm to -10 °C. A colour change to deep orange occurred over the course of 1 h with deposition of a copper mirror on the walls of the Schlenk tube. Stirring was continued overnight at room temperature. The deep orange-red solution was filtered and the filtrate was concentrated to 30 mL. Cooling at -10 °C overnight produced a small yield of orange crystals. Several subsequent crops were isolated from the mother liquors. Yield: 0.35 g (61 %). m.p. 229 - 231 °C. IR (Nujol, CsI): 2720 (w-m), 1306 (vw), 1260 (m), 1151 (w), 1095 (m), 1064 (vw), 1020 (s), 958 (s), 800 (br s), 723 (br m-s), 661 (vs), 623 (w), 432 (br m), 380 (br w), 326 (s), 279 (s) cm⁻¹. ¹H NMR (C₆D₁₂, 32 °C): δ 7.4 ppm (ν_{1/2} = 310 Hz) Only resonance observed. M.S.(E.I.) m/e = 459 amu (Yb(C₅Me₅)₂Me⁺), 444 (Yb(C₅Me₅)₂⁺). Anal. Calcd for C₄₂H₆₆Yb₂: C, 55.0; H, 7.25 %. Found: C, 54.0; H, 6.96 %.

The magnetic susceptibility of 7 was measured at 5kG from 5 to 280 K and the two linear regions were fit to the Curie-Weiss law: low

temperature (T=5-30 K): $\mu = 5.88$ B.M. (per molecule), $\theta = -1$ K; high temperature (T=100-280 K): $\mu = 6.71$ B.M., $\theta = -16$ K.

Yb(C₅Me₅)₂(acac); 8

This compound was originally isolated from the third crop of crystals obtained in the preparation of 7 above. Complex 8 was also prepared by stirring Yb(C₅Me₅)₂(OEt₂) (0.35 g, 0.68 mmol) with Cu(acac)₂ (0.10 g, 0.38 mmol) in 100 mL of toluene for 3 h. The red-orange solution was filtered and the filtrate concentrated to 20 mL. Cooling at -78 °C for several days produced red-orange crystals. Yield: 0.29 g (79 %). m.p. 237 - 241 °C. IR (Nujol, CsI): 2720 (w), 1585 (vs), 1540 (sh w), 1520 (vs), 1388 (sh w), 1268 (s), 1194 (w), 1165 (vw), 1152 (vw), 1094 (vw), 1061 (vw), 1021 (s), 949 (vw), 929 (m), 898 (vw), 800 (w-m), 774 (m-s), 724 (w), 694 (w), 667 (br m), 636 (vw), 623 (vw), 589 (vw), 541 (m), 419 (w), 403 (w-m), 352 (vw), 312 (vs) cm⁻¹. ¹H NMR (C₆D₆, 32 °C): δ 11.1 (6H, $\nu_{1/2} = 22$ Hz), 8.8 (30H, $\nu_{1/2} = 65$ Hz), - 40.6 (1H, $\nu_{1/2} = 23$ Hz). M.S.(E.I.) m/e = 543 amu (M⁺), 408 (M⁺ - C₅Me₅), 273 (M⁺ - 2 C₅Me₅). Anal. Calcd for C₂₅H₃₇O₂Yb: C, 55.3; H, 6.87 %. Found: C, 54.9; H, 6.86 %.

Reactions with Methyllithium.

Yb(C₅Me₅)₂(ER)(OEt₂) was dissolved in toluene or diethyl ether and cooled to -78 °C. One or two equivalents of MeLi was added by syringe with stirring. The solution was allowed to warm to room temperature overnight. The cloudy orange solution was then filtered to produce a clear orange solution. Concentration or cooling the filtrate resulted

in precipitation of a white powder. This material gives a positive lithium flame test. IR (Nujol, CsI): 2720 (m), 1635 (vw), 1304 (vw), 1170 (m), 1083 (vw), 1024 (vw), 970 (br w-m), 791 (w), 723 (s), 553 (br vs), 476 (br m) cm^{-1} .

After several cycles of cooling at $-10\text{ }^{\circ}\text{C}$ followed by filtration, an orange precipitate was isolated from the mother liquor. This material was insoluble in hexane and diethyl ether once it had been isolated from the latter solvent. The solid redissolved in toluene but produced orange powders upon cooling. Warming above ca. $65\text{ }^{\circ}\text{C}$ resulted in decomposition with deposition of a white powder. Attempts to recrystallize the orange powder from thf gave oily orange solids. The same results were obtained regardless of the identity of the organic chalcogenide. The infrared spectrum of the orange powder was recorded. IR (Nujol, CsI): 2720 (w), 1306 (w), 1262 (w), 1204 (w), 1086 (m), 1062 (w), 1023 (w), 970 (w), 722 (br m-s), 670 (s), 660 (s), 585 (m), 510 (m), 445 (m), 385 (br w), 350 (vw), 298 (m-s) cm^{-1} .

The addition of a large excess (> 10 equivalents) of MeLi produced a bright yellow solution. Concentration produced the same white powder obtained above. The solution was refiltered and the filtrate cooled slowly to $-78\text{ }^{\circ}\text{C}$. A bright yellow powder precipitated on prolonged cooling. This material proved to be insoluble in hexane, diethyl ether, and toluene. A positive lithium flame test was obtained. IR (Nujol, CsI): 1160 (w), 1065 (m), 1023 (w), 950 (br m-s), 660 (m), 641 (m-s), 585 (m-s), 455 (m), 280 (br m) cm^{-1} .

Reactions with t-Butyllithium

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{ER})(\text{L})$ was dissolved in hexane and precooled to -78°C . One equivalent of t-BuLi was added to the solution by syringe. The solution was allowed to warm slowly to room temperature. After stirring overnight, the suspension was allowed to settle. The colourless supernatant was filtered off and discarded, leaving a dark red powder. This material redissolved in thf to give a red-brown solution. Cooling at -78°C resulted in precipitation of the white solid observed in the MeLi reactions above. After removal of this precipitate by filtration, hexane was slowly diffused into the thf filtrate precipitating a pyrophoric pink solid. IR (Nujol, CsI): 2720 (w), 1306 (w), 1262 (m), 1170 (vw), 1154 (m), 1106 (s), 1059 (s'), 1021 (w), 985 (vw), 974 (vw), 946 (vw), 888 (m-s), 797 (br m-s), 722 (w-m), 598 (br s), 550 (br vs), 491 (br w), 310 (br m) cm^{-1} .

