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PENTAMETHYLCYCLOPENTADIENYL AND BIS(TRIMETHYLSILYL) AMIDO COMPLEXES OF THE DI- AND TRIVALENT LANTHANIDES

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to my parents

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Pentamethylcyclopentadienyl and Bis(trimethylsilyl)amido Complexes of the Di- and Trivalent Lanthanides

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ABSTRACT

The reaction of the divalent iodides YbI_2 and EuI_2 with $NaN(SiMe_3)_2$ has provided pentane-soluble, monomeric derivatives of the divalent lanthanides. These compounds are isolated as the solvated species $Eu[N(SiMe_3)_2]_2L_2$ (L = thf or 1,2-dme), $Yb[N(SiMe_3)_2]_2(thf)_{1.5}$ and $Yb[N(SiMe_3)_2]_2L_2$ (L = 1,2-dme or OEt_2), or as the sodium salts $NaM[N(SiMe_3)_2]_3$ (M = Eu or Yb). The crystal structure of $NaEu[N(SiMe_3)_2]_3$ reveals four short Eu-C(methyl) contacts that appear to result from electrostatic attractions between the metal and the methyl carbon atoms. Diethyl ether and $NaN(SiMe_3)_2$ can be displaced from $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ and $NaEu[N(SiMe_3)_2]_3$, respectively, to yield phosphine coordination complexes. Thus, $Yb[N(SiMe_3)_2]_2(dmpe)$, $Yb[N(SiMe_3)_2]_2L_2$ (L = $Pn\text{-}Bu_3$, dmpm), $Eu[N(SiMe_3)_2]_2(dmpe)_{1.5}$ and $Eu[N(SiMe_3)_2]_2(Pn\text{-}Bu_3)_2$ are obtained. The crystal structure of $Yb[N(SiMe_3)_2]_2(dmpe)$ provides the first structural evidence for lanthanide-phosphine bonding, and exhibits two metal-C(methyl) interactions.

The pentamethylcyclopentadienyl ligand has been used to obtain trivalent derivatives of the type $(C_5Me_5)_2MCl_2M'L_x$ (M = Nd, Sm or Yb; M' = Li or Na; L = OEt_2 or tmed) or $(C_5Me_5)_2MCl(thf)$ (M = Nd or Yb). These compounds undergo metathesis reactions that yield $(C_5Me_5)_2MO_2CR$, $(C_5Me_5)_2MS_2CNEt_2$ or $(C_5Me_5)_2MN(SiMe_3)_2$ (M = Nd or Yb).

The interaction of NaC_5Me_5 with $EuCl_3$ yields only the divalent $(C_5Me_5)_2EuL$ (L = thf or OEt_2). Analogous compounds of ytterbium are obtained by reaction of YbI_2 with NaC_5Me_5 in thf or OEt_2. Displacement of the ether ligands by aromatic amines yields $(C_5Me_5)_2ML_2$ complexes (M = Eu, L = $\frac{1}{2}$bipy; M = Yb, L = py, $\frac{1}{2}$bipy or p - $Me_2NC_5H_4N$). The ytterbium amine complexes are weakly paramagnetic, apparently due to charge transfer from ytterbium to the aromatic rings. The divalent phosphine complexes $(C_5Me_5)_2ML$ (M = Eu or Yb; L = dmpe or dmpm) are also described.

Whereas oxidizing agents fail to yield isolable Eu(III) species, the $(C_5Me_5)_2Yb(L)$ complexes are taken to trivalent $(C_5Me_5)_2YbX(L)$ derivatives (X = Cl, I or O_2CR). The $(C_5Me_5)_2Yb(OEt_2)$ is shown to reduce binary transition metal carbonyls, affording the Yb(III) species $[(C_5Me_5)_2Yb]_2[Mo(CO)_5]$, $[(C_5Me_5)_2Yb(thf)][Co(CO)_4]$, $[(C_5Me_5)_2Yb(thf)]_2[Fe(CO)_4]$ and $[(C_5Me_5)_2Yb]_2[Fe_3(CO)_{11}]$. Infrared and X-ray crystallographic data reveal the presence of isocarbonyl (YbOCM) linkages. In $[(C_5Me_5)_2Yb(thf)][Co(CO)_4]$, one isocarbonyl linkage is observed in the crystal structure. The structure of $[(C_5Me_5)_2Yb]_2[Fe_3(CO)_{11}]$ shows an unusual bent geometry for the triiron fragment, with only two Fe-Fe bonds. Four carbonyls bridge the Fe-Fe bonds, and form two chelating, $Fe(CO)_2Yb$ rings.

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CHAPTER 1

INTRODUCTION

Since 1956, when Wilkinson first described the preparations of the trivalent tris(cyclopentadienyl) lanthanides [1], interest in organometallic lanthanide chemistry has grown steadily. To date, most of this chemistry has been developed with the six-electron (three-coordinate) cyclopentadienide as a solubilizing ligand, though σ-bonded complexes (with two-electron donor groups) such as $Ln(CH_2SiMe_3)_3(thf)_2$ [2,3], $[Li(thf)_4][Ln(CH_2SiMe_3)_4]$ [2,3], $[Li(thf)_4][Ln(CMe_3)_4]$ [4], $[Li(tmed)]_3[LnMe_6]$[5], $[Li(thf)_4][Ln(CH(SiMe_3)_2)_3Cl]$ [2] and $[Li(thf)_4][LnAr_4]$ [6,7], where Ar is phenyl or 2,6-dimethylphenyl, have been reported.

The development of mixed-ligand cyclopentadienyl complexes was pioneered by Dubeck et. al., who reported preparations for the halide derivatives $LnCp_2X$ (X = halide) [8] and $LnCpCl_2(thf)_3$ [9]. These compounds were readily obtained by the following methods:

$$LnCl_3 + 2NaCp \longrightarrow LnCp_2Cl$$

$$2LnCp_3 + LnCl_3 \longrightarrow LnCp_2Cl$$

$$LnCp_3 + HCl \longrightarrow LnCp_2Cl$$

$$LnCp_3 + I_2 \longrightarrow LnCp_2I + CpI$$

$$LnCp_3 + 2LnCl_3 + 3thf \longrightarrow LnCpCl_2(thf)_3$$

More recently, Dornberger et. al. have shown that $SmCp_2Cl$ and $YbCp_2Cl$ can be conveniently synthesized by protonation of a C_5H_5 ligand with ammonium chloride [10]:

$$LnCp_3 + NH_4Cl \longrightarrow LnCp_2Cl + NH_3 + C_5H_6$$

The bis(cyclopentadienyl)chloro species have proven to be useful starting materials for the preparations of a variety of substituted $LnCp_2X$ derivatives. Chloride-metathesis reactions have generated bis(cyclopentadienyl)-carboxylate [8], -alkyl [11], -alkynyl [11], -(η^3-allyl) [12], -hydride [13], -borohydride [14], -phosphide [15], -stannyl [16] and -germyl [16] derivatives. A number of excellent reviews covering organometallic lanthanide chemistry have appeared recently [17-19].

Divalent lanthanide chemistry has received much less attention. Liquid ammonia solutions of europium(II) and ytterbium(II) cations, prepared by dissolving the metals in liquid ammonia, have been used to obtain the insoluble species $LnCp_2$ [20], Ln(COT) [21] and $Ln(C \equiv CR)_2$ [22,23], upon reaction with the appropriate hydrocarbon. The preparation of $YbCp_2$ from the metal and diene in liquid ammonia is not straightforward, since two ytterbium(III) products, $YbCp_3$ and $Yb_2Cp_4N_2H_4$, have also been isolated from this reaction [24]. An alternative synthetic scheme, reduction of $YbCp_2Cl$ by sodium or ytterbium metal in tetrahydrofuran, has been devised [25]. Ytterbium, samarium and europium analogues to Grignard reagents, RLnX, can be

prepared by the reaction of the metal and the alkyl halide in tetrahydrofuran [26]. Ytterbium metal also reacts with $Hg(C_6F_5)_2$ [22] or $Hg(C \equiv CPh)_2$ [22] to give the ether-soluble $Yb(C_6F_5)_2(thf)_4$ or $Yb(C \equiv CPh)_2$. An insoluble, purple, paramagnetic (3.6 B.M.) derivative of samarium(II), $SmCp_2(thf)$, is isolated from reduction of $SmCp_3$ with potassium naphthalene in tetrahydrofuran [27]. Johnson has produced a detailed review of divalent lanthanide chemistry, including discussions on the electronic and thermodynamic factors influencing relative stabilities of the di- and trivalent oxidation states [28].

The difficulty in studying the solution chemistry of the divalent compounds results from their lack of solubility in hydrocarbon solvents. This property is undoubtedly related to the tendency of these large, electropositive metals to achieve a high coordination number <u>via</u> polymerization. The divalent $EuCp_2$ and $YbCp_2$ have been shown to be isostructural with $SrCp_2$ and $CaCp_2$ [20], respectively. The $CaCp_2$ compound has been shown to have a polymeric structure, with η^5-C_5H_5, η^3-C_5H_5, and η^1-C_5H_5 bonding [29]. The structure of $Yb(C_5H_4Me)_2(thf)_2$ reveals a polymeric structure with C_5H_4Me groups bridging two ytterbium atoms by penta-hapto bonding to both metals [30].

The bonding in all lanthanide compounds is thought to be highly ionic, and much of the coordination chemistry of these metals reflects this. The lanthanide ions, which have a high charge-to-ionic radius ratio, can be considered as hard Lewis acids, which typically bind to

as many donor ligands as is sterically possible. Therefore, typical coordination numbers are high, ranging from seven to eleven. The question of valence-orbital participation in bonding is somewhat controversial, but since the 4f orbitals are well-shielded by the $5s^2$ and $5p^6$ shells, little covalency is to be expected. The possible role of 5d orbital participation in bonding is unclear, though these orbitals may play a role as acceptor-orbitals in coordination by donor ligands [31].

So far, lanthanide research has resulted in little reason to expect chemical properties that are strikingly unique to the lanthanide series. The placement of the lanthanide series in the periodic table suggests properties intermediate between those of the alkaline earth metals and the Group IV transition metals. This observation is substantiated by known chemical properties. However, a number of fundamental questions remain unanswered. For instance, how do chemical and redox properties change from metal to metal? Also, the capacity of soft donor molecules, for example CO, olefins and acetylenes, to serve as ligands in lanthanide complexes is still an open question, since no evidence for such bonding has been observed. This may be a result of the inability of these potential ligands to compete with harder Lewis bases that are generally present at some point during the preparation of the lanthanide compounds. Evans has reported that lanthanide metal vapors condense with butadienes to yield the compounds $Ln(C_4H_6)_3$ [32], where Ln is La, Nd, Sm and Er, and $Ln(Me_2C_4H_6)_2$, where Ln is La or Er. The mode of bonding to the butadiene ligands has

not been established, but the metals in these complexes are most likely not trivalent. Another interesting observation is that $SmCp_3$ is known to trimerize phenylacetylene and to polymerize olefins [33].

It is reasonable to expect fo find new and interesting reactivity patterns among more reactive lanthanide systems, such as ones exhibiting a low coordination number and/or low oxidation state. The reaction chemistry of these compounds with various organic and inorganic substrate molecules can best be studied if solubility in non-coordinating hydrocarbons can be obtained. This will eliminate complications due to coordination of polar solvents, such as tetrahydrofuran.

The aim of the research reported here is to investigate the use of sterically demanding ligands in preparing hydrocarbon-soluble derivatives of the lanthanides. Bulky ligands that can block coordination sites around the metal should lead to monomeric, electron-poor species that might display new and interesting chemical properties. Of particular interest are coordinatively unsaturated, hydrocarbon-soluble divalent compounds.

Two ligands that fit this description are the pentamethylcyclopentadienyl and bis(trimethylsilyl)amide groups. The utility of the pentamethylcyclopentadienyl ligand in this regard is illustrated by the observation that dicyclopentadienylmanganese has a polymeric constitution in the solid state [34], whereas bis(pentamethylcyclopentadienyl) manganese is monomeric and pentane-soluble [35].

Although the coordination chemistry of bis(trimethylsilyl)amide has been extensively investigated for main group metals, first-row

transition metals and the actinides [36], its use in lanthanide chemistry has been largely unexplored. Exhaustive reviews on the chemistry of this ligand have appeared [37-39]. It is potentially a very valuable ligand in lanthanide systems due to its steric bulk, and has been used to prepare monomeric, three-coordinate $Ln[N(SiMe_3)_2]_3$ complexes [40]. In addition, the tendency of the silylamide ligand to bridge two metal atoms, resulting in associated species, is relatively low. The basicity of the lone pair of electrons on nitrogen is much less than that of the lone pairs in dialkylamides, due to the electron-withdrawing effect of the $SiMe_3$ groups. The $SiMe_3$ group is more electron-withdrawing than an alkyl group, and possesses low-lying d_π-orbitals that may be able to delocalize the lone pair on nitrogen. However, there are a few examples of silylamide bridged species in low-coordination number complexes. The alkali-metal derivatives are associated, as is the divalent $Mn[N(SiMe_3)_2]_2$, which has been shown to exist as dimeric units in the solid state, with each manganese atom bound to one terminal and two bridging silylamides [41].

The divalent chemistry will focus upon europium and ytterbium, since the thermodynamic stability of these divalent metals is greatest among the lanthanides [28]. This is a consequence of the stability of the half-filled 4f shell ($4f^7$) in europium(II), and the full 4f shell ($4f^{14}$) in ytterbium(II).

During the course of this research, the compound $[Li(thf)_2][(C_5Me_5)_2NdCl_2]$ was briefly described by Evans [42], and the preparation of $Yb(C_5Me_5)_2(thf)_2$ was communicated [43]. The

latter publication also reports some halo and alkyl-pentamethylcyclopentadienyl derivatives of ytterbium(III).

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CHAPTER 2

EXPERIMENTAL DETAILS

General

Infrared spectra were recorded on a Perkin-Elmer 597 spectrometer as Nujol mulls between CsI windows. Mass spectra were obtained with an AEI-MS 12 mass spectrometer. The ^{1}H (90 MHz), $^{13}C\{^{1}H\}$ (22.5 MHz) and $^{31}P\{^{1}H\}$ (36.2 MHz) nuclear magnetic resonance spectra were recorded on a JEOL FX-90Q spectrometer and referenced to Me_4Si (δ 0, ^{1}H and ^{13}C spectra) or 85 percent H_3PO_4 (δ 0, ^{31}P spectra). Elemental analyses were performed by the analytical laboratories at the University of California, Berkeley. Melting points were taken in sealed capillaries and are uncorrected.

Low temperature magnetic susceptibility studies were conducted on solid samples using a Princeton Applied Research Model 155 vibrating sample magnetometer, equipped with a Janus Research Model 153 liquid helium dewar. The spectrometer was calibrated with $HgCo(SCN)_4$, and field strength was monitored with a George Associates rotating coil gaussmeter. Temperatures were measured with a calibrated GaAs diode. Solution magnetic moments were obtained using the Evans' NMR method [1].

All operations were conducted under a nitrogen atmosphere, using standard Schlenk techniques or a vacuum atmospheres inert atmosphere box. For reactions carried out under elevated pressures, a Fischer-Porter bottle, equipped with a pressure release valve, was used.

Reagent grade diethyl ether, tetrahydrofuran, 1,2-dimethoxyethane, pentane, benzene and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pyridine and N,N,N',N'-tetramethylethylene-diamine were distilled from sodium. Deuterated solvents for NMR studies were stored over molecular sieves and degassed prior to use. All other chemicals were of reagent grade quality unless specified otherwise.

The preparation of 1,2,3,4,5-pentamethylcyclopentadiene was according to the method of Threlkel and Bercaw [2]. Sodium pentamethylcyclopentadienide was prepared by adding the diene to $NaNH_2$ in liquid ammonia. The crude product was purified by extraction with tetrahydrofuran, evaporating the solvent and washing the residue with diethyl ether. The grey residue was dried in vacuo. Unlike LiC_5Me_5, which is insoluble in ethers, $Na(C_5Me_5$ is soluble in tetrahydrofuran and 1,2-dimethoxyethane, but not diethyl ether.

Sodium bis(trimethylsilyl)amide [3], the lanthanide dihalides [4], and the $Ln[N(SiMe_3)_2]_3$ [5] were prepared according to literature procedures.

The phosphine 1,2-dimethylphosphinoethane was prepared by reaction of bis(1,2-dichlorophosphino)ethane with methyl magnesium chloride [6]. The 1,2-dimethylphosphinomethane was prepared by the method of Schmidbaur [7].

Tetra(n-butyl)ammonium borohydride, $[n\text{-}Bu_4N][BH_4]$, was prepared by soxhlet extraction of a sodium borohydride-tetra(n-butyl)-ammonium bromide mixture [8]. Sodium 2,2-dimethylpropionate (which is insoluble

in diethyl ether and tetrahydrofuran) was prepared by stirring equal molar amounts of sodium hydride and pivalic acid in diethyl ether for 12 h. Lithium diethylamide was prepared by the addition of n-butyl lithium to diethyl amine in pentane at 0°C. Ferrocinium hexafluorophosphate was obtained by combining ferrocinium tetrachloroferrate (8 g) and potassium hexafluorophosphate (3.8 g) in 120 mL of water. After stirring for 30 min., the mixture was cooled to 0°C, and the product isolated by filtration.