Attempted Reaction of Methylolithium with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{CNET}_2)$.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{CNET}_2)$ was dissolved in thf and one equivalent of MeLi was added by syringe. The solution immediately changed colour from purple to orange. After stirring overnight, the solution was filtered and the solvent removed under reduced pressure. The wine-red solid was redissolved in toluene to give a red-purple solution. Concentration and cooling at -10°C produced purple needles and white powder. The purple crystals were identified as $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{S}_2\text{CNET}_2)$. m.p. 225 - 228 $^\circ\text{C}$. IR (Nujol, CsI): 2724 (w), 1483 (vs), 1423 (s), 1356 (w), 1300 (w), 1271 (vs), 1200 (vs), 1135 (vs), 1088 (m), 1023 (m), 986 (s), 910 (m-s), 844 (w-m), 799 (w), 777 (w), 608 (m), 596 (vw), 567 (m), 392 (m), 350 (w), 312 (vs) cm^{-1} .

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Chapter 4: Reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with Weak Acids.

The reactions of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with weakly acidic organic molecules, such as amines and phosphines, were of interest because recent work in this group ¹ indicated that uranium(III)-amine coordination compounds readily oxidize on heating to the corresponding uranium(IV) amides (Equation 1). The similarity in oxidation potential between $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$ and $\text{U}(\text{C}_5\text{H}_4\text{Me})_3(\text{L})$ complexes, mentioned in earlier chapters, suggested that the analogous reactions might occur with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$ (Equation 2). These reactions were intriguing because very few molecular amides or phosphides of ytterbium(III) are known ^{2 3 4 5}.

Equation 1



Equation 2



E = N or P

R = alkyl, aryl, H

Reactions with Ammonia and Amines.

The reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ with ammonia produces the dark red complex, $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ 1 (Equation 3). This complex was originally isolated as an insoluble byproduct in the synthesis of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ due to residual ammonia in YbI_2 prepared from Yb metal and NH_4I in liquid ammonia (see Introduction). Some physical properties of this complex are given in Table 1. Complex 1 is insoluble in hexane and sparingly soluble in toluene or diethyl ether. The low solubility makes it impossible to obtain a proton NMR spectrum in hydrocarbon solvents. The complete displacement of diethyl ether clearly demonstrates that ammonia is a stronger Lewis base towards $\text{Yb}(\text{C}_5\text{Me}_5)_2$ than diethyl ether. Nitrogen bases such as pyridine have previously been shown ⁶ to displace diethyl ether and tetrahydrofuran (thf) from divalent ytterbium.

Equation 3



Heating 1 at 250 °C in vacuum or under nitrogen does not result in simple oxidation to the ytterbium(III) amide as depicted in Equation 2. Instead sublimation occurs, with loss of one coordinated ammonia molecule, to form brick red crystals of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)$ 2 (Equation 4). Unlike complex 1, the mono-ammonia adduct is soluble in hydrocarbons. This may be because 2 adopts the asymmetric dimer structure found in $[\text{Lu}(\text{C}_5\text{Me}_5)_2\text{Me}]_2$ ⁷ (Figure 1a), whereas 1 exists as a coordinatively

saturated monomer (Figure 1b). An asymmetric dimer would be expected to pack less efficiently in the solid state than a compact monomer, so this would explain the increase in solubility and decrease in melting point going from 1 to 2

Table 1 Physical Properties of Complexes 1 - 5

	<u>Colour</u>	<u>m.p. (°C)</u>	<u>ν Yb-C₅Me₅ (cm⁻¹)</u> (a)
<u>1</u>	dark red	275 - 280	255
<u>2</u>	brick red	219 - 221	278
<u>3</u>	dark brown	115 - 118	276
<u>4</u>	red-orange	193 - 195 dec.	256
<u>5</u>	lime green	86 - 88	268

(a) Recorded as Nujol mulls between CsI plates

Equation 4

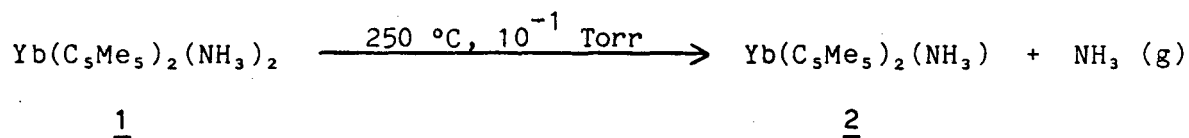
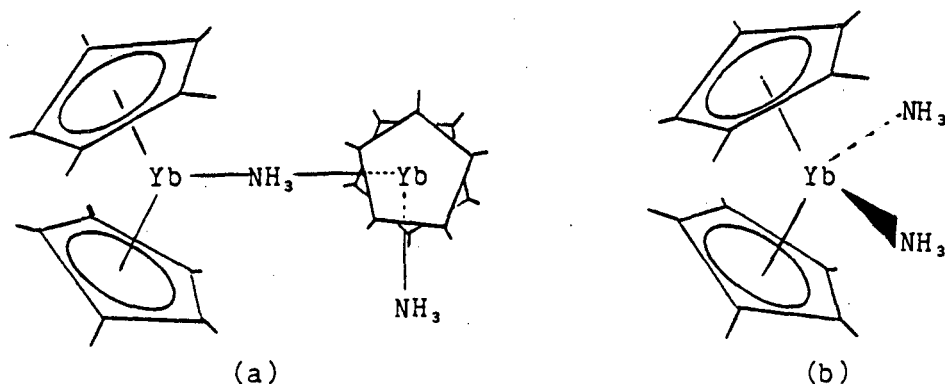
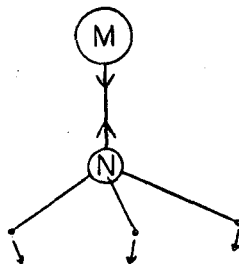


Figure 1



The physical properties of complex 2 are given in Table 1. As expected, 2 shows only two NH_3 stretching modes in the infrared spectrum compared with four such modes for 1. The NH_3 symmetric deformation frequency (Figure 2), the dominant feature in the infrared spectrum of all metal ammine complexes ⁸, is found at 1150 cm^{-1} in 1 and at 1186 cm^{-1} in 2. The Yb-N stretching frequency is assigned to the bands at 440 and 432 cm^{-1} for 1 and 2, respectively, by comparison with a wide range of metal ammine complexes ⁸. Two NH_3 deformation modes and two M-N stretching frequencies are expected for the asymmetric dimer structure proposed for 2. In fact only one band is observed for both of these modes. However, given the broadness of these bands in 2, this observation does not convincingly rule out an asymmetric structure.

Figure 2 The NH_3 Symmetric Deformation Mode of Ammine Complexes.



The proton NMR spectrum of 2 is given in Table 2. The chemical shift of the C_5Me_5 resonance is typical of divalent ytterbium complexes as discussed in Chapter 1. The NH_3 protons are not observed, presumably due to chemical exchange between coordinated and free ammonia.

Table 2 NMR Data for Complexes 2 - 4

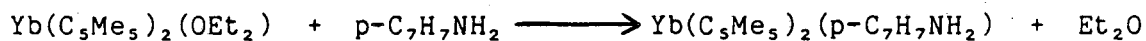
	<u>Solvent</u>	¹ H NMR (a)		³¹ P NMR (J_{PH}) (b)
		<u>C₅Me₅</u>	<u>Other</u>	
<u>2</u> ^(c)	C ₇ D ₈	1.91		
<u>3</u>	C ₆ D ₆	1.90	2.18 s (3H) 3.70 s (2H) 6.57 m (2H) 6.95 m (2H)	
<u>4</u> ^(d)	C ₄ D ₈ O	1.97	6.62 t (1H) 6.85 t (2H) 7.21 dd (2H)	-89.9 d (185)

(a) Recorded at 32 °C unless specified. Chemical shifts in ppm downfield of TMS. Relative intensities given in brackets. (b) Chemical shifts in ppm downfield of external 85 % H_3PO_4 . Coupling constants expressed in Hertz. (c) Coordinated NH_3 is not observed. (d) Recorded at 21 °C. The P-H protons are obscured by the α -protons of thf.

In the preparation of 2 a variable amount of a non-volatile, pyrophoric yellow powder is also produced. Hydrolysis clearly shows that this material contains C_5Me_5 rings while ammonia gas is given off on exposure to air. The infrared spectrum shows a $Yb-C_5Me_5$ ring stretching frequency of 302 cm^{-1} , indicative of trivalent ytterbium (Chapter 1). These facts, combined with the insolubility of this material in hydrocarbons or diethyl ether, suggests a $Yb(III)$ polymeric amide formulation. It seems most likely that this product contains only one ring per ytterbium (eg. $[Yb(C_5Me_5)(NH_2)_2]_x$), since complexes with two rings per ytterbium atom are invariably monomeric or dimeric ^{6 9}. This result indicates that both ring loss and oxidation occur under the reaction conditions employed. Further characterization of this material has not been carried out.

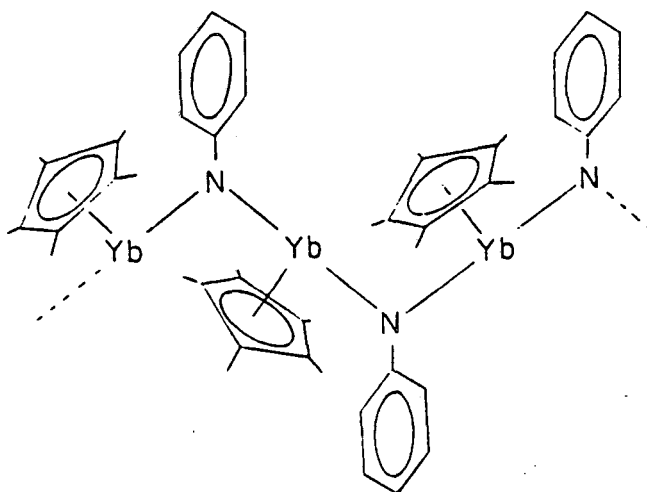
The reaction of $Yb(C_5Me_5)_2(OEt_2)$ with p-toluidine proceeds rapidly in toluene to produce the dark brown coordination compound, $Yb(C_5Me_5)_2(p-C_7H_7NH_2)$ 3 (Equation 5). The physical properties and proton NMR spectrum of this complex, given in Tables 1 and 2, respectively, are consistent with a simple $Yb(II)$ coordination compound. The NMR spectrum is similar to that of free p-toluidine and $Yb(C_5Me_5)_2$ which may indicate that this complex is dissociated in C_6D_6 .

Equation 5



Heating 3 under nitrogen at 250 °C results in outgassing and formation of a glassy brown-black solid. This material is completely insoluble in all hydrocarbon and ethereal solvents. A yellow liquid is liberated during pyrolysis which condenses in the cooler regions of the Schlenk flask. This liquid is identified as C_5Me_5H from its characteristic odour and proton NMR spectrum. The infrared spectrum of the black solid shows the presence of C_5Me_5 ($2725, 722, 290\text{ cm}^{-1}$) and *p*-tolyl (815 cm^{-1}) rings, but no N-H stretching frequency is observed between 3100 and 3500 cm^{-1} . The Yb- C_5Me_5 stretching frequency of 290 cm^{-1} is consistent with trivalent ytterbium. These observations suggest the formation of a polymeric imide complex similar to that shown in Figure 3.

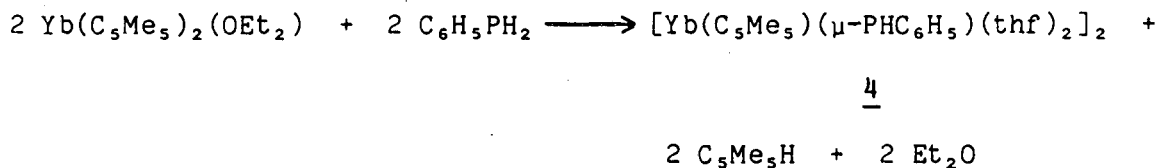
Figure 3



Reactions with Primary Phosphines.