Experimental Procedures for Chapter 3

Attempted Preparation of Bis[bis(trimethylsilyl)amido]chloro-europium(III)

Tris[bis(trimethylsilyl)amido]europium(III) (1.12 g, 1.77 mmol) in tetrahydrofuran (75 mL) was added to $EuCl_3$ (0.23 g, 0.89 mmol) in tetrahydrofuran (50 mL). After 24 h of stirring, during which time the $EuCl_3$ dissolved, the solution was filtered. Attempts to crystallize a product by concentration and cooling failed.

Attempted Preparations of Bis[bis(trimethylsilyl)amido]-chlorosamarium(III)

1) Tris[bis(trimethylsilyl)amido]samarium(III) (1.47 g, 2.33 mmol) in tetrahydrofuran (75 mL) was added to $SmCl_3$ (0.30 g, 1.2 mmol) in tetrahydrofuran (50 mL). The solution was stirred for 24 h, the solvent was removed under vacuum, and the residue was extracted with pentane (50 mL). Concentration and cooling (-10°C) resulted in crystallization of the starting material, $Sm[N(SiMe_3)_2]_3$, characterized by its infrared spectrum and melting point. 2) Sodium bis(trimethylsilyl)amide (1.12 g, 6.11 mmol) in tetrahydrofuran (75 mL) was added to $SmCl_3$ (0.70 g, 3.1 mmol) in tetrahydrofuran (50 mL) and the solution was stirred for 12 h. The solvent was removed under vacuum and the residue extracted with pentane (40 mL). Concentration and cooling (-10°C) led to isolation of only $Sm[N(SiMe_3)_2]_3$, as shown by its infrared spectrum and melting point.

Attempted Preparation of Bis[bis(trimethylsilyl)amido]-iodosamarium(III)

Iodine (0.24 g, 0.96 mmol) in diethyl ether (25 mL) was added to Tris[bis(trimethylsilyl)amido]samarium(III) (1.21 g, 1.92 mmol) in diethyl ether (25 mL). A white precipitate formed immediately. The reaction mixture was stirred for 12 h, the volatile material was removed under vacuum, and the residue was extracted with pentane. Concentration and cooling (-10°C) yielded $Sm[N(SiMe_3)_2]_3$, as shown by IR and melting point. No attempt was made to characterize the insoluble product of the residue.

Attempted Preparation of Bis[bis(trimethylsilyl)amido]-chloroytterbium(III)

Sodium bis(trimethylsilyl)amide (2.02 g, 11.0 mmol) in tetrahydrofuran (30 mL) was added to $YbCl_3$ (1.54 g, 5.51 mmol) in tetrahydrofuran (50 mL), and the solution stirred for 12 h. The solvent was removed under vacuum and the residue was extracted with pentane (40 mL). Concentration and cooling (-10°C) resulted in the crystallization of $Yb[N(SiMe_3)_2]_3$, as shown by its IR spectrum and melting point.

Attempted Preparations of Bis[bis(trimethylsilyl)amido]-samarium(III) Complexes

1) A solution of sodium naphthalene (0.055 M, 50 mL, 2.7 mmol) in tetrahydrofuran was added to a solution prepared by adding $Sm[N(SiMe_3)_2]_3$ (1.14 g, 1.81 mmol) in tetrahydrofuran (30 mL) to $SmCl_3$ (0.23 g, 0.90 mmol) in tetrahydrofuran (50 mL). An intense purple color developed immediately that yielded a reddish-brown color

after ca. 2 h. After 12 h of stirring, the solvent was removed and naphthalene was sublimed (40°C, 10^{-2} mm Hg). The residue was extracted with pentane, from which only $Sm[N(SiMe_3)_2]_3$ could be crystallized (by IR and mp) in very low yield.

2. A sodium naphthalene solution (one molar equivalent in tetrahydrofuran, 50 mL) was added to $SmCl_3$ (0.76 g, 2.96 mmol) in tetrahydrofuran (50 mL). The purple solution was stirred for 12 h, and the tetrahydrofuran removed under vacuum. The dark brown-red residue was washed with toluene (2 x 75 mL), and sodium bis(trimethylsilyl)amide (1.08 g, 5.89 mmol) in 75 mL of tetrahydrofuran was added. The purple solution was stirred for 24 h, and the volatile material removed under vacuum. Addition of pentane gave a dark red solution, from which only the white $Sm[N(SiMe_3)_2]_3$ (by IR, mp) could be obtained.

Bis[bis(trimethylsilyl)amide]bis(tetrahydrofuran)europium(II), $Eu[N(SiMe_3)_2]_2(thf)_2$

Sodium bis(trimethylsilyl)amide (2.13 g, 11.6 mmol) and europium diiodide (2.36 g, 5.82 mmol) were stirred together in tetrahydrofuran (70 mL) for 8 h. After removal of the solvent, pentane (100 mL) was added, and the solution filtered. Concentration and cooling (-10°C) gave orange-yellow prisms, m.p. = 128-130°C, in an overall yield of 73 percent (2.62 g). The mass spectrum contained peaks at m/e 471 and 473, corresponding to $^{151}Eu[N(SiMe_3)_2]_2$ and $^{153}Eu[N(SiMe_3)_2]_2$. The $Eu[N(SiMe_3)_2]_2(thf)_2$ sublimes with much decomposition, 100-110°C/10^{-2} mm Hg. It is soluble in hydrocarbons and ethers.

Anal. Calcd. for $C_{20}H_{52}N_2EuO_2Si_4$: C, 38.9; H, 8.50; N, 4.54.

Found: C, 39.4; H, 7.73; N, 4.63. IR data: 1245 s, 1008 w sh, 998 s, 987 s, 865 m, 835 s br, 788 m, 770 m, 753 w, 668 m, 602 m, 447 w, 442 m, 375 m cm^{-1}.

Bis[bis(trimethylsilyl)amido]bis(1,2-dimethoxyethane)europium(II), $Eu[N(SiMe_3)_2]_2(dme)_2$

Europium diiodide (1.78 g, 4.39 mmol), sodium bis(trimethylsilyl) amide (1.61 g, 8.78 mmol) and 1,2-dimethoxyethane (75 mL) were added to a flask, and the mixture stirred for 10 h. After removal of solvent, the residue was extracted and crystallized from pentane (ca. 30 mL, -10°C) in an overall yield of 79 percent (2.26 g), m.p. = 83-86°C (the compound turned orange at ca. 77°C). The compound follows Curie behavior from 5 to 45 K with C = 8.82 and μ_{eff} = 8.43 B.M. Yellow $Eu[N(SiMe_3)_2]_2(dme)_2$ is soluble in hydrocarbons and ethers. Anal. Cald. for $C_{20}H_{56}N_2O_4Si_4Eu$: C, 36.8; H, 8.64; N, 4.29. Found: C, 35.7; H, 8.40; N, 4.28. IR data: 1303 m, 1245 s br, 1212 w, 1188 m, 1120 w sh, 1102 s, 1063 s, 1020 vs br, 988 w sh, 977 w, 929 w, 873 s br, 852 w sh, 822 vs br, 758 w sh, 745 m br, 692 w, 654 s, 603 m, 584 m, 562 w, 453 w br, 363 m cm^{-1}.

Bis[bis(trimethylsilyl)amido](bipyridine)europium(II), $Eu[N(SiMe_3)_2]_2(bipy)$

2,2'-Bipyridine (0.064 g, 0.41 mmol) in benzene (30 mL) was added to $Eu[N(SiMe_3)_2]_2(thf)_2$ (0.25 g, 0.41 mmol) in benzene (20 mL). The dark brown solution was stirred for 1 h, and the solvent removed under vacuum. The residue was extracted with toluene (10 mL), the toluene extract filtered, and the volume decreased to ca. 5 mL. Yellow

needles were obtained upon cooling (0°C) in a yield of 0.16 g (62 percent), m.p. = 85–87°C (decomp). The $Eu[N(SiMe_3)_2]_2(bipy)$ is soluble in toluene, benzene and ethers. It is only slightly soluble in saturated hydrocarbons. Anal. Calcd. for $C_{22}H_{44}N_4Si_4Eu$: C, 42.0; H, 7.05; N, 8.91. Found: C, 42.0; H, 6.66; N, 8.85. IR data: 1600 m, 1594 m, 1580 w, 1575 w, 1568 w, 1558 w, 1490 w, 1438 m, 1324 m, 1240 vs br, 1170 m, 1152 m, 1098 w, 1088 w, 1049 w, 1029 w, 1014 m, 1006 w, 965 vs br, 881 s, 866 m, 830 vs br, 775 w, 756 s, 738 m, 693 w, 666 m br, 643 m, 625 w, 602 m br, 428 m br, 415 w sh, 377 m cm^{-1}.

Sodium Tris[bis(trimethylsilyl)amido]europate(II), $NaEu[N(SiMe_3)_2]_3$

Europium diiodide (5.41 g, 0.0133 mol) and sodium bis(trimethylsilyl)amide (4.89 g, 0.0267 mol) were stirred together for 14 h in diethyl ether (100 mL). The diethyl ether was removed under reduced pressure, and the residue extracted with toluene (60 mL). The yellow toluene solution was filtered, the volume was reduced to ca. 15 mL under vacuum and cooled (-10°C) to give large yellow prisms (m.p. = 132–134°C) in an overall yield of 41 percent (3.58 g). The compound was dissolved in benzene and hydrolyzed with D_2O. Only the resonance due to $DN(SiMe_3)_2$ was observed in the ^1H NMR spectrum of the benzene extract. A qualitative test for sodium (with uranyl zinc acetate reagent) was positive. Anal. Calcd. for $C_{18}H_{54}N_3Si_6NaEu$: C, 32.9; H, 8.30; N, 6.40. Found: C, 30.8; H, 8.11; N, 5.45. IR data: 1240 s, 1206 w, 1069 s, 982 s, 858 s, 811 vs br, 753 m, 739 w sh, 720 w sh, 652 s, 602 w, 577 m, 389 m, 359 m cm^{-1}.

When extraction and crystallization were carried out with pentane or diethyl ether rather than toluene, a compound having different physical properties was obtained. The yellow needles (m.p. = 152-153°C) that crystallized from pentane (-10°C) or diethyl ether (-70°C) also contained sodium (by a qualitative test with uranyl zinc acetate reagent) and did not contain solvent of crystallization (by examinatin of hydrolysis products in benzene by ^{1}H NMR). The mass spectrum of this compound contained a peak due to the $Eu[N(SiMe_3)_2]_2$ species at m/e = 473, as well as groups of higher mass peaks centered at 504, 515, 536, 552, 603, 618, 625, 697 and 712. The compound crystallizes in space group $P\bar{1}$, with Z = 4 and a unit cell volume of 3454 Å^3 [9]. This volume is roughly one-half the unit cell volume observed for the product crystallized from toluene, 6996 Å^3 (space group $P2_1/n$, Z = 8) [9]. These data suggest that the compound crystallized from pentane or diethyl ether can also be formulated as $NaEu[N(SiMe_3)_2]_3$, and that this compound simply crystallizes in a different form from pentane and diethyl ether. Anal. C, 29.0; H, 7.26; N, 5.50 IR data: 1242 m sh, 1232 s, 1006 s, 868 m, 850 w, 817 s, 756 m, 718 m, 653 m, 602 w, 587 m, 551 w, 390 m, 364 m cm^{-1}.

Bis[bis(trimethylsilyl)amido]europium(II)-1,2-dimethylphosphinoethane complex, $Eu[N(SiMe_3)_2]_2(dmpe)_{1.5}]_x$

To $NaEu[N(SiMe_3)_2]_3$ (0.49 g, 0.75 mmol) in pentane (20 mL) was added 1,2-dimethylphosphinoethane (0.32 g, 2.1 mmol), and the resulting orange solution was stirred for 6 h. The solution was filtered, concentrated to ca. 10 mL and cooled (-10°C) to yield large orange prisms in an overall yield of 67 percent (0.35 g). When heated

in a sealed capillary, the compound partially melted at 78–80°C and the remaining solid melted at 94–95°C. The compound was hydrolyzed in benzene with D_2O. The ^1H NMR spectrum of the benzene extract contained resonances due to $DN(SiMe_3)_2$ and dmpe [10]. The mass spectrum contained an envelope of peaks centered at m/e 623 due to $Eu[N(SiMe_3)_2]_2(dmpe)$. Anal. Calcd. for $C_{21}H_{60}N_2P_3Si_4Eu$: C, 36.1; H, 8.67; N, 4.01; P, 13.3. Found: C, 35.4; H, 8.34; N, 3.80; P, 13.0. IR data: 1424 m, 1300 w, 1282 w, 1243 s, 1173 w, 1147 w, 1094 w, 1046 s, 986 w, 938 m, 925 w sh, 864 s, 822 s, 751 m, 740 w sh, 718 w, 652 m, 600 m, 578 m, 356 s, 238 w cm^{-1}.

Bis[bis(trimethylsilyl)amido]bis[tri(n-butyl)phosphine]europium(II)

$Eu[N(SiMe_3)_2]_2(PBu^n_3)_2$

Tri(n-butyl)phosphine (1.6 mL, 6.4 mmol) was added to $NaEu[N(SiMe_3)_2]_3$ (1.00 g, 1.52 mmol) dissolved in pentane (50 mL). After stirring for 12 h, the pentane solution was filtered, concentrated to ca. 10 mL under reduced pressure and cooled (-70°C). The orange cyrstals (m.p. = 48–49°C) were isolated and dried in vacuo. Yield was 48 percent (0.64 g). The hydrosylate of this compound in benzene consisted of tri(n-butyl)phosphine and $HN(SiMe_3)_2$ in a 1:1 molar ratio (by ^1H NMR). The $^{31}P\{^1H\}$ NMR spectrum of the above solution contained a single resonance at δ -29.7 due to free tri-(n-butyl)phosphine [11]. The mass spectrum contained groups of peaks centered at m/e 783, 873 and 944. The $Eu[N(SiMe_3)_2]_2(PBu^n_3)_2$ requires 877. The effective magnetic moment, determined by Evans' method (30°C, benzene) was 7.4 B.M. Anal. Calcd. for $C_{36}H_{90}N_2P_2Si_4Eu$: C, 49.3; H, 10.3; N, 3.19; P, 7.06. Found: C, 49.0; H, 10.2; N, 2.79; P, 6.82. When heated to 100°C under vacuum,

tri(n-butyl)phosphine is slowly evolved from the compound. IR data: 1413 w, 1339 w, 1241 s, 1043 s, 978 s, 861 s, 817 s, 749 s, 653 m, 598 m, 577 w, 380 w sh, 361 m cm^{-1}.

Bis[bis(trimethylsilyl)amido]ytterbium(II)-tetrahydrofuran complex, $Yb[N(SiMe_3)_2]_2(thf)_{2.5}$

Sodium bis(trimethylsilyl)amide (2.30 g, 13.0 mmol) and ytterbium diiodide (2.78 g, 6.51 mmol) were stirred together in tetrahydrofuran (75 mL) for 12 h. After removal of solvent, the orange residue was extracted with pentane (50 mL). The pentane solution was filtered, concentrated (to ca. 15 mL) and cooled to -10°C. The orange prisms (m.p. = 173-174°C) were collected and dried in vacuum in an overall yield of 68 percent (3.0 g). This compound can also be prepared by the additon of tetrahydrofuran to $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ in pentane, followed by crystallization from pentane. ^1H NMR (26°C, d_6-PhH): δ 0.49 (s, 36H, $N(SiMe_3)_2$), 1.40 (m, 10H, β-protons of thf) and 3.68 (m, 10H, α-protons of thf). $^{13}C\{^1H\}$ NMR (-30°C, d_8-PhMe): δ 5.47, $N(SiMe_3)_2$; 25.0, β-carbons of thf and 69.6, α-carbons of thf. The highest mass peak observed in the mass spectrum was at 494, corresponding to $Yb[N(SiMe_3)_2]_2$. Anal. Calcd. for $C_{22}H_{56}N_2O_{2.5}Si_4Yb$: C, 39.2; H, 8.37; N, 4.16. Found: C, 35.3; H, 8.02; N, 3.57. IR data: 1250 s, 1182 w, 1079 m, 1047 s, 972 s, 866 s, 832 s, 776 m, 756 m, 664 s, 609 m, 590 m, 369 s cm^{-1}.

Bis[bis(trimethylsilyl)amido]bis(1,2-dimethoxyethane)ytterbium(II), $Yb[N(SiMe_3)_2]_2(dme)_2$

Ytterbium diiodide (3.92 g, 9.18 mmol), sodium bis(trimethylsilyl) amide (3.37 g, 18.4 mmol) and 1,2-dimethoxyethane (75 ml) were added

to a flask, and the mixture was stirred for 10 h, resulting in a blue solution. Removal of solvent under vacuum gave a blue residue, which was extracted with toluene (40 mL). Concentration of the filtrate (to ca. 10 mL) and cooling (-10°C) led to crystallization of blue prisms (m.p. = 162-165°C) in an overall yield of 63 percent (3.9 g). The mass spectrum contained a parent peak at m/e 674. Anal. Calcd. for $C_{20}H_{56}N_2O_4Si_4Yb$: C, 35.6; H, 8.37; N, 4.16. Found: C, 34.5; H, 8.07; N, 4.11. IR data: 1248 s, 1194 w, 1127 m, 1086 s, 1062 w sh, 968 s, 864 m, 832 s, 776 m, 757 m, 662 s, 601 m, 587 w, 387 m sh, 372 m cm^{-1}.