The reaction of phenylphosphine with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ in toluene produces a dark red powder which redissolves in thf to give $[\text{Yb}(\text{C}_5\text{Me}_5)(\mu\text{-PhC}_6\text{H}_5)(\text{thf})_2]_2$ 4 (Equation 6). The presence of only one C_5Me_5 ring per ytterbium is readily established by proton and phosphorus NMR. The proton NMR spectrum (Table 2) indicates that the complex is diamagnetic. The ratio of C_5Me_5 to phenyl protons of 15:5 immediately suggests a mono-ring, ytterbium(II)-phosphide formulation. The presence of a phenylphosphide unit is confirmed by the observation of a doublet ($^1J_{\text{P-H}} = 185 \text{ Hz}$) at -89.7 ppm in the proton-coupled phosphorus NMR spectrum. The phosphorus resonance appears 33 ppm downfield of the signal for free phenylphosphine as a result of the strong electron withdrawing effect of the Yb(II) center. The P-H coupling constant only decreases by ca. 12 Hz going from free phenylphosphine to complexed phenylphosphide. Unfortunately $^{31}\text{P} - ^{171}\text{Yb}$ ($I = 1/2$, 14.3 % natural abundance) coupling is not observed, despite the fact that the phosphorus resonance is less than 5 Hz wide at half peak height. The infrared spectrum shows a single P-H stretch at 2259 cm^{-1} , consistent with a coordinated RPH^- ligand.

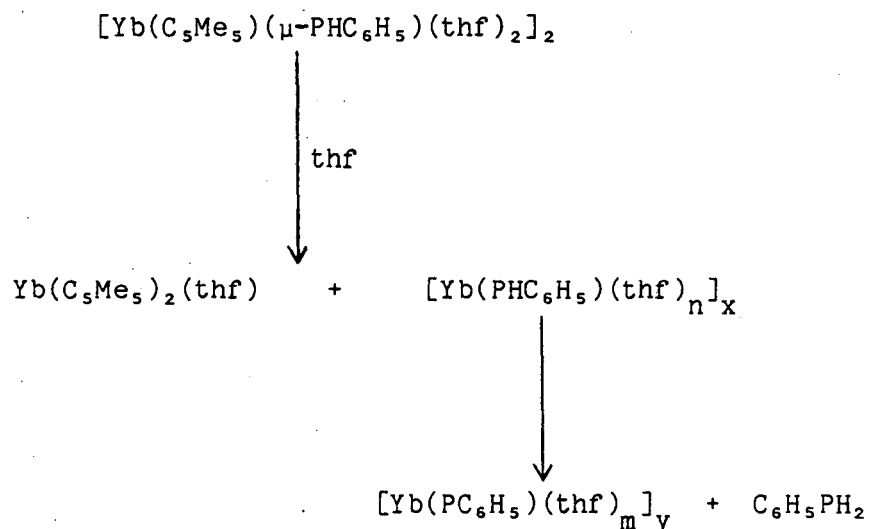
Equation 6



Complex 4 slowly decomposes in thf to produce a new diamagnetic species with a C_5Me_5 resonance at 1.87 ppm. The C_5Me_5 resonance of 2 decreases to half its original intensity after heating at 65 °C for 2 h while the new resonance at 1.87 ppm increases in intensity by a corresponding amount. Free phenylphosphine is detected in the proton NMR after heating, but no other species can be positively identified in the decomposition products. The addition of stronger bases such as pyridine or acetonitrile leads to rapid formation of $Yb(C_5Me_5)_2(L)_2$ ($L = py, CH_3CN$) complexes. The pyridine complex has been isolated and identified by its melting point and infrared spectrum.

These results suggest that ligand redistribution reactions similar to Equation 7 are occurring in solution. The rate of redistribution appears to depend on the base strength of the ligand, L. Rapid ligand redistribution is not unexpected in complex 2 because dissociation of thf in solution leads to highly reactive, coordinatively unsaturated metal centers (5-coordinate Yb). The coordination environment is much more congested in compounds containing two C_5Me_5 rings so ligand redistribution reactions present much less of a problem. The tendency of mono-ring complexes to satisfy coordinative vacancies by forming insoluble polymers and by undergoing ligand redistribution reactions is probably the primary reason why so few of these complexes have been isolated^{3 10 11}. Obviously the successful isolation of discrete molecular compounds containing only one C_5Me_5 ring per metal center depends on a subtle balance between ligand base strength, steric bulk of the ancillary ligands and crystal packing forces.

Equation 7



The X-ray crystal structure of 4 has been determined by Zalkin ¹². An ORTEP diagram is shown in Figure 4 and selected bond distances and angles are tabulated in Table 3. The structure consists of a dimer in which two ytterbium centers are bridged by two phenylphosphide ligands. A crystallographic inversion center, located at the midpoint of the Yb-Yb vector, renders both ytterbium atoms equivalent. There is no plane of symmetry in this molecule. Each ytterbium ion is surrounded by one C₅Me₅ ring, two bridging phenylphosphides and two thf molecules so that the metal center is formally seven-coordinate and divalent. The Yb-O bond lengths of 2.445(7) and 2.497(7) Å are slightly longer than the value of 2.412(5) Å found in Yb(C₅Me₅)₂(thf) ¹³. The two unique Yb-P distances in 4 are 2.957(2) and 3.066(2) Å. The only other structurally characterized lanthanide phosphide complex,

Figure 4 ORTEP Diagram of $[\text{Yb}(\text{C}_5\text{Me}_5)(\mu\text{-PhC}_6\text{H}_5)(\text{thf})_2]_2$ 4

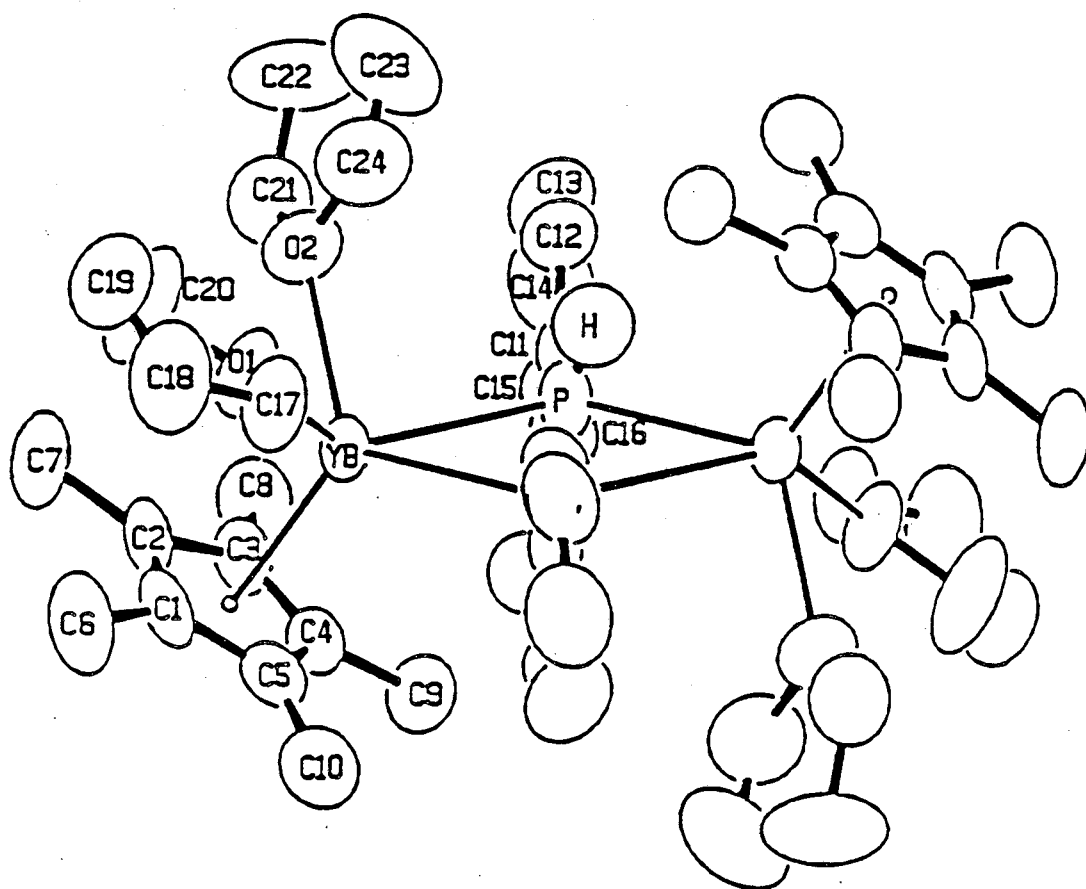
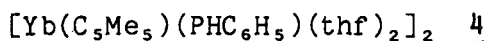


Table 3 Selected Distances (Å) and Angles (°) for



Yb - Cp ^(a)	2.43
<Yb - C(Cp)>	2.71(3)
<C(Cp) - C(Cp)>	1.41(3)
<C(Cp) - C(Me)>	1.53(1)
Yb - P	2.957(2)
Yb - P' ^(b)	3.066(2)
Yb - O(1)	2.445(7)
Yb - O(2)	2.497(7)
P - C(aryl)	1.834(9)
P...P ^(c)	3.301
Cp - Yb - P	112.5
Cp - Yb - P'	121.8
Cp - Yb - O(1)	109.9
Cp - Yb - O(2)	118.4
P - Yb - P'	66.5(1)
P - Yb - O(1)	91.2(2)
P - Yb - O(2)	118.9(2)
O(1) - Yb - O(2)	77.4(3)
Yb - P - C(aryl)	124.7(3)
Yb - P - Yb'	113.5(1)

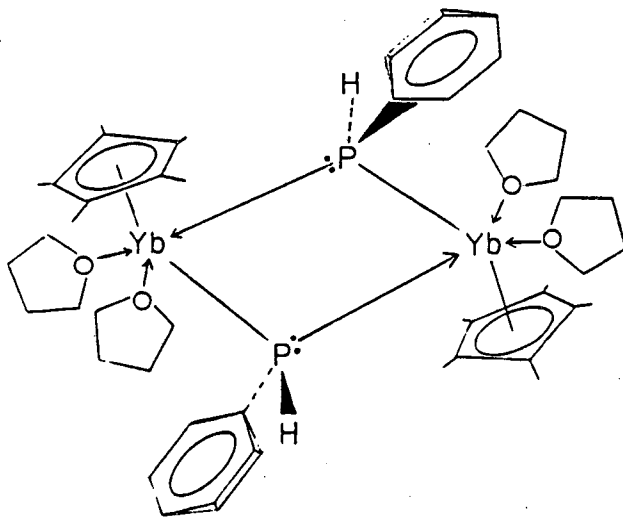
(a) Cp denotes the centroid of C(1)-C(5)

(b) ' denotes atom at -x, -y, -z.

(c) Non-bonding distance.

$(C_5Me_5)_2Lu(\mu-P(C_6H_5)_2)_2Li(tmed) \cdot 1/2C_7H_8$ ⁵, has Lu-P distances of 2.782 and 2.813 Å. After correcting for the change in oxidation state and coordination number going from eight-coordinate Lu(III) to seven-coordinate Yb(II), the Yb-P bond is predicted to be ca. 0.10 Å longer than the Lu-P bond ¹⁴. In fact the Yb-P distance in 4 are 0.175 and 0.253 Å longer. Another interesting feature of this structure is the pronounced asymmetry of the Yb-P distances. This would appear to be a function of the steric congestion about the metal center since both the Yb-P and Yb-O bond distances are longer than expected by comparison with similar compounds. It appears that there is a significant contribution to this structure from the localized bonding model shown in Figure 5.