Bis[bis(trimethylsilyl)amido](1,2-dimethoxyethane)ytterbium(II), $Yb[N(SiMe_3)_2]_2(dme)$

Blue $Yb[N(SiMe_3)_2]_2(dme)_2$ (1.78 g, 2.64 mmol) was dissvoled in pentane (40 mL) giving a red solution. Concentration to ca. 10 mL and cooling (-10°C) led to crystallization of red prisms (m.p. = 118-120°C) in quantitative yield. ^1H NMR (30°C, d_6-PhH): δ 0.42 (s, 36H, $N(SiMe_3)_2$), 2.93 (s, 6H, OCH_3) and 3.26 (m, 4H, $MeOCH_2$). The mass spectrum contained a parent peak at m/e 584. Anal. Calcd. for $C_{16}H_{46}N_2O_2Si_4Yb$: C, 32.9; H, 7.94; N, 4.80. Found: C, 33.1; H, 7.95; N, 4.60. IR data: 1249 s, 1238 w sh, 1112 w sh, 1092 w sh, 1054 s, 1024 w sh, 962 s, 887 w sh, 862 m, 828 s, 749 m, 662 m, 604 w, 589 w, 373 w sh, 363 m cm^{-1}.

Bis[bis(trimethylsilyl)amido](1,2-dimethoxyethane)iodoytterbium(III), $Yb[N(SiMe_3)_2]_2I(dme)$

A solution of blue $Yb[N(SiMe_3)_2]_2(dme)_2$ (0.74 g, 1.10 mmol) in toluene (40 mL) was added to solid silver iodide (0.26 g, 1.1 mmol)

with stirring. The resulting yellow solution, with a very dark suspended solid, was stirred for 5 h. After removal of toluene under reduced pressure, diethyl ether (ca. 50 mL) was used to extract the product from the residue and for crystallization of the product (-10°C, ca. 8 mL). The yellow needles (m.p. = 153-155°C) were obtained in 49 percent yield. A qualitative test for iodide (with silver nitrate solution) was positive. Anal. Calcd. for $C_{16}H_{46}N_2O_2Si_4IYb$: C, 27.0; H, 6.52; N, 3.94. Found: C, 26.7; H, 6.54; N, 3.93. IR data: 1302 w, 1261 w sh, 1200 m, 1203 w sh, 1192 w, 1079 m, 1031 s, 989 w sh, 970 w sh, 953 m, 933 s, 889 w sh, 856 m, 832 s, 780 w, 759 w, 669 m, 620 m, 402 w, 383 m cm^{-1}.

Bis[bis(trimethylsilyl)amido]bis(diethyl ether)ytterbium(II), $Yb[N(SiMe_3)_2]_2(OEt_2)_2$

Diethyl ether (125 mL), cooled to 0°C, was added to a flask containing ytterbium diiodide (4.76 g, 11.2 mmol) and sodium bis(trimethylsilyl)amide (4.09 g, 22.3 mmol). The blue reaction mixture was stirred at 0°C for 1 h. Upon warming to room temperature, the solution color changed to red. After 10 h of additional stirring, the solution was filtered, concentrated (to ca. 20 mL) and cooled (-70°C). The yellow prisms that were isolated gradually turned orange upon warming to ambient temperature. The orange crystals (m.p. 69-71°C) were isolated in 56 percent (4.0 g) yield. The compound gives a red solution in aromatic or aliphatic hydrocarbons. ^1H NMR (26°C, d_6-PhH): δ 0.41 (s, 36 H, $N(SiMe_3)_2$), 1.06 (t, 12H, $OCH_2\underline{C}H_3$) and 3.51 (q, 8H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (26°C, d_6-PhH): δ 5.57 ($N(SiMe_3)_2$), 14.1 ($OCH_2\underline{C}H_3$) and 65.2 ($O\underline{C}H_2CH_3$). Mass

spectrum: m/e 639 ($Yb[N(SiMe_3)_2]_2(OEt_2)_2$ - 3), 567 ($Yb[N(SiMe_3)_2]_2(OEt_2)$ - 1) and 493 ($Yb[N(SiMe_3)_2]_2$ - 1). IR data: 1249 s, 1187 m, 1151 m, 1122 m, 1091 w, 1040 m br, 968 s, 862 m sh, 830 s br, 774 m, 753 w sh, 732 w sh, 663 w sh, 662 m, 609 m, 592 w, 503 w, 391 m, 372 m cm^{-1}. Anal. Calcd. for $C_{20}H_{56}N_2O_2Si_4Yb$: C, 37.4; H, 8.79; N, 4.36. Found: C, 33.3; H, 8.06; N, 4.18.

The complex was freed of diethyl ether by stirring it (0.56 g, 0.87 mmol) in toluene (30 mL) at 80°C for 5 h, then removing the solvent under reduced pressure at 80°C. The resulting red compound (0.14 g) was crystallized from pentane (6 mL, -10°C). ^1H NMR (26°C, d_8-PhMe): δ 0.32, s, $N(SiMe_3)_2$. $^{13}C\{^1H\}$ NMR (26°C, d_8-PhMe): δ 6.45, s, $N(SiMe_3)_2$. IR data: 1252 s, 1022 s, 927 s, 876 s, 818 s, 763 s, 659 s, 604 w sh, 594 m, 412 m, 391 w sh, 374 m, 363 w sh, 284 w, 244 w cm^{-1}.

Sodium Tris[bis(trimethylsilyl)amido]ytterbate(II), $NaYb[N(SiMe_3)_2]_3$

Sodium bis(trimethylsilyl)amide (3.76 g, 0.0205 mol) and ytterbium diiodide (4.38 g, 0.0103 mol) were stirred together in diethyl ether (100 mL) at 0°C for 1 h. The mixture was then warmed to room temperature and stirred for an additional 10 h. After removal of the diethyl ether, the residue was extracted with toluene (60 mL) to give a red solution. This solution was evaporated to dryness under vacuum, and the red residue dissolved in pentane (40 mL). The red pentane solution was filtered, concentrated to ca. 15 mL and cooled (-10°C). The red needles (m.p. = 154-157°C) were isolated in 46 percent yield (3.20 g). ^1H NMR (26°C, d_6-PhH): δ 0.24, s, $N(SiMe_3)_2$. $^{13}C\{^1H\}$ NMR

(26°C, d_6-PhH): δ 6.38, s, $N(SiMe_3)_2$. Upon lowering the temperature to -80°C, the silylamide resonance in the $^{13}C\{^1H\}$ NMR spectrum (d_8-PhMe) gradually decreased in intensity as a broad resonance (δ 7.01, $\nu_{1/2}$ = ca. 120 Hz) increased in intensity. A qualitative test for sodium (with uranyl zinc acetate reagent) was positive. Anal. Calcd. for $C_{18}H_{54}N_3Si_6NaYb$: C, 31.9; H, 8.04; N, 6.20. Found: C, 28.9; H, 7.29; N, 5.36. IR data: 1241 s, 1203 w, 1046 s, 964 s, 857 s, 818 s, 752 s, 653 m, 602 w, 579 w, 392 m, 357 m cm^{-1}.

Bis(1,2-dimethylphosphinomethane)bis(trimethylsilyl)ytterbium(II), $Yb[N(SiMe_3)_2]_2(dmpm)_2$

The addition of 1,2-dimethylphosphinomethane (0.14 mL, 0.83 mmol) to a pentane solution (20 mL) of $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ (0.53 g, 0.83 mmol) resulted in a deep red colored solution. The solution was stirred for 3 h, filtered and concentrated to ca. 6 mL. Cooling to -10°C resulted in crystallization of thin, dark red plates (m.p. = 60-61°C). The compound dissolves in diethyl ether to give a solution that has the orange-yellow color characteristic of $Yb[N(SiMe_3)_2]_2(OEt_2)_2$. ^1H NMR (26°C, d_8-PhMe): δ 0.35 (s, 36H, $N(SiMe_3)_2$); 0.87 (s, 24H, PMe_2) and 1.14 (t, J_{PH} = 3Hz, 4H, PCH_2P). $^{13}C\{^1H\}$ NMR (26°C, d_8-PhMe): δ 5.91 (s, $N(SiMe_3)_2$); 14.9 (s, PMe_2) and 31.6 (s, PCH_2P). $^{31}P\{^1H\}$ NMR (-40°C to +25°C, d_8-PhMe): δ - 44.7. The mass spectrum did not contain a parent ion (m/e = 766), but peaks at 825, 756 and 639 were observed, as well as the $Yb[N(SiMe_3)_2]_2$ -1 peak (493). Anal. Calcd. for $C_{22}H_{64}N_2P_4Si_4Yb$: C, 34.5; H, 8.42; N, 3.66; P, 16.2. Found: C, 33.9; H, 8.25; N, 3.38; P, 15.8.

IR data: 1423 m, 1414 m, 1291 m, 1278 w, 1238 s, 1030 s, 968 s, 932 s, 860 s, 822 s, 748 s, 723 w sh, 710 w, 654 s, 600 m, 584 m, 387 w sh, 361 s cm^{-1}.

(1,2-Dimethylphosphinoethane)bis[bis(trimethylsilyl)amido]ytterbium(II), $Yb[N(SiMe_3)_2]_2(dmpe)$

To orange $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ (0.57 g, 0.89 mmol) in pentane (30 mL) was added 1,2-dimethylphosphinoethane (0.3 mL, ca. 2 mmol). The color of the solution turned purple. After stirring for 2 h, the solution was filtered, concentrated to ca. 13 mL and cooled (-10°C). Purple prisms (m.p. = 195-197°C) were isolated in 70 percent yeild (0.4 g). The color of $Yb[N(SiMe_3)_2]_2(dmpe)$ is discharged by dissolution in diethyl ether to give the yellow-orange color of $Yb[N(SiMe_3)_2]_2(OEt_2)_2$. ^1H NMR (26°C, d_6-PhH): δ 0.46 (s, 36H, $N(SiMe_3)_2$), 0.86 (s, 12H, PMe_2) and 1.04 (t, 4H, PCH_2CH_2P). $^{13}C\{^1H\}$ NMR (26°C, d_6-PhH): δ 5.75, $N(SiMe_3)_2$; 11.6, PMe_2 and 25.8, t ($^1J_{PC}$ = 8 Hz), PCH_2CH_2P. $^{31}P\{^1H\}$ NMR (26°C, d_6-PhH): δ -40.9, s. The mass spectrum gave a molecular ion for $Yb[N(SiMe_3)_2]_2(dmpe)$, m/e = 644. Anal. Calcd. for $C_{18}H_{52}N_2P_2Si_4Yb$: C, 33.6; H, 8.14; N, 4.35; P, 9.62. Found: C, 31.6; H, 7.98; N, 3.81; P, 9.02. IR data: 1423 m, 1300 w, 1283 w, 1243 s, 1245 w, 1052 s, 962 s, 940 s sh, 862 s, 821 s, 748 s, 722 w sh, 692 w, 656 s, 600 m, 579 m, 455 w, 369 s, 352 s cm^{-1}.

Bis[bis(trimethylsilyl)amido]bis[tri(n-butyl)phosphine]ytterbium(II), $Yb[N(SiMe_3)_2]_2(PBu^n_3)_2$

Tri(n-butyl)phosphine (0.34 mL, 1.4 mmol) was added to a pentane solution (20 mL) of $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ (0.43 g, 0.67 mmol). After 14 h of stirring, the solution was filtered,

concentrated to ca. 10 mL under reduced pressure and cooled (-70°C). Brown-red prisms (m.p. = 46-48°C) crystallized in 70 percent yield (0.42 g). In the mass spectrum, groups of peaks centered at m/e 493 ($Yb[N(SiMe_3)_2]_2$ - 1), 505, 517, 531, 543, 567, 581, 593, 605, 617, 639, 655, 693 and 705 were observed. ^1H NMR (26°C, d_6-PhH): δ 0.48 (s, 36H, $N(SiMe_3)_2$), 1.00 (t, 18H, $P(CH_2)_3\underline{CH_3}$) and 1.49 (s, 36H, $P(\underline{CH_2})_3CH_3$). $^{13}C\{^1H\}$ NMR (26°C, d_6-PhH): δ 6.27 (s, $N(SiMe_3)_2$), 14.0 (s, $P(CH_2)_3\underline{CH_3}$), 24.9 (d, J_{PC} = 10 Hz, $-\underline{CH_2}-$), 26.9 (d, J_{PC} = 10 Hz, $-\underline{CH_2}-$) and 28.3 (d, J_{PC} = 11 Hz, $-\underline{CH_2}-$) $^{31}P\{^1H\}$ NMR (26°C, d_6-PhH): δ 29.6. Anal. Calcd. for $C_{36}H_{90}N_2P_2Si_4Yb$: C, 48.1; H, 10.1; N, 3.12; P, 6.89. Found: C, 48.8; H, 10.0; N, 2.87; P, 7.47. IR data: 1413 w, 1244 s, 1089 w, 1031 m, 964 s, 862 m, 824 s, 769 w, 749 w, 656 w, 602 w, 586 w, 386 w, 367 m cm^{-1}.

Bis[bis(trimethylsilyl)amido](1,2-diphenylphosphinoethane)ytterbium(II), $Yb[N(SiMe_3)_2]_2$(disphos)

A solution of $NaYb[N(SiMe_3)_2]_3$ (0.81 g, 1.20 mmol) in pentane (50 ML) was added to 1,2-diphenylphosphinoethane (0.48 g, 1.20 mmol), and the solution was stirred for 12 h. The product separated from solution as a red solid. The pentane was filtered off, and the red solid washed with pentane (2 x 40 mL). The compound is sparingly soluble in toluene, from which it was crystallized (0.11 g from 15 mL at -10°C, after extraction with 60 mL). When heated in a sealed capillary, the compound gradually moistens above ca. 140°C and melts at 206-209°C. Anal. Calcd. for $C_{38}H_{60}N_2P_2Si_4Yb$: C, 51.2; H, 6.78; N, 3.14; P, 6.94. Found: C, 51.3; H, 6.50; N, 2.79; P, 6.64.

IR data: 1583 w, 1570 w, 1433 w, 1246 w sh, 1233 s, 1174 m, 1154 w, 1098 w, 1052 s, 1023 w sh, 997 w, 929 m, 882 m, 869 m, 822 s, 749 m sh, 741 m, 726 w, 691 s, 661 m, 590 m, 551 w, 510 m, 502 w sh, 480 w, 448 w, 379 w sh, 363 m, 243 w cm^{-1}.

Bis[bis(trimethylsilyl)amido]tris(t-butylnitrile)ytterbium(II), $Yb[N(SiMe_3)_2]_2(NCCMe_3)_3$

To $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ (0.55 g, 0.86 mmol) in toluene (10 mL) was added t-butylnitrile (0.40 mL, 3.6 mmol) in toluene (25 mL). The reaction mixture was stirred for 10 h, the toluene removed under vacuum, and the residue extracted with pentane (40 mL). The red pentane solution was concentrated to ca. 6 mL and cooled (-10°C) to afford dark red prisms (m.p. = 68–70°C) in 38 percent yield (0.24 g). ^1H NMR (26°C, d_6-PhH): δ 0.63 (s, $N(SiMe_3)_2$) and 1.62 (s, $\nu_{1/2}$ = 41 Hz, $NCCMe_3$). $^{13}C\{^1H\}$ NMR (26°C, d_6-PhH): δ 5.89, $N(SiMe_3)_2$ and 28.3, $NCCMe_3$. No other resonances were observed. Anal. Calcd. for $C_{27}H_{63}N_5Si_4Yb$: C, 43.6; H, 8.54; N, 9.42. Found: C, 42.5; H, 8.33; N, 9.13. IR data: 2254 m, 1242 s, 1207 w, 1041 s, 940 w, 884 w sh, 873 m, 817 s, 763 m, 742 m, 689 m, 652 s, 593 m, 360 m cm^{-1}.

Reaction of methyl lithium with $Yb[N(SiMe_3)_2]_2I(dme)$

Methyl lithium (1.3 mL of a 0.6 M solution in diethyl ether, 0.78 mmol) was added to $Yb[N(SiMe_3)_2]_2I(dme)$ in diethyl ether at 0°C. The solution was stirred for 6 h, the solvent removed and the residue extracted with pentane (40 mL). The $Li(OEt_2)N(SiMe_3)_2$, identified by m.p. and IR, was crystallized from the pentane solution (ca. 8 mL, -10°C).

Reaction of phenylacetylene with $Yb[N(SiMe_3)_2]_2(OEt_2)_2$

Phenylacetylene (0.16 mL, 1.5 mmol) in toluene (10 mL) was added to $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ (0.48 g, 0.75 mmol) in toluene (20 mL) at 0°C. After stirring for 1 h, a dark purple solid had separated from solution. This solid was isolated by filtration, and crystallized from tetrahydrofuran (8 mL, -70°C). The compound was identified as $Yb(C \equiv CPh)_2$ by its infrared spectrum and analyses (C, 51.6; H, 2.83; $C_{16}H_{10}Yb$ requires C, 51.2; H, 2.69) [12].

Experimental Procedures for Chapter 4

Bis(diethyl ether)sodium pentamethylcyclopentadienyltrichloroneodymate(III), $[Na(OEt_2)_2][(C_5Me_5)NdCl_3]$

Sodium pentamethylcyclopentadienide (3.38 g, 0.0214 mol) in tetrahydrofuran (50 ml) was added to a stirred suspension of $NdCl_3$ (5.36 g, 0.0214 mol) in tetrahydrofuran (75 mL). The resulting solution was refluxed for 12 h. The blue-green solution was evacuated to dryness, and the residue extracted with diethyl ether (2 x 100 mL). The combined diethyl ether extracts were concentrated to ca. 80 mL and cooled to -10°C, yielding light blue prisms. Overall yield: 7.40 g (62 percent). When heated in a sealed capillary, the compound turned pink (decomp.) at ca. 125°C. Anal. Calcd. for $C_{18}H_{35}O_2Cl_3NaNd$: C,38.8; H, 6.33. Found: C, 38.6; H, 5.69. IR data: 2720 w, 1296 W br, 1181 w, 1150 w, 1090 s, 1063 s, 1018 w sh, 1007 m, 968 w, 911 m, 862 m, 833 w sh, 799 w, 791 w, 721 m, 588 w, 392 m cm^{-1}.

Bis(diethyl ether)lithium bis(pentamethylcyclopentadienyl)dichloroytterbate(III), $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$

A flask was charged with $YbCl_3$ (2.62 g, 9.38 mmol) and LiC_5Me_5 (2.67 g, 18.8 mmol). Tetrahydrofuran (75 mL) was added, and the violet

mixture was refluxed for 6 h. The tetrahydrofuran was removed under vacuum, and the residue extracted with diethyl ether (2 x 60 mL). The combined extracts were concentrated to ca. 30 mL and cooled to -10°C to give violet needles in 72 percent (4.50 g) yield. When heated in a sealed capillary, the compound decomposed (turned grey) at 128-130°C. Anal. Calcd. for $C_{28}H_{50}O_2Cl_2LiYb$: Cl 50.2; H, 7.53; Cl, 10.59. Found: C, 50.5; H, 7.59; Cl, 9.38. IR data: 2723 w, 1300 m, 1262 w, 1183 m, 1153 w, 1120 w sh, 1090 s, 1061 s, 1021 s, 911 m, 836 m, 791 m, 722 w, 592 w, 502 m, 382 vs br, 305 vs br cm^{-1}.

(N,N,N',N'-Tetramethylethylenediamine)lithium bis(pentamethylcyclopentadienyl)dichloroytterbate(III), $[Li(tmed)][(C_5Me_5)_2YbCl_2]$

N,N,N',N'-Tetramethylethylenediamine (0.3 mL, ca. 2 mmol) was added to $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ (0.60 g, 0.90 mmol) in 40 mL of diethyl ether. The violet solution was stirred for 5h and the volatile material removed under vacuum to yield a pink residue. The residue was dissolved in 30 mL of diethyl ether and the volume reduced to ca. 20 mL under reduced pressure. Cooling (-10°C) resulted in crystallization of violet needles in 53 percent (0.30 g) yield. The compound turned grey (decomposed) at 254-256°C when heated in a sealed capillary. Anal. Calcd. for $C_{26}H_{46}N_2Cl_2LiYb$: C, 49.0; H, 7.27; N, 4.39. Found: C, 50.0; H, 7.43; N, 4.50. IR data: 2723 w, 1410 m, 1360 m, 1290 s, 1248 m, 1186 m, 1161 s, 1131 s, 1099 w, 1070 s, 1033 s, 1016 s, 947 s, 792 s, 773 m, 722 w, 631 w, 618 w, 594 m, 472 s br, 445 s, 417 m, 389 s, 357 m, 308 vs br, 240 s cm^{-1}.

Bis(diethyl ether)lithium bis(pentamethylcyclopentadienyl)dichloroneodymate(III), $[Li(OEt_2)_2][(C_5Me_5)_2NdCl_2]$

Tetrahydrofuran (100 mL) was added to a flask containing $NdCl_3$ (3.55 g, 0.0142 mol) and LiC_5Me_5 (4.03 g, 0.0283 mol) and the dark blue solution was refluxed for 12 h. After removal of solvent under vacuum, the residue was extracted with diethyl ether (2 x 100 mL). The combined red extracts were concentrated to ca. 100 mL and cooled (-10°C), resulting in isolation of large blue prisms in 66 percent yield (6.0 g). Heating in a sealed capillary results in decomposition (to a white substance) at 114-116°C. Anal. Calcd. for $C_{28}H_{50}O_2Cl_2LiNd$: C, 52.5; H, 7.87. Found: C, 52.2; H, 7.78. IR data: 2728 w, 2184 w, 1949 w, 1299 m, 1182 s, 1154 m, 1089 s br, 1059 s br, 1018 s br, 909 m, 834 m, 790 s, 722 w, 632 w, 619 w, 592 w, 552 w, 503 m, 384 vs br, 304 vs br cm^{-1}.

Bis(N,N,N'N'-tetramethylethylenediamine)lithium bis(pentamethylcyclopentadienyl)dichloroneodymate(III), $[Li(tmed)_2][(C_5Me_5)_2NdCl_2]$

N,N,N',N'-Tetramethylethylenediamine (0.3 mL, 2 mmol) was added to $[Li(OEt_2)_2][(C_5Me_5)_2NdCl_2]$ (0.58 g, 0.91 mmol) in 30 mL of diethyl ether. The solution was stirred for 3 h, the volatile material removed under vacuum, and the residue extracted with diethyl ether (30 mL). This solution was concentrated to ca. 20 mL and cooled (-10°C) to yield small, light blue needles in 58 percent yield (0.38 g). When heated in a sealed capillary, the compound did not undergo an observable change below 300°C. Anal. Calcd. for $C_{32}H_{62}N_4Cl_2LiNd$: C, 53.0; H, 8.62; N, 7.73. Found: C, 53.3; H, 8.47; N, 7.69. IR data: 2720 w, 1369 m, 1290 s, 1249 m, 1188 m,

1163 s, 1131 s, 1100 m, 1070 m, 1034 s, 1017 s, 948 s, 789 s, 776 w, 722 w, 593 m, 496 m br, 446 m, 378 m sh, 342 m, 300 s br, 229 s br cm^{-1}.

(N,N,N'N'-Tetramethylethylenediamine)lithium bis(pentamethylcyclopentadienyl)dichlorosamarate(III), $[Li(tmed)][(C_5Me_5)_2SmCl_2]$

Lithium pentamethylcyclopentadienide (2.1 g, 15 mmol) was added to $SmCl_3$ (1.94 g, 7.6 mmol) and tetrahydrofuran (60 mL) was added. After refluxing for 8 h, the suspension was evaporated to dryness. The residue was extracted with toluene (50 mL) and evaporated to dryness. Tetrahydrofuran (10 mL) and N,N,N',N'-tetramethylethylenediamine (1.5 mL, ca. 10 mmol) were added to the residue. After stirring the orange solution for 2 h, the volatile material was removed under vacuum. The residue was washed with pentane (20 mL), then crystallized from tetrahydrofuran (10 mL, -10°C) as yellow prisms in 33 percent yield (1.5 g). When heated in a sealed capillary, the compound turned orange at 201-203°C and dark red at 287-289°C. Anal. Calcd. for $C_{26}H_{46}N_2Cl_2LiSm$: C, 50.8; H, 7.54; N, 4.56. Found: C, 50.5; H, 7.71; N, 4.40. IR data: 2721 w, 1358 w, 1293 s, 1263 w sh, 1250 m, 1186 m, 1161 m, 1130 m, 1099 w, 1067 m, 1033 s, 1014 w sh, 947 s, 913 w, 892 w, 792 s, 773 w, 722 w, 592 w, 471 m br, 443 m, 416 w, 384 w, 309 vs, 236 s cm^{-1}.

Bis(diethyl ether)sodium bis(pentamethylcyclopentadienyl)dichloroytterate(III), $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$

To a stirred suspension of $YbCl_3$ (3.33 g, 0.0119 mol) in tetrahydrofuran (25 mL) was added NaC_5Me_5 (3.77 g, 0.0238 mol) in tetrahydrofuran (75 mL). The solution was stirred for 15 h, the solvent removed under vacuum and the purple residue extracted with

diethyl ether (2 x 100 mL). The diethyl ether extracts were concentrated to ca. 100 mL and cooled to -10°C to yield large violet prisms. Subsequent crystallizations from the mother liquors resulted in isolation of $Yb(C_5Me_5)_2Cl(thf)$, which could be separated by fractional crystallization. Overall yields: $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$, 2.70 g (33 percent); $Yb(C_5Me_5)_2Cl(thf)$, 2.75 g (42 percent). When heated in a sealed capillary, $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ decomposed (turned grey) at 278-280°C. A sample was dissolved in benzene and hydrolyzed with D_2O. Examination of the benzene extract (^1H NMR) showed only resonances due to diethyl ether and C_5Me_5D. The magnetic moment (5-45k) was 3.91 B.M., with θ = -3.7K and C = 1.90. Anal. Calcd. for $C_{28}H_{50}O_2Cl_2NaYb$: C, 49.1; H, 7.36; Cl, 10.35. Found: C, 49.0; H, 7.16; C, 9.00. IR data: 2723 w, 1307 w, 1290 w, 1187 w sh, 1172 w sh, 1152 m, 1124 m, 1084 vs br, 1046 w, 1024 m, 931 m, 845 m, 824 w, 804 w, 723 w, 598 m, 444 w, 390 m br, 309 vs br cm^{-1}.

(N,N,N',N'-Tetramethylethylenediamine)sodium bis(pentamethylcyclopentadienyl)dichloroytterbate(III), $[Na(tmed)][(C_5Me_5)_2YbCl_2]$

N,N,N',N'-Tetramethylethylenediamine (0.30 mL, ca. 2 mmol) was added to a solution of $[Na(OEt)_2][(C_5Me_5)_2YbCl_2]$ (0.83 g, 1.2 mmol) in 30 mL of diethyl ether. The reaction mixture was stirred for 1 h, and then evacuated to dryness. Extraction with diethyl ether (2 x 50 mL), concentration of the combined extracts to ca. 40 mL and cooling (-10°C) resulted in crystallization of violet prisms in 41 percent yield (0.32 g). When heated in a sealed capillary, the

compound gradually decomposed (turned grey) above ca. 120°C. Anal. Calcd. for $C_{26}H_{46}N_2Cl_2NaYb$: C, 47.8; H, 7.09; N, 4.28. Found: C, 46.3; H, 7.05; N, 3.10. A qualitative test for sodium (uranyl zinc acetate reagent) was positive. Attempted sublimation of the compound at 250°C and 10^{-4} mm Hg led to decomposition. IR data: 2719 w, 1289 s, 1248 m, 1176 m, 1152 m, 1129 w, 1070 s br, 1032 w sh, 1017 s br, 943 s, 927 w sh, 913 w sh, 837 m, 782 s, 720 w, 612 w, 590 m, 550 w, 451 w, 424 m, 378 s br, 305 s br cm^{-1}.

(Diethyl ether)sodium bis(pentamethylcyclopentadienyl)dichloroneodymate(III), $[Na(OEt_2)][(C_5Me_5)_2NdCl_2]$

Addition of NaC_5Me_5 (4.56 g, 0.0288 mol) in tetrahydrofuran (75 mL) to $NdCl_3$ (3.61 g, 0.0144 mol) suspended in tetrahydrofuran (25 mL) resulted in a green solution. The mixture was refluxed for 8 h, evacuated to dryness and the residue extracted with diethyl ether (2 x 10 mL). The combined extracts were concentrated to ca. 150 mL and cooled to -10°C, resulting in crystallization of light blue prisms, m.p. > 300°C. Overall yield: 4.03 g, 48 percent. Anal. Calcd. for $C_{24}H_{40}OCl_2NaNd$: C, 49.7; H, 6.92. Found: C, 50.1; H, 6.66. IR data: 2722 w, 2180 w, 1943 w, 1306 w, 1186 m, 1157 m, 1123 s, 1098 s, 1069 s, 1021 s, 913 w, 841 w, 802 w, 796 w sh, 722 w, 628 w, 618 w, 594 w, 379 m br, 312 vs br cm^{-1}.

Bis(pentamethylcyclopentadienyl)chlorotetrahydrofuranneodymium(III), $(C_5Me_5)_2NdCl(thf)$

Upon further concentration and cooling, the mother liquors from the above reaction also yielded green $(C_5Me_5)_2NdCl(thf)$, m.p.

220-223°C, in an overall yield of 1.73 g (23 percent). Anal. Calcd. for $C_{24}H_{38}OClNd$: C, 55.2; H, 7.33. Found: C, 55.4; H, 7.28. IR data: 2721 w, 1948 w, 1343 w, 1298 w, 1262 w, 1179 m, 1151 w, 1122 s, 1076 w, 1019 vs, 953 w, 917 m, 863 vs, 845 w sh, 802 w, 723 w, 671 m, 628 w, 617 w, 593 m, 551 w, 382 w, 309 vs br, 243 m cm^{-1}. The ^1H NMR spectrum (36°C, d_6-PhH) consisted of a broad resonance ($\nu_{1/2}$ = 75 Hz) at δ 2.95 due to the C_5Me_5 group. The thf resonances were not observed.

The neutral species, $(C_5Me_5)_2NdCl(thf)$, may also be prepared by extraction of the residue from reaction of NaC_5Me_5 (2 molar equivalents) and $NdCl_3$ in tetrahydrofuran with pentane in 20 percent yield. The complex was identified by IR and m.p.

(Diethyl ether)sodium bis(pentamethylcyclopentadienyl)dichlorosamarate(III), $[Na(OEt_2)][(C_5Me_5)_2SmCl_2]$

Sodium pentamethylcyclopentadienide (2.19 g, 13.8 mmol) in tetrahydrofuran (75 mL) was added to a $SmCl_3$ (1.77 g, 6.9 mmol) suspension in tetrahydrofuran (25 mL). The resulting brown solution was stirred for 24 h, and then evaporated to dryness in vacuum. The residue was extracted with diethyl ether (2 x 75 mL) and the combined, orange extracts were concentrated to ca. 70 mL and cooled (-10°C). The large, orange prisms, obtained in 36 percent yield (2.9 g), were collected and dried under vacuum. When heated in a sealed capillary, there was no observable change in the compound up to 280°C. The ^1H NMR spectrum (d_6-PhH, 26°C) consisted of a singlet at δ 7.27, a quartet centered at δ 3.35 (J = 7 Hz), and a triplet centered at δ 1.20 (J = 7 Hz) in

area ratio 30:4:6 due to $\underline{Me}_5C_5$, $MeCH_2O$ and $\underline{Me}CH_2O$, respectively. The resonances are narrow, $\nu_{1/2}$ being ca. 1 Hz. Anal. Calcd. for $C_{24}H_{10}OClNaSm$: C, 49.0; H, 6.85. Found: C, 48.5; H, 6.49. IR data: 3563 w, 2725 w, 2275 w, 1305 w, 1187 m, 1157 m, 1123 s, 1098 s, 1068 s, 1022 s, 912 w, 835 m, 803 w sh, 796 m, 723 w, 629 w, 618 w, 596 w, 553 w, 506 w, 381 m br, 312 vs br, 238 m cm^{-1}.

(N,N,N',N'-Tetramethylethylenediamine)sodium bis(pentamethylcyclopentadienyl)dichlorosamarate(III), $[Na(tmed)][(C_5Me_5)_2SmCl_2]$

Addition of N,N,N',N'-tetramethylethylenediamine (0.3 mL, ca. 2 mmol) to a solution of $[Na(OEt_2)][(C_5Me_5)_2SmCl_2]$ (0.80 g, 1.4 mmol) in diethyl ether (15 mL) resulted in precipitation of a yellow solid that crystallized from tetrahydrofuran as yellow needles. The yellow needles did not melt or undergo a noticeable change when heated in a sealed capillary to 280°C. Overall yield: 0.56 g (65 percent). Anal. Calcd. for $C_{26}H_{46}N_2Cl_2NaSm$: C, 49.5; H, 7.35; N, 4.44. Found: C, 49.7; H, 7.36; N, 3.20. IR data: 2724 w, 1297 s, 1256 m, 1181 m, 1160 m, 1137 m, 1099 w, 1078 m, 1040 m sh, 1023 s, 953 s, 918 w, 896 w, 838 w, 804 w sh, 788 s, 724 m, 592 m br, 456 w, 432 w, 383 m br, 310 s br cm^{-1}.

Bis(pentamethylcyclopentadienyl)chlorotetrahydrofuranytterbium(III), $(C_5Me_5)_2YbCl(thf)$

a. By crystallization from toluene. Sodium pentamethylcyclopentadienide (4.74 g, 0.030 mol) in tetrahydrofuran (75 mL) was added to a cooled (-70°C) suspension of $YbCl_3$ (4.19 g, 0.015 mol) in tetrahydrofuran (50 mL). The blue suspension turned to red as the

solution was allowed to warm to room temperature. The red suspension was stirred for 15 h. Tetrahydrofuran was removed under vacuum and the residue extracted with toluene (2 x 100 mL). The extracts were combined, concentrated to ca. 70 mL and cooled (-10°C). The violet needles, m.p. 221-223°C, were collected and dried in vacuum. Yield was 5.2 g (63 percent). The compond is soluble in hydrocarbons and ethers. Attempted sublimation at 120-125°C and 10^{-3} mm Hg led to decomposition of the compound. A sample was dissolved in benzene and hydrolyzed with water. Examination of the benzene extract (^{1}H NMR) showed only resonances due to tetrahydrofuran and C_5Me_5H. The mass spectrum contained groups of peaks centered about m/e = 479, 444, 343, and 309, corresponding to the fragments $Yb(C_5Me_5)_2Cl^+$, $Yb(C_5Me_5)_2^+$, $Yb(C_5Me_5)Cl^+$ and $Yb(C_5Me_5)^+$, respectively. The magnetic moment, determined at 28°C (in PhH) by the Evans method, was 4.2 B.M. Anal. Calcd. for $C_{24}H_{38}ClOYb$: C, 52.4; H, 6.96; Cl, 6.44. Found: C, 52.6; H, 7.05; Cl, 6.04. IR data: 2723 w, 1612 w, 1342 w, 1297 w, 1246 w, 1178 m, 1062 w, 1036 w sh, 1014 s, 954 w, 922 m, 913 w sh, 862 s, 841 w sh, 803 w, 728 m, 693 w, 677 m, 628 w, 595 m, 552 w, 382 m, 308 vs, 258 s cm^{-1}.

b. From $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$. The anionic complex (0.65 g, 9.5 mmol) was suspended in toluene (60 mL) and tetrahydrofuran (0.5 mL) was added, yielding a purple solution that was stirred for 8 h. The volatile material was removed under vacuum and the residue was crystallized from toluene (ca. 10 mL, -10°C). The m.p. and IR spectrum were identical to those of an authentic specimen.