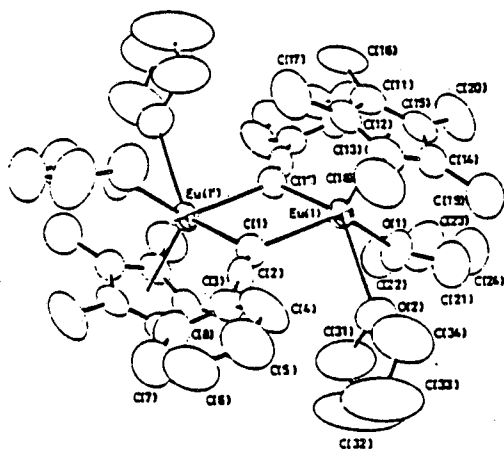
Figure 5



The coordination environment about phosphorus is distorted tetrahedral. The hydrogen atom on phosphorus was located and refined isotropically. The P...P non-bonding distance is only 3.301 Å in 4 compared with a value of 3.845 Å in the lutetium phosphide. Obviously the larger $(C_6H_5)_2P^-$ bridging ligands cannot be expected to approach one another as closely as the $(C_6H_5)PH^-$ ligands, nevertheless the close contact probably reflects significant steric crowding in 2.

The structure ¹⁰ of $[Eu(C_5Me_5)(\mu-CCC_6H_5)(thf)_2]_2$ shown in Figure 6 is very similar to that of 4. In this case the Eu-bridging C distances are identical within experimental error although the two Eu-C-C angles are slightly different. It is not surprising that this structure exhibits essentially symmetric bridges because the sp hybridization at the acetylide carbon allows the phenyl group to remain in the central Eu_2C_2 plane and this minimizes steric interactions within the molecule. In 4, sp^3 hybridization at P forces the phenyl group out of the central Yb_2P_2 plane so that unfavourable steric interactions with the C_5Me_5 rings on ytterbium occur.

Figure 6 ORTEP Plot of $[Eu(C_5Me_5)(\mu-CCC_6H_5)(thf)_2]_2$ (Reference 10)



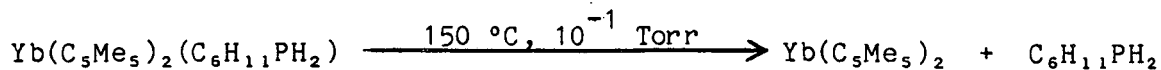
No reaction is observed between $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ and cyclohexylphosphine. Base-free $\text{Yb}(\text{C}_5\text{Me}_5)_2$ does however react with this base to form a lime-green, diamagnetic coordination compound $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{C}_6\text{H}_{11}\text{PH}_2)$ 5 (Equation 8). This indicates that cyclohexylphosphine is a poorer base than diethyl ether; consistent with established trends in Lewis base strength towards divalent ytterbium ⁶. The physical properties of 5 are given in Table 1. The low melting point is probably a reflection of the poor packing properties of the cyclohexyl group in the solid state. The proton NMR is identical with that of base-free $\text{Yb}(\text{C}_5\text{Me}_5)_2$ and free cyclohexylphosphine indicating that this ligand is essentially dissociated in hydrocarbon solvents.

Equation 8



Heating 5 to 150 °C under vacuum does not result in oxidation of ytterbium or C_5Me_5 ring loss. Instead cyclohexylphosphine is lost and base-free $\text{Yb}(\text{C}_5\text{Me}_5)_2$ is recovered in 50 % isolated yield (Equation 9). The low recovery of $\text{Yb}(\text{C}_5\text{Me}_5)_2$ is due to the high solubility of this compound because no insoluble solids remain after pentane extraction of the pyrolysis residue. Phosphine coordination is so weak that the ligand is lost before any thermal chemistry can be observed.

Equation 9



Acidity Effects.

The product obtained in the reaction of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ or $\text{Yb}(\text{C}_5\text{Me}_5)_2$ with amines and phosphines appears to depend on the acidity of the organic substrate. The pK_a 's of some amines, phosphines and hydrocarbons are given in Table 4. Ring loss is observed in the reaction with phenylphosphine. This is not surprising since Table 4 indicates that phenylphosphine is 3.7 pK_a units more acidic than $\text{C}_5\text{Me}_5\text{H}$ in dimethylsulphoxide. The reaction with diphenylamine slowly produces an insoluble red-brown precipitate suggesting that ring loss also takes place in this reaction, even though this amine is only slightly more acidic than $\text{C}_5\text{Me}_5\text{H}$. Earlier work in this group ¹⁰ showed that phenylacetylene ($\text{pK}_a = 23.2$) reacts with $\text{Eu}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ to give the mono-ring acetylide $[\text{Eu}(\text{C}_5\text{Me}_5)(\mu\text{-CCC}_6\text{H}_5)(\text{thf})_2]_2$. It was also shown in Chapter 2 that the reaction of benzylthiol ($\text{pK}_a = 10$) with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ in the presence of dibenzyl disulphide produces the mono-ring Yb(III) complex, $[\text{Yb}(\text{C}_5\text{Me}_5)(\text{S-CH}_2\text{C}_6\text{H}_5)_2]_2$. Cyclohexylphosphine, p-toluidine and ammonia are all weaker acids than $\text{C}_5\text{Me}_5\text{H}$ (Table 4), allowing isolation of simple coordination compounds, $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$.

Table 4 pK_a Values for Selected Organic Acids.^(a)

<u>Acid</u>	<u>pK_a</u>	<u>Reference</u>
Methane	55	15
Toluene	42	15
Ammonia	41	15
Cyclohexylphosphine	32.3	16
p-Toluidine ^(b)	32	17, 18
Aniline	30.7	17
C ₅ Me ₅ H	26.1	19
Diphenylamine	25.1	17
Phenylacetylene	23.2	20
Fluorene	22.6	19
Phenylphosphine	22.4	17
C ₅ H ₆	18.0	19
Benzylthiol ^(c)	10	21

(a) Measured in dimethylsulphoxide (DMSO) at 25 °C.

(b) Estimated for DMSO by comparison with other solvents

(c) Estimated value.

The importance of coordination prior to protonation is not certain. The acidic hydrocarbon fluorene does not react with $\text{Yb}(\text{C}_5\text{Me}_5)_2$ although phenylacetylene does. It seems reasonable to assume that coordination through a lone pair weakens the N-H or P-H bonds in amines and phosphines which facilitates ring protonation. Thus coordination should lower the pK_a (increase the acidity) of any substrate which can form a complex. The magnitude of this effect is not known and cannot be estimated from the data in hand. It should also be pointed out that fluorene may fail to react for kinetic reasons. Steric repulsion may prohibit close approach of the bulky fluorene ligand, thus preventing proton transfer to C_5Me_5 .