Bis(pentamethylcyclopentadienyl)chloropyridineytterbium(III), $(C_5Me_5)_2YbCl(py)$

To $(C_5Me_5)_2YbCl(thf)$ (0.84 g, 1.53 mmol) dissolved in diethyl ether (10 mL) was added 1 mL of pyridine (an excess), and the solution was stirred for 2 h. The volatile material was removed under vacuum, and the residue dissolved in diethyl ether (30 mL). Upon concentration to ca. 20 mL and cooling (-10°C), purple prisms (m.p. 270-272°C) were obtained in 47 percent yield (0.4 g). Anal. Calcd. for $C_{25}H_{35}NClYb$: C, 53.8; H, 6.32; N, 2.51; Cl, 6.35. Found: C, 54.4; H, 6.37; N, 2.53; Cl, 5.96. IR data: 3048 w, 2720 w, 1947 w, 1640 m, 1600 s, 1570 w, 1233 w, 1215 m, 1153 w, 1062 m, 1039 w, 1019 w sh, 1009 m, 959 w, 800 w, 756 s, 707 s, 627 m, 592 w, 433 m, 389 m, 310 s br cm^{-1}.

(Diethyl amine)bis(pentamethylcyclopentadienyl)chloroytterbium(III), $(C_5Me_5)_2YbCl(NHEt_2)$

Diethyl amine (1 mL, excess) was added to a suspension of $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ (1.47 g, 25.1 mmol) in toluene (25 mL). The resulting solution was stirred for 6 h and then evaporated to dryness. The purple residue was crystallized from toluene (ca. 8 mL, -10°C) to give purple prisms in 84 percent yield (1.0 g). When heated in a sealed capillary, the prisms decomposed at ca. 181°C. Anal. Calcd. for $C_{24}H_{41}NClYb$: C, 52.2; H, 7.49; N, 2.54; Cl, 6.42. Found: C, 51.9; H, 7.24; N, 2.42; Cl, 6.16. IR data: 3300 w, 2723 w, 1192 w, 1153 w, 1119 m, 1053 m, 1017 m, 963 s, 838 m, 785 s, 728 w, 593 w, 382 m, 300 s, 250 m cm^{-1}.

Tetrabutylammonium bis(pentamethylcyclopentadienyl)dichloroytterbate (III), $[n\text{-}Bu_4N][(C_5Me_5)_2YbCl_2]$

To $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ (0.77 g, 1.15 mmol) in 20 mL of toluene was added $[n\text{-}Bu_4N][BH_4]$ (0.28 g, 1.2 mmol) in toluene (60 mL). After stirring 10 h, the solution was filtered and concentrated to ca. 15 mL. Cooling (-10°C) gave purple needles (m.p. 204-205°C) in 69 percent yield (0.6 g). ^1H NMR (26°C, d_8-PhMe): δ 2.85 ($\nu_{1/2}$ = 15 Hz), 12 H; 3.52 ($\nu_{1/2}$ = 37 Hz), 30H; 4.45 ($\nu_{1/2}$ = 23 Hz), 8 H; 6.75 ($\nu_{1/2}$ = 23 Hz), 8H and 10.17 ($\nu_{1/2}$ = 23 Hz), 8H. Anal. Calcd. for $C_{36}H_{66}NCl_2Yb$: C, 57.1; H, 8.79; N, 1.85. Found: C, 54.7; H, 8.46; H, 1.82. IR data: 2718 w, 1159 m, 1127 w, 1103 w, 1061 w, 1021 m, 923 w, 898 w sh, 879 m, 800 w, 782 w, 736 m, 599 w, 382 m, 296 s cm^{-1}.

Phenylpyridinemagnesium bis(pentamethylcyclopentadienyl)bromochloroytterbate(III), $(C_5Me_5)_2Yb(Cl)BrMgPh(py)$

The Grignard reagent PhMgBr (1.05 mL of a 1.0 M diethyl ether solution) was added to a diethyl ether solution (40 mL) of $(C_5Me_5)_2YbCl(py)$ (0.57 g, 1.0 mmol) cooled to 0°C. After 1 h, the solution was warmed to room temperature and stirred for 8 h. The solution was then filtered, concentrated to ca. 12 mL and cooled (-10°C) to yield purple needles (m.p. 279-281°C, dec.) in 61 percent yield. The mass spectrum contained peaks due to $(C_5Me_5)_2$-$Yb(Cl)BrMg(py)^+$ (661), $(C_5Me_5)_2YbBr^+$ (523) and $(C_5Me_5)_2YbCl^+$ (479). Anal. Calcd. for $C_{31}H_{40}NBrClMgYb$: C, 50.4; H, 5.45; N, 1.89. Found: C, 50.3; H, 5.99; N, 2.30. IR data: 3045 w, 2707 w, 1600 s, 1485 w, 1441 m,

1235 w, 1214 s, 1064 m, 1040 m, 1020 m, 1009 m, 757 s, 707 s, 630 m, 387 m, 306 s, 278 m, 245 m cm^{-1}.

Bis(pentamethylcyclopentadienyl)[bis(trimethylsilyl)amido]neodymium(III), $(C_5Me_5)_2NdN(SiMe_3)_2$

Sodium bis(trimethylsilyl)amide (0.16 g, 0.87 mmol) in toluene (25 mL) was added to $[Li(OEt_2)_2][(C_5Me_5)_2NdCl_2]$ (0.55 g, 0.86 mmol) in toluene (20 mL). The blue solution was stirred for 8 h, then the solvent was removed under vacuum. The residue was extracted with pentane (2 x 20 mL). The combined extracts were concentrated to ca. 13 mL and cooled (-10°C) to obtain large hexagonal needles in 51 percent yield (0.25 g). The compound does not melt below 300°C. Anal. Calcd. for $C_{26}H_{48}NSi_2Nd$: C, 54.3; H, 8.41; N, 2.44. Found: C, 53.3; H, 8.28; N, 2.36. IR data: 2722 w, 1257 w sh, 1242 s, 1032 s br, 863 vs br, 813 vs br, 762 vs br, 669 m, 592 s, 383 w sh, 370 s, 290 vs br cm^{-1}.

Pentamethylcyclopentadienylbis[bis(trimethylsilyl)amido]neodymium(III), $(C_5Me_5)Nd[N(SiMe_3)_2]_2$

Sodium bis(trimethylsilyl)amide (0.72 g, 3.9 mmol) in toluene (50 mL) was added to $[Na(OEt_2)_2][(C_5Me_5)NdCl_3]$ (1.08 g, 1.94 mmol), and the mixture was stirred for 12 h. After evaporation to dryness, the residue was extracted with pentane (50 mL). Concentration to ca. 10 mL under vacuum, followed by cooling (-10°C) resulted in crystallization of large blue prisms (m.p. 234-236°C) in 72 percent yield (0.84 g). A parent ion, an envelope of peaks centered about m/e = 600, was observed in the mass spectrum. Anal. Calcd. for $C_{22}H_{51}N_2Si_4Nd$: C, 44.0; H, 8.56; N, 4.67. Found: C, 42.0; H,

8.46; N, 4.30. IR data: 1246 vs br, 990 vs br, 878 s sh, 830 s br, 763 s, 752 w sh, 723 m, 670 s, 660 w sh, 598 s, 371 s, 306 s cm^{-1}.

Bis(pentamethylcyclopentadienyl)bis(trimethylsilyl)amidoytterbium(III), $(C_5Me_5)_2YbN(SiMe_3)_2$

Sodium bis(trimethylsilyl)amide (0.21 g, 1.1 mmol) in diethyl ether (30 mL) was added to $(C_5Me_5)_2YbCl(py)$ (0.64 g, 1.1 mmol) in diethyl ether (20 mL). After stirring for 10 h, the volatile material was removed under reduced pressure and the residue was extracted with pentane (50 mL). After filtration, the pentane solution was concentrated to ca. 10 mL. Cooling (-10°C) afforded large, purple prisms (m.p. 294-295°C) in 61 percent yield (0.42 g). Anal. Calcd. for $C_{26}H_{48}NSi_2Yb$: C, 51.7; H, 8.01; N, 2.32. Found: C, 50.9; H, 7.82; N, 2.18. IR data: 2710 w, 1256 w sh, 1242 s, 988 s br, 868 s br, 820 s br, 777 m, 749 m, 655 m, 383 m, 298 s cm^{-1}.

Bis(pentamethylcyclopentadienyl)(2,2-dimethylpropionato)ytterbium(III), $(C_5Me_5)_2YbO_2CCMe_3$

The anionic complex $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ (1.72 g, 2.51 mmol) in diethyl ether (30 mL) was added to a suspension of sodium 2,2-dimethylpropionate (0.31 g, 2.50 mmol) in diethyl ether (20 mL). After stirring 6 h, the red solution was evaporated to dryness and the residue extracted with 35 mL of pentane. After filtering and cooling (-70°C), red prisms (m.p. 154-155°C) were obtained. The yield was 48 percent (0.65 g). The mass spectrum showed dimeric peaks at m/e = 924, 889, 820, 802, 749, 612 and 571, as well as the monomeric peak at m/e = 545. ^1H NMR (26°C, d_8-PhMe): δ 10.95 ($\nu_{1/2}$ = 107

Hz), 30 H; δ -26.45 ($\nu_{1/2}$ = 21 Hz), 9 H. The magnetic susceptiblity followed Curie behavior from 5-35K, with μ_{eff} = 3.29 B.M. and C = 1.34. Anal. Calcd. for $C_{25}H_{39}O_2Yb$: C, 55.1; H, 7.22. Found: C, 55.2; H, 7.19. IR data: 2713 w, 1503 m, 1489 m, 1430 m, 1225 s, 1169 w, 1064 w, 1026 m, 940 w, 896 s, 810 m, 793 m, 617 m, 474 w, 408 m, 388 m, 319 s cm^{-1}.

Bis(pentamethylcyclopentadienyl)trifluoroacetatoytterbium(III), $(C_5Me_5)_2YbO_2CCF_3$

The complex $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ (1.08 g, 1.58 mmol) in tetrahydrofuran (30 mL) was added to NaO_2CCF_3 (0.22 g, 1.6 mmol) in tetrahydrofuran (10 mL). The dark red solution was stirred for 12 h, the tetrahydrofuran removed under vacuum, and the residue extracted with diethyl ether (2 x 40 mL). Concentration and cooling (-10°C) of the combined extracts led to crystallization of violet prisms (m.p. 262-263°C) in 57 percent yield (0.5 g). The mass spectrum contained a molecular ion at 557. Anal. Calcd. for $C_{22}H_{30}O_2F_3Yb$: C, 47.5; H, 5.43. Found: C, 47.7; H, 5.49. IR data: 3140 w, 3092 w, 2726 w, 1680 s, 1204 s, 1158 s, 1023 w, 847 m, 785 m, 718 m, 614 w, 592 w, 523 w, 468 w, 385 m, 312 s cm^{-1}.

Diethyldithiocarbamatobis(pentamethylcyclopentadienyl)ytterbium(III), $(C_5Me_5)_2YbS_2CNEt_2$

The anionic complex, $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ (1.39 g, 2.03 mmol) in diethyl ether (40 mL) was added to NaS_2CNEt_2 (0.35 g, 2.04 mmol) in diethyl ether (20 mL). After stirring for 8 h, the red diethyl ether solution was evaporated to dryness. Addition of pentane (40 mL) gave a deep purple solution, that upon concentration

and cooling (-10°C) gave purple prisms (m.p. 226-227°C) in 81 percent yield (0.97 g). The mass spectrum contained peaks at m/e = 592, $Yb(C_5Me_5)_2S_2CNEt_2^+$; 457, $Yb(C_5Me_5)S_2CNEt_2^+$; 444, $Yb(C_5Me_5)_2^+$; 322, $YbS_2CNEt_2^+$; 309, $YbC_5Me_5^+$. ^1H NMR (26°C, d_8-PhMe): δ 7.45 ($\nu_{1/2}$ = 61 Hz), 30 H; -5.76 ($\nu_{1/2}$ = 18 Hz), 4 H; -9.00 ($\nu_{1/2}$ = 13 Hz), 6H. The magnetic susceptability followed Curie behavior (5-55K), with μ_{eff} = 3.39 B.M. and C = 1.43. Anal. Calcd. for $C_{25}H_{40}NS_2Yb$: C, 50.7; H, 6.81; N, 2.37; S, 10.8. Found: C, 50.7; H, 6.76; N, 2.29; S, 10.7. IR data: 2723 w, 1487 s, 1424 s, 1360 m, 1306 w, 1277 s, 1209 m, 1241 m, 1089 m, 1023 w, 987 m, 911 m, 841 m, 800 w, 779 w, 608 w, 593 w, 564 m, 473 w, 392 m, 360 m, 311 s cm^{-1}.

Diethyldithiocarbamatobis(pentamethylcyclopentadienyl)neodymium(III), $(C_5Me_5)_2NdS_2CNEt_2$

To NaS_2CNEt_2 (0.58 g, 3.39 mmol) in diethyl ether (20 mL) was added $[Li(OEt_2)_2][(C_5Me_5)_2NdCl_2]$ (2.17 g, 3.39 mmol) in diethyl ether (40 mL). After 8 h of stirring, the green solution was filtered, concentrated to ca. 30 mL and cooled (-10°C). Large green prisms (m.p. 229-231°C) were obtained in an overall yield of 72 percent (1.37 g). ^1H NMR (d_8-PhMe, 70°C): δ 7.00 ($\nu_{1/2}$ = 23 Hz), 30 H; -0.10 ($\nu_{1/2}$ = 17 Hz), 4 H; -0.94 ($\nu_{1/2}$ = 16 Hz), 6H. The mass spectrum contained peaks at m/e = 562, $Nd(C_5Me_5)_2S_2CNEt_2^+$; 427, $Nd(C_5Me_5)S_2CNEt_2^+$; 414, $Nd(C_5Me_5)_2^+$; 292, $NdS_2CNEt_2^+$; 279, $NdC_5Me_5^+$. Anal. Calcd. for $C_{25}H_{40}NS_2Nd$: C, 53.3; H, 7.16; N, 2.49. Found: C, 53.5; H, 7.03;

N. 2.47. IR data: 2722 w, 1482 s, 1420 s, 1357 m, 1402 w, 1273 s, 1203 s, 1138 m, 1087 m, 1063 w, 1021 w, 979 m, 905 m, 836 m, 798 w, 773 w, 607 w, 560 m, 470 w, 430 w, 382 m, 348 m, 310 s cm^{-1}. The magnetic susceptibility followed Curie behavior (5-50K), with μ_{eff} = 2.75 B.M. and C = 0.94.

Attempted Preparation of $(C_5Me_5)_2YbNEt_2$

The anionic complex $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ (0.81 g, 1.21 mmol) in 40 mL of diethyl ether was added to a cold (-70°C) suspension of lithium diethylamide (0.10 g, 1.3 mmol) in diethyl ether. After ca. 1 h, the stirred solution was allowed to warm to room temperature, and was then stirred for an additional 7 h. The red solution was filtered away from a white precipitate. Concentration of the solution and cooling (-10°C) led to isolation of only the starting material, $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$, in 60 percent yield. Refluxing the reactants in tetrahydrofuran for 14 h led to the same result.

Experimental Procedures for Chapter 5

(Diethyl ether)bis(pentamethylcyclopentadienyl)(tetrahydrofuran) europium(II), $Eu(C_5Me_5)_2(thf)(OEt_2)$

Sodium pentamethylcyclopentadienide (9.72 g, 0.0614 mol) in tetrahydrofuran (75 mL) was added to a stirred suspension of europium trichloride (5.30 g, 0.0205 mol) in tetrahydrofuran (75 mL). A blue solution developed immediately which slowly turned brown-red. The suspension was refluxed for 12 h. Tetrahydrofuran was removed under vacuum, the residue was extracted with diethyl ether (2 x 150 mL), and the combined extracts were concentrated to ca. 100 mL. Cooling (-10°C)

yielded red prisms in 65 percent yield (7.5 g); m.p. 181–182°C. The complex is soluble in aliphatic and aromatic hydrocarbons and in ethereal solvents. It decomposed upon attempted sublimation under vacuum at ca. 140°C. A sample of the complex was dissolved in benzene and hydrolyzed with water. The ^1H NMR spectrum of the benzene solution showed tetrahydrofuran and diethyl ether in equal amounts. The compound follows Curie behavior from 5–50K with μ_{eff} = 7.99 B.M. and C = 7.91. Anal. Calcd. for $C_{28}H_{48}O_2Eu$: C, 59.1; H, 8.51. Found: C, 59.1; H, 8.43. IR data: 2713 w, 1629 w, 1313 w, 1286 w, 1248 w, 208 w, 1185 w, 1147 m, 1119 w, 1089 w, 1054 m, 1032 s, 1003 w sh, 927 w, 896 s, 837 w, 828 w, 818 w, 795 m, 777 m, 766 w, 649 w br, 624 w, 585 m, 506 m br, 353 w br, 248 s br cm^{-1}.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)europium(II), $Eu(C_5Me_5)_2(thf)$

(Diethyl ether)bis(pentamethylcyclopentadienyl)(tetrahydrofuran)-europium(II) (1.5 g, 2.7 mmol) was dissolved in toluene (25 mL), and the solution was concentrated to ca. 10 mL. Cooling (-70°C) yielded red prisms in quantitative yield; m.p. 178–181°C. Recrystallization of this complex from diethyl ether yields $Eu(C_5Me_5)_2(thf)(OEt_2)$. Anal. Calcd. for $C_{24}H_{38}EuO$: C, 58.3; H, 7.74. Found: C, 58.6; H, 7.56. IR data: 2714 w, 1637 w br, 1292 w sh, 1281 w, 1243 m, 1209 m, 1027 s br, 952 w, 928 w, 898 s br, 834 w sh, 794 w, 691 w, 637 m br, 587 w, 462 w, 357 m br, 258 s br cm^{-1}.