Pyrolysis of the p-toluidine complex 3 results in ring loss and oxidation of the metal. As discussed earlier in this chapter, the insoluble yellow residue produced in the pyrolysis of 1 indicates that both reactions take place here as well. It is interesting to note that phenylacetylene reacts ¹⁰ with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ to form a mixed valence Yb(II,III) complex, $\text{Yb}_3(\text{C}_5\text{Me}_5)_4(\mu\text{-CCC}_6\text{H}_5)_2(\text{thf})_4$. Once again this represents a reaction where both ring loss and oxidation occur, although this is the only example where these reactions both take place at room temperature. The pyrolysis of $\text{Yb}(\text{C}_5\text{H}_5)_3(\text{NH}_3)$ has been reported to give $\text{Yb}(\text{C}_5\text{H}_5)_2(\text{NH}_2)$ ²², demonstrating that ring loss during pyrolysis is not restricted to Yb(II) or the C_5Me_5 system.

Clean oxidation reactions, analogous to those in the $(\text{C}_5\text{H}_4\text{Me})_3\text{U}(\text{L})$ system, are not observed with $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{L})$. Instead ring loss via protonation dominates this chemistry. The tendency of lanthanide cyclopentadienyl derivatives to undergo ring displacement reactions by protonation appears to be much greater than similar uranium complexes.

Whether or not this is due to more covalent bonding in the actinide series ²³ is still open for discussion.

Experimental.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$; 1

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$ (1.50 g, 2.90 mmol) was dissolved in 40 mL of toluene with stirring. Toluene (50 mL) was saturated with ammonia gas then added to the green solution of $\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{OEt}_2)$. Immediate precipitation of a dark red powder occurred. After stirring 1 h, the suspension was allowed to settle and the toluene supernatant was filtered off and discarded leaving a muddy red solid. Drying under reduced pressure produced a free-flowing, pyrophoric red powder. Yield: 1.31 g (95 %). m.p. 275 - 280 °C. IR (Nujol, CsI): 3390 (m), 3350 (m), 3260 (m), 3180 (w), 2720 (m-s), 1640 (w-m), 1550 (br w), 1150 (vs), 1012 (m), 790 (w), 718 (s), 630 (br m), 440 (s), 330 (vw), 255 (vs) cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{N}_2\text{Yb}$: C, 50.3; H, 7.60; N, 5.86 %. Found: C, 49.6; H, 7.19; N, 5.47 %.

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)$; 2

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{NH}_3)_2$ (2.72 g, 5.70 mmol) was heated at 250 °C under vacuum (10^{-1} Torr). Brick red crystals were collected on a water-cooled probe. Yield: 1.32 g (50 %). m.p. 219 - 221 °C. IR (Nujol, CsI): 3344 (m), 3263 (m), 2724 (m), 1657 (vw), 1578 (w), 1224 (sh vw), 1186 (br vs), 1093 (vw), 1019 (w), 801 (vw), 722 (vw), 698 (vw), 432 (br s), 309 (w), 301 (vw), 278 (vs), 268 (sh w) cm^{-1} . $^1\text{H NMR}$ (C_7D_8 , 21 °C): diamagnetic δ 1.91 ppm (s). M.S.(E.I.) $m/e^- = 461$ amu (M^+), 444 ($\text{M}^+ - \text{NH}_3$). Anal. Calcd for $\text{C}_{20}\text{H}_{33}\text{NYb}$: C, 52.2; H, 7.22; N, 3.04 %. Found: C, 51.4; H, 7.30; N, 2.94 %.

The yellow, non-volatile residue which was recovered from the sublimator failed to dissolve in hydrocarbon solvents or diethyl ether. This material proved to be extremely air sensitive. Hydrolysis showed the presence of C_5Me_5H by proton NMR. The vapour produced on exposure to air gave a positive test with red litmus paper indicating the presence of ammonia gas. m.p. > 300 °C. IR (Nujol, CsI): 3358 (w), 3252 (w), 3174 (w), 2720 (m), 1608 (w), 1542 (m), 1312 (w), 1261 (m-s), 1170 (m), 1155 (m), 1096 (m), 1062 (w), 1019 (m), 938 (br w), 897 (w), 860 (vw), 801 (br s), 722 (br s), 651 (br vs), 583 (br w), 393 (br s), 302 (vs), 283 (sh m) cm^{-1} .

$Yb(C_5Me_5)_2(p-C_6H_4NH_2)$; 3

$Yb(C_5Me_5)_2(OEt_2)$ (1.18 g, 2.28 mmol) and p-toluidine (0.25 g, 2.3 mmol) were weighed into a Schlenk flask and dissolved in 100 mL of toluene with stirring. The dark brown solution was stirred 1 h, filtered, and the filtrate was concentrated to 20 mL. Cooling at -10 °C for several days produced large brown crystals. Yield: 0.65 g (52 %). m.p. 115 - 118 °C. IR (Nujol, CsI): 3339 (s), 3273 (s), 2726 (w-m), 1603 (m), 1573 (m-s), 1515 (vs), 1234 (m), 1151 (vw), 1103 (vw), 1089 (vw), 1020 (w), 966 (vs), 957 (vs), 930 (m), 836 (w), 821 (sh w), 812 (s), 799 (sh w), 732 (m-s), 705 (w), 509 (vs), 447 (m), 407 (m), 373 (vw), 353 (vw), 313 (vw), 302 (w), 276 (br vs) cm^{-1} . 1H NMR (C_6D_6 , 32 °C): diamagnetic δ 6.95 ppm (2H, m), 6.57 (2H, m), 3.70 (2H, br s), 2.18 (3H, s), 1.90 (30H, s). Anal. Calcd for $C_{27}H_{39}NYb$: C, 58.9; H, 7.14; N, 2.54 %. Found: C, 58.7; H, 7.17; N, 2.59 %.

Pyrolysis of 3 at 250 °C for 1 h under nitrogen caused the solid to melt with outgassing. The red-brown liquid resolidified to an

insoluble brown solid after the outgassing was completed. m.p. > 300 °C
IR (Nujol, CsI): 2725 (w), 1600 (m), 1543 (w), 1504 (sh vw), 1486 (vs),
1302 (vw), 1232 (vs), 1207 (w), 1176 (m-s), 1107 (w), 1025 (vw), 862
(vw), 845 (m), 815 (s), 770 (s), 722 (w-m), 647 (m), 541 (m), 526 (w),
514 (m), 421 (br s), 290 (br vs) cm^{-1} .