(Diethyl ether)bis(pentamethylcyclopentadienyl)europium(II), $Eu(C_5Me_5)_2(OEt_2)$

Sodium pentamethylcyclopentadienide (2.18 g, 13.8 mmol) and europium diiodide (2.79 g, 6.88 mmol) were stirred together in diethyl ether (100 mL). After 12 h, the red solution was filtered, concentrated (to ca. 60 mL) and cooled (-10°C). Large red needles (m.p. = 192-195°C) were obtained in 72 percent yield (2.46 g). The highest mass peak in the mass spectrum corresponded to the base-free fragment (m/e = 423). Anal. Calcd. for $C_{24}H_{40}OEu$: C, 58.1; H, 8.12. Found: C, 57.9; H, 8.07. IR data: 2721 w, 1488 w, 1284 m, 1163 w, 1144 s, 1079 s, 1037 s, 1017 m, 929 m, 838 s, 819 w, 797 m, 590 m, 551 w, 442 w, 358 s, 270 s cm^{-1}.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(II), $Yb(C_5Me_5)_2(thf)$

Sodium pentamethylcyclopentadienide (3.97 g, 0.0251 mol) in tetrahydrofuran (75 mL) was added to a suspension of ytterbium dichloride (3.06 g, 0.0125 mol) in tetrahydrofuran (75 mL). After refluxing for 12 h, the deep purple suspension was evaporated to dryness, and the residue was extracted with diethyl ether (2 x 100 mL). The combined, green extracts were concentrated to ca. 100 mL and cooled (-10°C). The red prisms were collected and dried under vacuum; yield 5.5 g (85 percent). When heated in a sealed capillary, the complex shrank at ca. 120°C and melted at 206-209°C. The compound is soluble in aromatic hydrocarbons and ethereal solvents. The complex decomposed upon attempted sublimation under vacuum at ca. 125°C. ^1H NMR (-25°C, d_8-PhMe): δ 1.41 (m, 4H, β-protons of thf), 2.12 (s, 30H, C_5Me_5)

and 3.42 (m, 4H, α-protons of thf). $^{13}C\{^1H\}$ NMR (-25°C, d_8-PhMe): δ 11.5 ($C_5\underline{Me}_5$), 25.7 ($\overline{O\underline{C}H_2\underline{C}H_2\underline{C}H_2CH_2}$), 69.5 ($\overline{O\underline{C}H_2CH_2CH_2\underline{C}H_2}$) and 111 ($\underline{C}_5Me_5$). Anal. Calcd. for $C_{24}H_{38}OYb$: C, 55.9; H, 7.43. Found: C, 56.2; H, 7.32. IR data: 2719 w, 1646 w br, 1322 w, 1297 w, 1249 m br, 1221 w, 1151 w, 1093 w, 1067 w sh, 1034 s br, 916 w, 882 s br, 801 w, 783 w, 668 m br, 628 w, 595 m, 483 w, 472 w, 361 m br, 304 m, 258 s br cm^{-1}.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)ytterbium(II)-Hemitoluene, $Yb(C_5Me_5)_2(thf)\cdot 1/2PhMe$

Sodium pentamethylcyclopentadienide (3.52 g, 0.0227 mol) in tetrahydrofuran (75 mL) and ytterbium dichloride (2.71 g, 0.0111 mol) in tetrahydrofuran (75 mL) were refluxed for 12 h. Tetrahydrofuran was removed under vacuum, the residue was extracted with toluene (150 mL), and the solution was concentrated to ca. 80 mL and was cooled to -70°C. The brown-red prisms were collected and dried under vacuum; yield 4.6 g (74 percent). When heated in a sealed capillary, the complex darkened at ca. 195°C and melted at 204-206°C. Anal. Calcd. for $C_{27.5}H_{42}OYb$: C, 58.8; H, 7.54. Found: C, 58.5; H, 7.27. IR data: 2719 m, 1604 m, 1337 w, 1259 m, 1242 w sh, 1174 m br, 1079 w, 1022 s, 918 m, 868 s br, 843 w sh, 795 w, 730 s, 694 s, 671 m, 589 w, 481 w sh, 466 m, 360 m br, 304 s br, 282 w sh, 268 s cm^{-1}.

(Diethyl ether)bis(pentamethylcylopentadienyl)ytterbium(II), $Yb(C_5Me_5)_2(OEt_2)$

A flask was charged with ytterbium diiodide (6.70 g, 0.0157 mol) and sodium pentamethylcyclopentadienide (4.97 g, 0.0314 mol). Diethyl ether (100 mL) was added, and the mixture stirred for 16 h. The green

ether solution was filtered, and the residue extracted once more with diethyl ether (100 mL). The combined extracts were concentrated to ca. 70 mL and cooled (-10°C). Green needles were isolated in an overall yield of 73 percent (5.9 g). The compound decomposed without melting at ca. 145°C. ^{1}H NMR (35°C, d_6-PhH): δ 1.04 (t, 6H, CH_3CH_2O), 2.16 (s, 30H, C_5Me_5) and 3.15 (q, 4H, CH_3CH_2O). Anal. Calcd. for $C_{24}H_{40}OYb$: C, 55.7; H, 7.79. Found: C, 55.7; H, 7.58. IR data: 2720 w, 1633 w, 1284 w, 1262 w, 1180 w sh, 1163 w sh, 1149 s, 1123 w, 1097 w sh, 1077 s br, 1041 m, 1019 w, 980 w sh, 948 w, 929 m, 839 s, 829 w sh, 797 w, 592 m, 552 w, 482 w, 443 w, 355 m br, 303 m, 268 s br cm^{-1}.

(Methyl vinyl ether)bis(pentamethylcyclopentadienyl)ytterbium(II), $Yb(C_5Me_5)_2(MeOC_2H_3)$

Toluene was enriched with methyl vinyl ether by adding triglyme and refluxing with sodium benzophenone ketyl. Ytterbium diiodide (1.25 g, 3.0 mmol), sodium pentamethylcyclopentadienide (0.94 g, 5.9 mmol) and methyl vinyl ether-containing toluene (50 mL) were added to a flask. The solution was stirred for 24 h, filtered, concentrated to ca. 10 mL and cooled (-70°C). Green prisms (m.p. = 185-188°C) were isolated in 63 percent yield (0.95 g). ^{1}H NMR (28°C, d_6-PhH): δ 2.23 (s, 30 H, C_5Me_5), δ 4.12 (m, 5H, $CH=CH_2$ and OMe) and 6.17 (q, 1H, $CH_2=CHO$). $^{13}C\{^1H\}$ NMR (28°C, d_6-PhH): δ 11.5 (C_5Me_5), 66.2 (OMe), 90.4 ($OCH=CH_2$), 112 (C_5Me_5) and 149 ($OCH=CH_2$). Anal. Calcd. for $C_{23}H_{36}OYb$: C, 55.1; H, 7.23. Found: C, 55.1; H, 7.35. The compound can be recrystallized from diethyl ether. IR data:

3120 w, 2726 w, 1637 s, 1328 m, 1288 w, 1252 w, 1208 m, 1123 m, 1200 s, 1060 w, 1040 s, 966 m, 952 m, 871 s, 829 w, 732 s, 699 m, 597 w, 470 w, 370 w, 310 m, 263 s cm^{-1}.

Bis(pentamethylcyclopentadienyl)(tetrahydrofuran)(triphenylphosphine-oxide)ytterbium(II), $Yb(C_5Me_5)_2(thf)(OPPh_3)$

Triphenylphosphineoxide (0.33 g, 1.19 mmol) in diethyl ether (50 mL) was added to $Yb(C_5Me_5)_2(OEt_2)$ (0.61 g, 1.18 mmol) in diethyl ether (20 mL). The solution was stirred for 10 h, resulting in precipitation of a red-brown solid. The diethyl ether was filtered off, and the residue washed with toluene (20 mL). The residue was then dissolved in 13 mL of tetrahydrofuran-diethyl ether (3:1) and cooled (-10°C). Small purple crystals (m.p. = 188-190°C) were isolated in 56 percent yield (0.53 g). The presence of tetranydrofuran was substantiated by ^1H NMR (d_6-PhH) of a hydrolyzed sample, and by absorptions in the IR spectrum (1041 and 892 cm^{-1}). The mass spectrum contained a peak due to $Yb(C_5Me_5)_2(OPPh_3)$ (m/e = 721). Anal. Calcd. for $C_{42}H_{53}PO_2Yb$: C, 63.5; H, 6.73; P, 3.90. Found: C, 63.8; H, 6.72; P, 4.11. IR data: 3052 m, 2719 m, 1592 m, 1438 m, 1170 s, 1119 s, 1093 w, 1077 w, 1041 m, 999 m, 916 w, 892 m, 851 w, 761 m, 746 m, 723 s, 703 m, 695 m, 593 w, 540 s, 513 w, 469 m, 411 w, 358 m, 313 w, 289 w, 256 m cm^{-1}.

(Bipyridine)bis(pentamethylcyclopentadienyl)europium(II), $Eu(C_5Me_5)_2(bipy)$

The complex was prepared by the addition of 2,2'-bipyridine (0.31 g, 2.0 mmol) in toluene (20 mL) to $Eu(C_5Me_5)_2(thf)(OEt_2)$ (1.14 g, 2.0 mmol) in toluene (15 mL). After stirring for 3 h and

removing the solvent, the resulting dark brown solid was crystallized from tetrahydrofuran (-70°C). The brown prisms did not melt below 300°C when heated in a sealed capillary. Yield was 91 percent (1.05 g). The mass spectrum contained a parent peak at m/e = 579. The compound follows Curie behavior (5-60K) with μ_{eff} = 7.73 B.M. and C = 7.41. Anal. Calcd. for $C_{30}H_{38}N_2Eu$: C, 62.3; H, 6.62; N, 4.84. Found: C, 60.9; H, 6.67; N, 4.75. IR data: 3044 w, 2720 w, 1591 s, 1562 w, 1433 w, 1312 m, 1152 m, 1004 m, 757 s, 741 w, 652 w, 639 w, 621 w, 416 w, 259 s cm^{-1}.

(Bipyridine)bis(pentamethylcyclopentadienyl)ytterbium(II), $Yb(C_5Me_5)_2(bipy)$

Upon addition of a toluene (10 mL) solution of 2,2'-bipyridine (0.46 g, 2.95 mmol) to a green solution of $Yb(C_5Me_5)_2(OEt_2)$ (1.53 g, 2.96 mmol) in toluene (25 mL), a very deep brown solution formed. The solution was stirred for 4 h and the toluene removed under vacuum. The brown solid was dissolved in pentane (40 mL), filtered and concentrated (to ca. 25 mL). Cooling (-10°C) yielded dark brown prisms in an overall yield of 85 percent (1.5 g). When heated in a sealed capillary, the compound did not melt below 300°C. ^1H NMR (26°C, d_6-PhH): δ - 13.11, s; 4.11, s, C_5Me_5; 5.24, s and 25.82, s. ^{13}C NMR (26°C, d_6-PhH): δ - 3.35 (q, $C_5\underline{Me}_5$, $^1J_{CH}$ = 123 Hz) and - 42.2 (s, $\underline{C}_5Me_5$). Anal. Calcd. for $C_{30}H_{38}N_2Yb$: C, 60.1; H, 6.39; N, 4.67. Found: C, 59.9; H, 6.32; N, 4.67. The magnetic moment, obtained by Evans' method (PhH, 30°C) was 2.4 B.M. IR data: 2720 w, 1553 m, 1510 m, 1492 w sh, 1426 w, 1399 m, 1281 s br, 1259 m br, 1147 s br, 1021 m, 942 s br, 743 w, 732 m, 638 w, 608 w, 448 w, 430 w, 290 s br cm^{-1}.

Bis(pentamethylcyclopentadienyl)bis(pyridine)ytterbium(II), $Yb(C_5Me_5)_2(py)_2$

To a solution of $Yb(C_5Me_5)_2(OEt_2)$ (1.75 g, 3.4 mmol) in toluene (20 mL) was added pyridine (1 mL, an excess). A dark green solid precipitated from solution. The mixture was stirred for 1 h, taken to dryness under vacuum, and the green residue was washed with pentane (50 mL). Extractions were taken by stirring the green residue in 100 mL of toluene overnight, filtering, and concentrating to ca. 20 mL. Cooling (-10°C) yielded ca. 300 mg. of $Yb(C_5Me_5)_2(py)_2$ (m.p. = 215-218°C). Overall yield was ca. 70 percent. ^1H NMR (26°C, d_6-PhH): δ 2.12 (s, C_5Me_5). Resonances due to the pyridine ligands were not observed. Anal. Calcd. for $C_{30}H_{40}N_2Yb$: C, 59.9; H, 6.66; N, 4.66. Found: C, 60.3; H, 6.70; N, 4.47. IR data: 3092 w, 3061 w, 3038 w, 2720 w, 1594 s, 1487 m, 1223 m, 1150 m, 1106 w br, 1069 m, 1034 m, 1000 m, 984 w, 942 w, 886 w, 800 w, 749 s, 729 w, 702 s, 652 w, 628 w, 619 w, 591 w, 418 m cm^{-1}.

Bis(p-dimethylaminopyridine)bis(pentamethylcyclopentadienyl)-ytterbium(II), $Yb(C_5Me_5)_2(p\text{-}Me_2NC_5H_5N)_2$

To $Yb(C_5Me_5)_2(OEt_2)$ (0.76 g, 1.5 mmol) in toluene (10 mL) was added p-dimethylaminopyridine (0.32 g, 2.9 mmol) in toluene (30 mL). The red color that developed in the solution gradually turned dark blue. The solution was stirred for 3 h and the toluene removed under vacuum. The blue residue was extracted with diethyl ether (2 x 100 mL) and the combined extracts concentrated (to ca. 110 mL) and cooled (-10°C). Dark blue prisms (m.p. = 241-242°C) were isolated in

an overall yield of 92 percent (0.93 g). ^{1}H NMR (26°C, d_8-PhMe): δ 2.18 (s, 30H, C_5Me_5), 2.28 (s, 6H, NMe_2), 6.18 (s, $\nu_{1/2}$ = 12 Hz, 2H, aromatic) and 8.37 (s, $\nu_{1/2}$ = 21 Hz, 2H, aromatic). Anal. Calcd. for $C_{34}H_{50}N_4Yb$: C, 59.4; H, 7.33; N, 8.15. Found: C, 59.2; H, 7.56; N, 7.78. IR data: 2719 w, 1612 s, 1531 s, 1288 w, 1228 s, 1181 w, 1120 w sh, 1111 m, 1067 m, 999 s, 959 m, 806 s, 757 m, 591 w, 537 m, 483 w, 468 w, 307 w, 251 m cm^{-1}.

(1,2-Dimethylphosphinoethane)bis(pentamethylcyclopentadienyl)-ytterbium(II), $Yb(C_5Me_5)_2(dmpe)$

1,2-Dimethylphosphinoethane (0.16 mL, 1 mmol) was added to $Yb(C_5Me_5)_2(OEt_2)$ (0.48 g, 0.93 mmol) in 25 mL of benzene. Stirring for 1 h resulted in a green precipitate and a colorless solution. The benzene was filtered off, and the green solid washed with toluene (75 mL). A small amount (0.20 g) of microcrystalline $Yb(C_5Me_5)_2(dmpe)$ (m.p. 283-285°C) was obtained by extraction with diethyl ether (70 mL), followed by concentration to ca. 20 mL and cooling (-10°C). Anal. Calcd. for $C_{26}H_{46}P_2Yb$: C, 52.6; H, 7.81; P, 10.4. Found: C, 51.8; H, 7.69; P, 10.0. IR data: 2721 w, 1421 m, 1302 m, 1284 w, 1150 w, 1091 w, 1015 w, 945 s, 926 m, 889 w, 829 w, 796 w, 720 s, 624 m, 672 w, 637 w, 589 w, 360 m, 349 m, 253 s cm^{-1}.

(1,2-Dimethylphosphinoethane)bis(pentamethylcyclopentadienyl)-europium(II), $Eu(C_5Me_5)_2(dmpe)$

1,2-Dimethylphosphinoethane (0.17 mL, 1 mmol) was added to $Eu(C_5Me_5)_2(OEt_2)$ (0.51 g, 1.0 mmol) in toluene (20 mL). The mixture was stirred for 1 h, the toluene filtered off, and the red

precipitate washed with toluene (75 mL). About 0.15 g of $Eu(C_5Me_5)_2(dmpe)$ (m.p. 288-292°C) was crystallized from diethyl ether (ca. 20 mL, -10°C). The compound was hydrolyzed in d_6-benzene, and the resulting solution was shown to contain C_5Me_5H and dmpe [10] in a 1:1 ratio by ^1H and $^{31}P\{^1H\}$ NMR. Anal. Calcd. for $C_{26}H_{46}P_2Eu$: C, 54.5; H, 8.10; P, 10.8. Found: C, 53.7; H, 7.83; P, 10.5. The infrared spectrum was identical to the one for $Yb(C_5Me_5)_2(dmpe)$.

(1,2-Dimethylphosphinomethane)bis(pentamethylcyclopentadienyl)-ytterbium(II), $Yb(C_5Me_5)_2(dmpm)$

1,2-Dimethylphosphinomethane (0.16 mL, 1.1 mmol) was added to $Yb(C_5Me_5)_2(OEt_2)$ in toluene (25 mL). The solution was stirred for 8 h, filtered and cooled (-10°). Dark green needles (m.p. 250-253°C) were collected and dried under vacuum. Yield was quantitative. ^1H NMR (26°C, d_6-PhH): δ 2.17, (s, 30H, C_5Me_5), 1.78 (d, 2H, PCH_2P) and 0.95 (s, 12H, PMe_2). $^{13}C\{^1H\}$ NMR (26°C, d_6-PhH): δ 112 (s, C_5Me_5), 44.6 (s, PCH_2P), 15.8 (s, PMe_2) and 12.0 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (26°C, d_6-PhH): δ - 39.6. Anal. Calcd. for $C_{25}H_{44}P_2Yb$: C, 51.8; H, 7.65; P, 10.7. Found: C, 50.6; H, 7.41; P, 10.2. IR data: 2720 w, 1420 m, 1300 m, 1284 m, 1161 w, 1109 m, 1055 w, 1015 m, 942 s, 925 m, 888 s, 830 m, 795 w, 749 s, 725 s, 705 w, 693 w, 674 w, 623 w, 589 w, 352 s, 253 s cm^{-1}.

(1,2-Dimethylphosphinomethane)bis(pentamethylcyclopentadienyl)-europium(II), $Eu(C_5Me_5)_2(dmpm)$

1,2-Dimethylphosphinomethane (0.30 mL, 1.8 mmol) was added to $Eu(C_5Me_5)_2(OEt_2)$ (0.87 g, 1.8 mmol) in toluene (40 mL), and

the solution cooled (-10°C). Red needles (m.p. 251-253°C) were isolated; yield was quantitative. Hydrolysis of the compound in d_6-benzene gave C_5Me_5H and dmpm [7] in a 1:1 ratio (by ^1H and $^{31}P\{^1H\}$ NMR). Anal. Calcd. for $C_{25}H_{44}P_2Eu$: C, 53.8; H, 7.94; P, 11.1. Found: C, 53.4; H, 7.85; P, 10.8. The infrared spectrum was identical to that for $Yb(C_5Me_5)_2(dmpm)$.

Experimental Procedures for Chapter 6

(Diethyl ether)sodium Bis(pentamethylcyclopentadienyl)bis(trimethylsilyl)amidoytterbium(II), $[Na(OEt_2)][(C_5Me_5)_2YbN(SiMe_3)_2]$

The divalent compex $Yb(C_5Me_5)_2(OEt_2)$ (0.62 g, 1.20 mmol) in toluene (15 mL) was cooled to 0°C, and sodium bis(trimethylsilyl)-amide (0.22 g, 1.2 mmol) in toluene (30 mL) was added. After stirring for 5h, a green solid had precipitated, leaving a clear solution. The toluene was filtered and the green residue dried in vacuo. Diethyl ether (50 mL) was added to the residue and the resulting green solution was filtered, concentrated to ca. 12 mL and cooled (-10°C). Green needles (mp. > 300°C) were obtained in 59 percent yield (0.5 g). The compound is insoluble in nonpolar hydrocarbons. It was dissolved in benzene and hydrolyzed. Analysis of the benzene extract by ^1H NMR showed resonances due to diethyl ether, C_5Me_5 and $HN(SiMe_3)_2$ in a 1:2:1 ratio. Anal. Calcd. for $C_{30}H_{58}NOSi_2NaYb$: C, 51.4; H, 8.34; N, 2.00. Found: C, 51.4; H, 7.55; N, 1.67. IR data: 2722 w, 1242 s, 1232 w sh, 1038 s, 983 w, 871 s, 823 w sh, 811 s, 757 m, 740 w, 652 m, 599 w, 580 w, 361 m, 324 m br cm^{-1}.

Reaction of $Yb(C_5Me_5)_2(thf)$ with NH_4Cl

To ammonium chloride (0.13 g, 2.4 mmol) was added $Yb(C_5Me_5)_2(thf)$ (1.21 g, 2.3 mmol) in tetrahydrofuran (40 mL) and the mixture was stirred for 10 h. The resulting red solution was filtered from a yellow precipitate, and evaporated to dryness giving a red residue. The $Yb(C_5Me_5)_2(thf)$ starting material was obtained by crystallization of the red residue from diethyl ether. The yield (based on the original amount of $Yb(C_5Me_5)_2(thf)$) was 33 percent. The yellow precipitate was washed with diethyl ether (40 mL) and dried under reduced pressure. This material was shown to be $YbCl_2(thf)_2$. Anal. Calcd. for $C_8H_{16}O_2Cl_2Yb$: C, 24.8; H, 4.16. Found: C, 24.5; H, 3.59. IR data: 1200 w, 1069 m, 1032 m, 913 w, 880 m, 721 m, 303 s cm^{-1}.

Reaction of $Eu(C_5Me_5)_2(thf)(OEt_2)$ with 2,6-di(t-butyl)cresol

2,6-Di(t-butyl)cresol (0.26 g, 1.2 mmol) in tetrahydrofuran (20 mL) was added to $Eu(C_5Me_5)_2(thf)(OEt_2)$ (0.68 g, 1.2 mmol) in tetrahydrofuran (30 mL). After stirring for 8 h, the tetrahydrofuran was removed, and the resulting yellow solid was crystallized from diethyl ether-tetrahydrofuran (4:1) at -10°C. Yellow needles (m.p. 217-219°C) were obtained in 42 percent yield (0.41 g) based on $Eu(OC_{15}H_{23})_2(thf)_3$. Anal. Calcd. for $C_{42}H_{70}O_5Eu$: C, 62.5; H, 8.74. Found: C, 62.7; H, 8.70. The mass spectrum contained peaks for $Eu(OC_{15}H_{23})_2$ at 1178/1181 for the ^{151}Eu and ^{153}Eu isotopes. IR data: 3651 w, 3200 w, 3144 w, 2720 w, 2561 w, 1745 w, 1602 w, 1548 w, 1412 m, 1272 s, 1217 m, 1198 m, 1121 w, 1029 s, 922 w, 911 m, 890 s, 878 s, 863 m, 818 s, 800 s, 789 m, 670 m, 632 w, 578 m, 498 s, 353 s cm^{-1}.

Reaction of 2,2-dimethylpropionic acid with $Eu(C_5Me_5)_2(thf)(OEt_2)$

To $Eu(C_5Me_5)_2(thf)(OEt_2)$ (0.94 g, 1.65 mmol) in 50 mL of diethyl ether was added 2,2-dimethylpropionic acid (0.17 g, 1.7 mmol) in diethyl ether (20 mL). A dull yellow solid precipitated. The diethyl ether solution was filterd off, and the residue washed with diethyl ether (50 mL). The residue was dissolved in tetrahydrofuran, the solution was filtered and concentrated to ca. 10 mL. Yellow microcrystals (ca. 0.5 g) were obtained (m.p. > 310°C). Anal. C, 37.2; H, 5.66. $Eu(O_2CCMe_3)_2(thf)$ requires C, 39.4; H, 6.15. IR data: 1567 s, 1531 s, 1481 s, 1411 s, 1244 s, 1058 s, 892 s, 801 m, 792 m, 600 m, 543 m, 383 m cm^{-1}.

Reaction of 2,2-dimethylpropionic acid with $Yb(C_5Me_5)_2(OEt_2)$

A solution of $Yb(C_5Me_5)_2(OEt_2)$ (0.90 g, 1.7 mmol) in diethyl ether (40 mL) was cooled to 0°C. A solution of 2,2-dimethylpropionic acid (0.18 g, 1.8 mmol) in diethyl ether was then added slowly. After 10 h of stirring at room temperature, a yellow solid had precipitated from solution. The diethyl ether was filtered, and the yellow residue dissolved in tetrahydrofuran-diethyl ether (1:1, 10 mL) to give a red solution. Cooling (-70°C) gave a yellow powder (m.p. 164-165°C). Anal. C, 40.7; H, 6.16. $Yb(O_2CCMe_3)_2(thf)_2$ requires C, 41.6; H, 6.60. IR data: 1567 s, 1472 m, 1409 m, 1351 m, 1220 m, 1050 m, 1018 m, 883 m, 785 m, 370 m cm^{-1}.

Reaction of phenylacetylene with $Yb(C_5Me_5)_2(OEt_2)$

Phenylacetylene (0.17 mL, 1.5 mmol) in toluene (15 mL) was added to $Yb(C_5Me_5)_2(OEt_2)$ (0.82 g, 1.16 mmol) in toluene (15 mL). With stirring, the green solution gradually turned red over a 12 h

period. The solution was filtered, concentrated to ca. 5 mL, and pentane (ca. 2 mL) was added. Cooling (-10°C) resulted in red prisms (m.p. = 275-278°C). The yield (based on $(C_5Me_5)YbC_2Ph$ as the product) was 47 percent (0.31 g). The mass spectrum contained peaks due to $Yb_2(C_5Me_5)_3(C_2Ph)_2$ (955), $Yb_2(C_5Me_5)_2(C_2Ph)_2$ (820), $Yb_2(C_5Me_5)(C_2Ph)_2$ (685), $Yb_2(C_5Me_5)(C_2Ph)$ (584) and $Yb(C_5Me_5)(C_2Ph)$ (410). ^1H NMR (26°C, d_6-PhH): δ 3.49, s, $\nu_{1/2}$ = 25 Hz, 30 H; 10.55, s, $\nu_{1/2}$ = 20 Hz, 1H; 12.69, s, $\nu_{1/2}$ = 20 Hz, 2H and 25.47, s, $\nu_{1/2}$ = 21 Hz, 2H. Anal. Calcd. for $C_{18}H_{30}Yb$: C, 52.8; H, 4.92. Found: C, 52.6; H, 5.30. IR data: 3076 w, 3047 w, 2718 w, 2040 m, 1593 w, 1571 w, 1483 m, 1441 w, 1193 m, 1070 w, 1023 m, 917 w, 756 s, 729 m, 690 s, 542 m, 502 m, 388 m, 310 s cm^{-1}.

Reaction of dichloromethane with $Yb(C_5Me_5)_2(thf)$ 1/2PhMe

Dichloromethane (0.50 mL, 7.8 mmol) was added to a toluene solution (20 mL) of $Yb(C_5Me_5)_2(thf)$ 1/2PhMe (0.66 g, 1.2 mmol) cooled to 0°C. After stirring at 0°C for 30 min. the volatile material was evaporated and the residue crystallized from toluene (ca. 8 mL, -10°C), in 70 percent yield (0.45 g). The m.p. and infrared spectrum were identical to those of an authentic specimen of $Yb(C_5Me_5)_2Cl(thf)$.

Reaction of ytterbium trichloride with $Yb(C_5Me_5)_2(thf)\cdot 1/2PhMe$

The $Yb(C_5Me_5)_2(thf)\cdot 1/2PhMe$ (0.52 g, 0.93 mmol), dissolved in toluene (30 mL), was added to a suspension of ytterbium trichloride (0.26 g, 0.93 mmol) in toluene (15 mL). After stirring for 12 h, the solution was filtered, concentrated to ca. 10 mL and cooled (-10°C). The violet crystals of $Yb(C_5Me_5)_2Cl(thf)$ (0.30 g, 59 percent) were identified by their m.p. and infrared spectrum.

Chloro(1,2-dimethylphosphinomethane)bis(pentamethylcyclopentadienyl)-ytterbium(III), $Yb(C_5Me_5)_2Cl(dmpm)$

The divalent $Yb(C_5Me_5)_2(dmpm)$ (0.74 g, 1.28 mmol) in toluene (75 mL) was added to a suspension of ytterbium trichloride (0.36 g, 1.3 mmol) in toluene (10 mL). The reaction mixture was stirred for 24 h. The compound was crystallized by filtering the solution, concentrating it to ca. 10 mL and cooling (-10°C). The purple prisms (dec. ca. 208°C) were collected and dried under vacuum. Yield was 66 percent (0.52 g). The effective magnetic moment (30°C in benzene by Evans' method) was 4.4 B.M. Anal. Calcd. for $C_{25}H_{44}P_2ClYb$: C, 48.8; H, 7.21; P, 10.07; Cl, 5.77. Found: C, 48.6; H, 7.06; P, 9.88; Cl, 5.54. IR data: 2718 w, 1292 m, 1276 w, 1149 m, 1087 w, 1014 m, 943 s, 908 s, 880 w, 830 w, 799 w, 759 m, 723 m, 709 w, 699 w, 683 w, 615 w, 590 w, 372 m, 298 s, 248 s cm^{-1}.

Iodobis(pentamethylcyclopentadienyl)tetrahydrofuranytterbium(III), $Yb(C_5Me_5)_2I(thf)$

The complex $Yb(C_5Me_5)_2(thf)$ (0.58 g, 1.12 mmol) in toluene (25 mL) was added to silver iodide (0.27 g, 1.15 mmol) and the mixture stirred for 14 h. The violet solution was filtered, concentrated to ca. 8 mL under reduced pressure, and cooled (-10°C). The violet crystals were isolated in 60 percent yield (0.43 g). When heated in a sealed capillary, the compound decomposes (turns grey) at ca. 130°C. Anal. Calcd. for $C_{24}H_{38}OIYb$: C, 44.9; H, 5.96. Found: C, 45.1; H, 6.10. IR data: 2723 w, 1344 m, 1248 w, 1178 w, 1039 w sh, 1012 s, 956 w, 926 w, 914 w sh, 860 s, 841 w sh, 730 m, 697 w, 676 w, 595 m, 467 w, 388 m, 308 s cm^{-1}.

Reaction of silver trifluoroacetate with $Yb(C_5Me_5)_2(OEt_2)$

Silver trifluoroacetate (0.24 g, 1.1 mmol) in toluene (40 mL) was added to $Yb(C_5Me_5)_2(OEt_2)$ (0.57 g, 1.1 mmol) in 15 mL of toluene. The resulting purple solution was stirred for 6 h, filtered and concentrated to ca. 30 mL under reduced pressure. Cooling (-10°C) gave violet crystals of $[Yb(C_5Me_5)_2O_2CCF_3]_2$, identified by its m.p. and infrared spectrum, in 68 percent yield.

Reaction of Iodine with $Eu(C_5Me_5)_2(thf)OEt_2$

Iodine (0.13 g, 0.51 mmol) in diethyl ether (20 mL) was added to $Eu(C_5Me_5)_2(thf)(OEt_2)$ (0.60 g, 1.06 mmol) in diethyl ether (30 mL), resulting in a red solution with a grey precipitate. After stirring for 10 h, the volatile material was removed under reduced pressure, and the residue washed with pentane. The solid was crystallized from tetrahydrofuran (ca. 8 mL, -10°C). The isolated crystals (m.p. > 300°C) were white. The yield of $EuI_2(thf)_2$ was 23 percent (0.13 g). Anal. Calcd. for $C_8H_{16}I_2O_2Eu$: C, 17.5; H, 2.91; I, 46.2. Found: C, 17.3; H, 2.98; I, 44.9. IR data: 1339 w, 1293 w, 1028 s, 917 m, 870 s, 671 m cm^{-1}.

Reaction of allylbromide with $Eu(C_5Me_5)_2(thf)(OEt_2)$

A diethyl ether solution (10 mL) of allyl bromide (0.19 g, 1.6 mmol) was added to a cooled (0°C) solution of $Eu(C_5Me_5)_2(thf)(OEt_2)$ (0.89 g, 1.6 mmol). A blue solution developed after ca. 1 min. The solution was allowed to warm to room temperature, and a yellow solid began to precipitate, leaving a red solution. After stirring 6 h, the $Eu(C_5Me_5)_2(thf)(OEt_2)$ starting material was isolated from the diethyl ether solution in 43 percent yield (identified by m.p. and

i.r.). The yellow solid was washed with diethyl ether (40 mL), and tetrahydrofuran was added (15 mL). The yellow solid was only slightly soluble in the tetrahydrofuran. The solvent was removed, and an infrared spectrum of the residue showed only bands due to tetrahydrofuran (1030 and 872 cm^{-1}). Characterization of this material was not pursued further.

Reaction of trimethylchlorosilane with $Eu(C_5Me_5)_2(thf)(OEt_2)$

Addition of trimethylchlorosilane (0.14 g, 1.3 mmol) to $Eu(C_5Me_5)_2(thf)(OEt_2)$ (0.75 g, 1.3 mmol) in diethyl ether (30 mL) resulted in precipitation of a yellow-green solid after 7 h. The $Eu(C_5Me_5)_2(thf)(OEt_2)$ starting material was isolated from the diethyl ether solution in 45 percent yield. The yellow-green solid, which was insoluble in tetrahydrofuran and pyridine, showed only coordinated tetrahydrofuran in its infrared spectrum (1028 and 881 cm^{-1}).