[Yb(C₅Me₅)(μ -PhC₆H₅)(thf)₂]₂; 4

Phenylphosphine was prepared by reduction of C₆H₅PCl₂ with lithium aluminum hydride in diethyl ether according to a literature procedure²⁴. The crude product was vacuum distilled (95 °C, 50 Torr) and the distillate was stored over molecular sieves under nitrogen. ¹H NMR (C₆D₆, 20 °C): δ 7.40 ppm (2H, m), 7.14 (3H, m), 3.98 (2H, d, ¹J_{P-H} = 197 Hz). ³¹P NMR: δ -122.7 ppm relative to external 85 % H₃PO₄ (t, ¹J_{P-H} = 197 Hz).

Yb(C₅Me₅)₂(OEt₂) (1.02 g, 1.97 mmol) was dissolved in 50 mL of toluene. Phenylphosphine (0.40 mL, \approx 3.6 mmol) was added to this solution by syringe with rapid stirring. The solution slowly changed colour (3-4 h) to brown with a dark red precipitate. After stirring overnight, the suspension was allowed to settle and the colourless supernatant was filtered and discarded. The red residue was washed with 100 mL of hexane and dried under reduced pressure. Tetrahydrofuran (100 mL) was added to the red solid to produce a deep red solution. This solution was filtered and the filtrate was concentrated to 50 mL. Slow cooling to -78 °C produced red-orange crystals. Yield: 0.35 g (32 %). m.p. dec. 193 - 195 °C. IR (Nujol, CsI): 3060 (w), 2718 (w), 2259 (m), 1575 (m), 1180 (w), 1095 (w), 1069 (w), 1033 (s), 919 (w), 880 (s), 848 (sh w), 732 (s), 697 (m-s), 480 (w-m), 308 (w), 256 (br s) cm^{-1} . ¹H NMR

(C₄D₈O, 21 °C): δ 7.21 ppm (2H, dd), 6.85 (2H, t), 6.62 (1H, t), 1.97 (30H, s) The PH proton was not observed and may be obscured by the α-H of thf. ³¹P NMR: δ -89.9 ppm relative to external H₃PO₄ (d, ¹J_{P-H} = 185 Hz). A satisfactory analysis could not be obtained for this compound, presumably due to loss of coordinated thf (calculated for base-free compound: C, 46.0; H, 5.07; P, 7.42 %). Anal. Calcd for C₄₈H₇₄O₄P₂Yb₂: C, 51.3; H, 6.64; P, 5.54 %. Found: C, 42.3; H, 5.74; P, 4.63 %.

The reaction of C₆H₅PH₂ with base-free Yb(C₅Me₅)₂ initially produced an intense green solution which slowly (ca. 4 h) turns brown with precipitation of a red solid. This solid is identical with the precipitate obtained in the Yb(C₅Me₅)₂(OEt₂) reaction.

Complex 4 slowly decomposed in C₄D₈O to unidentified products. The C₅Me₅ resonance of 4 slowly decreased in intensity with time, while a new C₅Me₅ resonance (1.87 ppm) increased in intensity by a corresponding amount. Heating at 65 °C for 2 h decreased the integrated intensity of the resonances due to 4 by 50 %. Since not all species were accounted for, no attempts were made to measure the rate of decomposition quantitatively.

The addition of pyridine to 4 produced a dark green solution. After stirring overnight, the solvent was removed under reduced pressure leaving a green, tarry solid. This residue was extracted with toluene and the extract filtered to remove black insoluble solids. Cooling the filtrate produced dark green-black crystals. The crystals were identified as Yb(C₅Me₅)₂(py)₂ by comparison of the melting point and infrared spectrum with an authentic sample ⁶. m.p. 209 - 212 °C. IR (Nujol, CsI): 3092 (w), 3062 (w), 3038 (w), 2719 (w), 1594 (s), 1486 (m), 1439 (s), 1215 (w), 1151 (m), 1094 (w-m), 1058 (w-m), 1037 (m),

1017 (vw), 1001 (w-m), 984 (vw), 945 (vw), 886 (vw), 799 (br w), 750 (vs), 730 (sh vw), 705 (vs), 655 (w), 629 (vw), 591 (vw), 416 (m), 380 (br w), 259 (br s) cm^{-1} .

$\text{Yb}(\text{C}_5\text{Me}_5)_2(\text{C}_6\text{H}_{11}\text{PH}_2)$; 5

$\text{Yb}(\text{C}_5\text{Me}_5)_2$ (0.55 g, 1.2 mmol) was dissolved in 100 mL of hexane. Cyclohexylphosphine (0.55 mL, = 4.1 mmol) was added to this solution by syringe with rapid stirring. The dark green solution was stirred 4 h and the solvent was removed under reduced pressure. The tacky yellow-green residue slowly solidified under vacuum (3 h). The solid was redissolved in 40 mL of pentane and the mint green solution was then filtered. Concentration of the filtrate to 10 mL, followed by prolonged cooling at -78°C , produced lime green flakes. Yield: 0.21 g (31 %). m.p. $86 - 88^\circ\text{C}$. IR (Nujol, CsI): 2720 (m), 2304 (m), 2289 (m), 1296 (vw), 1261 (m), 1080 (br m-s), 1018 (br m-s), 828 (sh w), 808 (br s), 724 (m), 674 (m), 385 (br w), 268 (s) cm^{-1} .

In another experiment, 5 (0.25 g, 0.45 mmol) was heated to 150°C under a nitrogen atmosphere for 1 h. After melting, outgassing was observed and the remaining solid turned red and resolidified. The Schlenk flask was then allowed to cool to room temperature under vacuum. The red residue redissolved completely in pentane to produce a red-brown solution. After filtration, the pentane extract was cooled to -78°C , producing green-brown crystals. These crystals were identified as $\text{Yb}(\text{C}_5\text{Me}_5)_2$ from their infrared spectrum and melting point. Yield: 0.10 g (50 %).

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*LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720*