Reaction of silver trifluorocecetate with $Eu(C_5Me_5)_2(thf)(OEt_2)$

The addition of silver trifluoroacetate (0.35 g, 1.6 mmol) in toluene (30 mL) to $Eu(C_5Me_5)_2(thf)(OEt_2)$ (0.91 g, 1.16 mmol) in toluene (30 mL) resulted in a brown suspension. The suspension was stirred for 10 h, then the solvent was removed under reduced pressure. The residue was extracted with tetrahydrofuran (60 mL). After concentration of the tetrahydrofuran solution to 10 mL, diethyl ether (3 mL) was added and the solution cooled to -70°C. Yellow microcrystals (0.32 g) were isolated and dried in vacuo (m.p. > 300°C). Anal. C, 29.9; H, 3.15. $Eu(O_2CCF_3)_2(thf)$ requires C, 29.4; H, 3.29. IR data: 3104 w, 1661 s, 1189 s, 1133 s, 1032 m, 880 m, 839 m, 797 m, 720 s, 602 w, 519 w, 270 s cm^{-1}.

Reaction of chloroform with $Eu(C_5Me_5)_2(thf)(OEt_2)$

Chloroform (1 mL, an excess) was added to a cooled (0°C) diethyl ether (25 mL) solution of $Eu(C_5Me_5)_2(thf)(OEt_2)$ (0.64 g, 1.1 mmol). The blue solution was stirred for 25 min., and the volatile material was removed at 0°C. The blue residue was extracted with pentane (25 mL). The pentane solution was concentrated to ca. 8 mL under reduced pressure and cooled (-70°C) to give blue prisms (ca. 40 mg) that contained chloride ($AgNO_3$ test). IR data: 2722 w, 1209 w, 1110 w sh, 1096 m, 1063 s, 1012 w, 876 m, 840 w cm^{-1}. Nothing further was done to characterize this substance.

Reaction of europium trichloride with $Eu(C_5Me_5)_2(thf)(OEt_2)$

The addition of $Eu(C_5Me_5)_2(thf)(OEt_2)$ (0.67 g, 1.12 mmol) in tetrahydrofuran (50 mL) to $EuCl_3$ (0.30 g, 1.2 mmol) resulted in a blue solution that quickly began to deposit a green precipitate. IR of green precipitate: 2720 w, 1260 m, 1062 w, 1032 s, 970 w, 912 w, 878 s, 800 m, 627 w cm^{-1}. This substance was not further characterized.

Pentamethylcyclopentadienyltris(tetrahydrofuran)europium(II) hexafluorophosphate, $[Eu(C_5Me_5)(thf)_3][PF_6]$

To solid ferrocinium hexafluorophosphate (0.77 g, 2.3 mmol), cooled to 0°C, was added $Eu(C_5Me_5)_2(thf)(OEt_2)$ (1.32 g, 2.3 mmol) in diethyl ether (40 mL). After warming to room temperature, the solution was stirred for 10 h, resulting in an orange solution and a pale green precipitate. Ferrocene, identified by its m.p. and infrared spectrum, was crystallized from the diethyl ether solution. The green solid was washed with pentane (2 x 40 mL), and dissolved in tetrahydrofuran (20

mL). Concentration of the tetrahydrofuran solution to ca. 3 mL and cooling (-10°C) led to crystallization of large green prisms (m.p.=108-110°C) in 39 percent yield (0.58 g). The effective magnetic moment (5-40K) was 7.52 B.M., with C = 7.02. Anal. Calcd. for $C_{22}H_{42}PF_6O_3Eu$: C, 40.7; H, 6.06; P, 4.78. Found: C, 40.3; H, 6.04; P, 4.74. IR data: 2724 w, 1346 w, 1299 w, 1178 m, 1038 s, 873 s, 840 s, 734 s, 668 m, 560 s, 478 w cm^{-1}.

Bis(pentamethylcyclopentadienyl)tetracarbonylcobaltate-tetrahydrofuranytterbium(III), $[(C_5Me_5)_2Yb(thf)][Co(CO)_4]$

The divalent $Yb(C_5Me_5)_2(OEt_2)$ (1.12 g, 2.16 mmol) in toluene (15 mL) was added to octacarbonyldicobalt (0.37 g, 1.08 mmol) in toluene (10 mL). The solution was stirred for 36 h, resulting in precipitation of a blue solid. After removing the toluene, the blue solid was dissolved in tetrahydrofuran (30 mL) and filtered. The tetrahydrofuran solution was concentrated to 10 mL. Addition of pentane (20 mL) and cooling (-10°C) gave blue prisms (m.p. > 300°C) in 74 percent yield (1.10 g). ^1H NMR (26°C, d_8-PhMe): δ 8.36, s, $\nu_{1/2}$ = 43 Hz. The effective magnetic moment, determined by Evans' method in benzene at 30°C, was 4.1 B.M. Anal. Calcd. for $C_{28}H_{38}O_5CoYb$: C, 49.0; H, 5.58. Found: C, 47.3; H, 5.39. IR data: 3496 w, 2731 w, 2023 s, 1973 w, 1939 s, 1917 s, 1823 w, 1798 m sh, 1761 s, 1318 w, 1300 w, 1251 w, 1179 w, 1060 w, 1041 w, 1010 s, 959 w, 828 w, 917 w, 858 s, 676 w, 563 s, 526 s, 511 s, 439 m, 380 m, 320 s cm^{-1}.

Bis[bis(pentamethylcyclopentadienyl)ytterbium(III)] pentacarbonylmolybdate, $[Yb(C_5Me_5)_2]_2[Mo(CO)_5]$

A toluene (60 mL) solution of $Yb(C_5Me_5)_2(OEt_2)$ (0.70 g, 1.35 mmol) was added to molybdenum hexacarbonyl (0.18 g, 0.68 mmol), and the solution was stirred for 36 h. The toluene was removed under reduced pressure, and the red residue dissolved in tetrahydrofuran (30 mL). Filtration, concentration to ca. 8 mL and cooling (-10°C) caused crystallization of red needles (m.p. > 310°C) in 41 percent yield (0.62 g). The compound was hydrolyzed in benzene. Analysis of the benzene extract by ^1H NMR showed resonances due to C_5Me_5H only. Anal. Calcd. for $C_{45}H_{60}O_5MoYb$: C, 48.1; H, 5.38. Found: C, 48.4; H, 5.64. IR data: 2723 w, 2008 m, 1991 w, 1920 s, 1902 s, 1882 s, 1632 s, 1414 m, 1136 s, 1063 w, 998 s, 843 s, 667 m, 609 w, 562 w, 537 m, 468 w, 404 w, 372 m, 311 m cm^{-1}.

Bis[bis(pentamethylcyclopentadienyl)tetrahydrofuranytterbium(III)] tetracarbonylferrate, $[Yb(C_5Me_5)_2(thf)]_2[Fe(CO)_4]$

Iron pentacarbonyl (0.21 g, 1.1 mmol) in toluene (10 mL) was cooled to 0°C, and $Yb(C_5Me_5)_2(OEt_2)$ (1.11 g, 2.14 mmol) in toluene (20 mL) was added. A purple solid separated from solution after 1 h of stirring. Toluene was filtered from the solid, which was washed with more toluene (2 x 20 mL). The infrared spectrum of the blue solid contained peaks at 2018 w, 1981 w, 1752 m sh, 1710 s br and 1609 s br cm^{-1}. The compound was dissolved in tetrahydrofuran (25 mL). This solution was filtered, concentrated to ca. 8 mL, and diethyl ether (20 mL) was added. Cooling (-10°C) afforded blue microcrystals in 72

percent yield (0.95 g). The ^{1}H NMR spectrum (26°C, d_8-thf) contained a peak ($\nu_{1/2}$ = 144 Hz) at δ 9.52. Hydrolysis of the compound in benzene gave a 2:1 mixture of C_5Me_5H and tetrahydrofuran (by ^{1}H NMR). Anal. Calcd. for $C_{52}H_{76}O_6FeYb_2$: C, 52.1; H, 6.39. Found: C, 51.6; H, 6.42. IR data: 2720 w, 2004 w, 1980 w, 1961 w, 1928 s, 1922 s, 1753 m sh, 1741 s, 1711 s, 1648 m sh, 1608 s br, 1162 w, 1059 w, 1008 m, 856 m, 798 w, 653 m, 568 s, 551 s, 382 m, 310 s cm^{-1}. The compound reacts with triphenylchlorosilane (two molar equivalents) in tetrahydrofuran to generate $Fe(CO)_4(SnPh_3)_2$ and $Yb(C_5Me_5)_2Cl(thf)$ (by IR).

Bis[bis(pentamethylcyclopentadienyl)ytterbium(III)] undecacarbonyltriferrate, $[Yb(C_5Me_5)_2]_2[Fe_3(CO)_{11}]$

The compound $Yb(C_5Me_5)_2(OEt_2)$ (0.77 g, 1.49 mmol) in toluene (30 mL) was added to $Fe_3(CO)_{12}$ (0.37 g, 0.73 mmol) in toluene (10 mL). After stirring for 48 h, the resulting solution was filtered, evaporated to ca. 15 mL and cooled (-70°C) to obtain dark violet prisms (m.p. = 307-310°C). Overall yield was 55 percent (1.13 g). ^{1}H NMR (26°C, d_8-PhMe): δ 6.11 ($\nu_{1/2}$ = 130 Hz) and 8.09 ($\nu_{1/2}$ = 130 Hz). The effective magnetic moment (5-60K) was 3.91 B.M. per ytterbium. The compound follows Curie behavior over this temperature range. Anal. Calcd. for $C_{51}H_{71}O_{11}Fe_3Yb_2$: C, 44.6; H, 5.21. Found: C, 44.8; H, 4.63. IR data: 3260 w, 3100 w, 2722 wm 2048 w, 1998 s, 1973 s, 1667 w, 1604 s br, 1261 m, 1098 m br, 1020 m, 800 m, 727 m, 692 w, 658 m, 612 w sh, 598 m sh, 580 s, 493 w, 451 s, 393 m, 310 s cm^{-1}.

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CHAPTER 3

DIVALENT BIS(TRIMETHYLSILYL)AMIDO LANTHANIDE COMPLEXES

Bis(trimethylsilylamido) Europium(II) Complexes

The reaction scheme initially devised for the preparation of bis(trimethylsilyl)amido derivatives of europium(II) and ytterbium(II) involved preparation of the trivalent mono-chloro compounds $Ln[N(SiMe_3)_2]_2Cl$, followed by reduction with sodium napthalene:

$$2Ln[N(SiMe_3)_2]_3 + LnCl_3 \longrightarrow 3Ln[N(SiMe_3)_2]_2Cl$$

$$Ln[N(SiMe_3)_2]_2Cl + NaNaph \longrightarrow Ln[N(SiMe_3)_2]_2 + NaCl + Napn.$$

Numerous attempts to prepare the mono-chloro species by the methods used to obtain Cp_2LnCl resulted in crystallization of the $Ln[N(SiMe_3)_2]_3$ starting material (see Experimental Section). It seems likely, however, that the mono-chloro derivative of europium exists, at least to some degree in solution, since europium trichloride, which is only sparingly soluble in tetrahydrofuran, dissolves in the presence of $Eu[N(SiMe_3)_2]_3$. Confirmation of this hypothesis was shown by the *in situ* reduction with sodium naphthalene giving small yields (*ca.* 10 percent) of $Eu[N(SiMe_3)_2]_2(thf)_2$.

A much improved synthesis of this europium(II) complex, as well as its 1,2-dimethoxyethane (dme) analogue utilizes europium diiodide:

$$EuI_2 + 2NaN(SiMe_3)_2 \xrightarrow[L = thf \text{ or } dme]{L} Eu[N(SiMe_3)_2]_2L_2$$

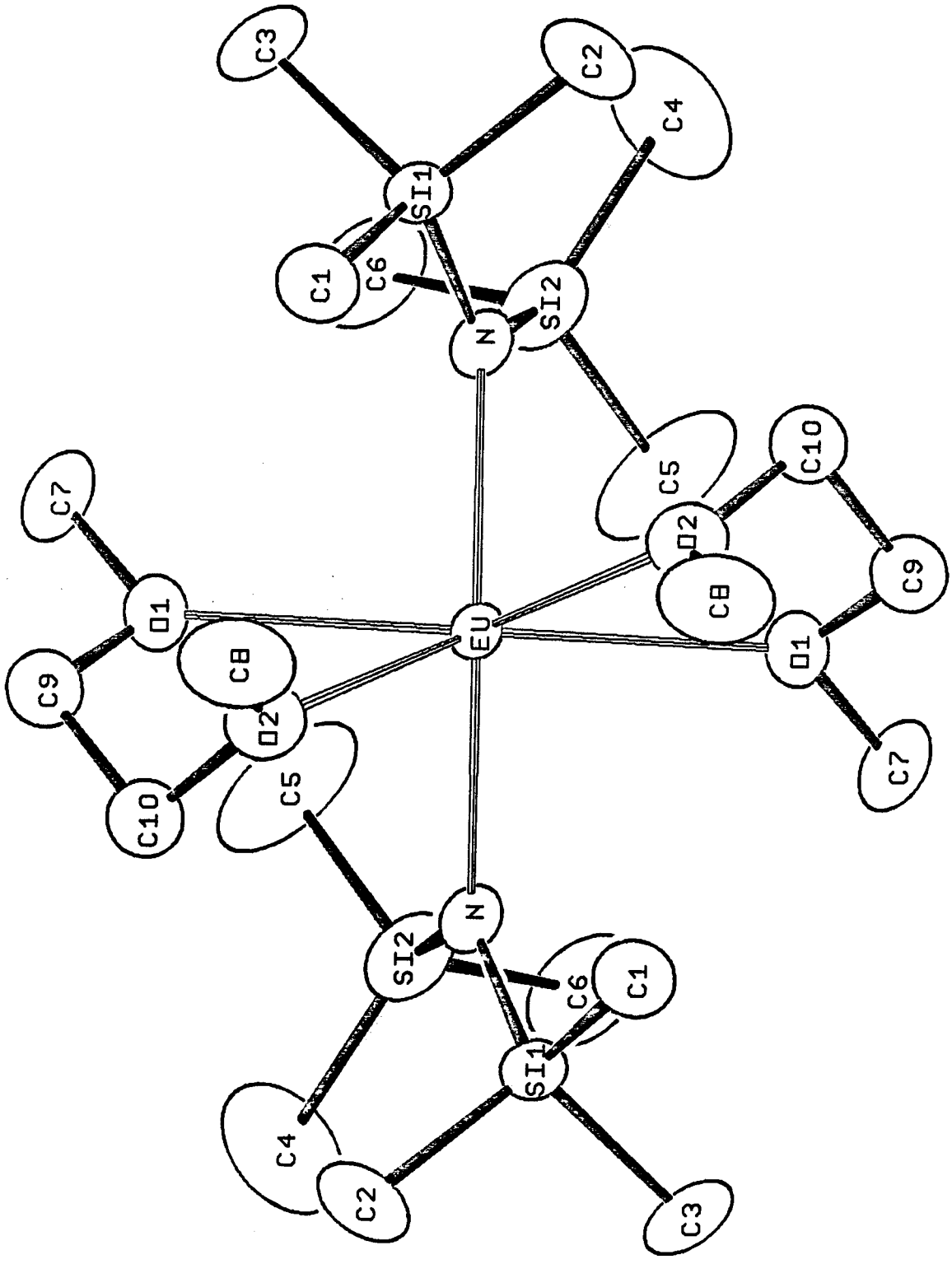
The yields from this reaction are much improved, 60-80 percent. The yellow $Eu[N(SiMe_3)_2]_2(thf)_2$ and $Eu[N(SiMe_3)_2]_2(dme)_2$ represent the first pentane-soluble derivatives of a divalent lanthanide. The tetrahydrofuran in $Eu[N(SiMe_3)_2]_2(thf)_2$ can be displaced by bipyridine, yielding yellow $Eu[N(SiMe_3)_2]_2(bipy)$.

The 1,2-dimethoxyethane complex follows Curie behavior, $\chi_m = CT^{-1}$, from 5 to 45 K with C = 8.82 and μ_{eff} = 8.43 B.M. The magnetic moment is similar to that found for the isoelectronic gadolinium(III) compound $Gd[N(SiMe_3)_2]_3$ (7.75 B.M. at 98K) [1], and is consistent with an $^8S_{7/2}$ ground state.

As further characterization, a single-crystal X-ray structure determination was performed on $Eu[N(SiMe_3)_2]_2(dme)_2$ [2]. The compound crystallizes in space group C2/c, with Z = 4. An ORTEP drawing, as viewed down the crystallographic two-fold axis, is shown in Figure 1. The carbon atoms in the ethylene units of the 1,2-dimethoxyethane ligands are disordered between the two positions shown in Figures 1 and 2. It is not apparent whether this disorder is static or dynamic, but the two structures represent two different puckered conformations for the five-membered chelate rings.

Figure 3 is a stereochemical view of the coordination geometry about the six-coordinate europium(II) ion. The coordination polyhedron cannot be described by a simple regular geometric figure. The two bulky silylamide groups are surprisingly close to one another, resulting in a N-Eu-N angle of only 134.5°C. Kepert has shown, from points-on-a-sphere repulsion energy calculations, that for six-coordinate

Figure 1. ORTEP drawing of $Eu[N(SiMe_3)_2]_2(dme)_2$ as viewed down the twofold axis.



XBL 7911-12675

Figure 2. ORTEP drawing of $Eu[N(SiMe_3)_2]_2(dme)_2$ showing the molecule in the other configuration due to disorder in C(9) and C(10).

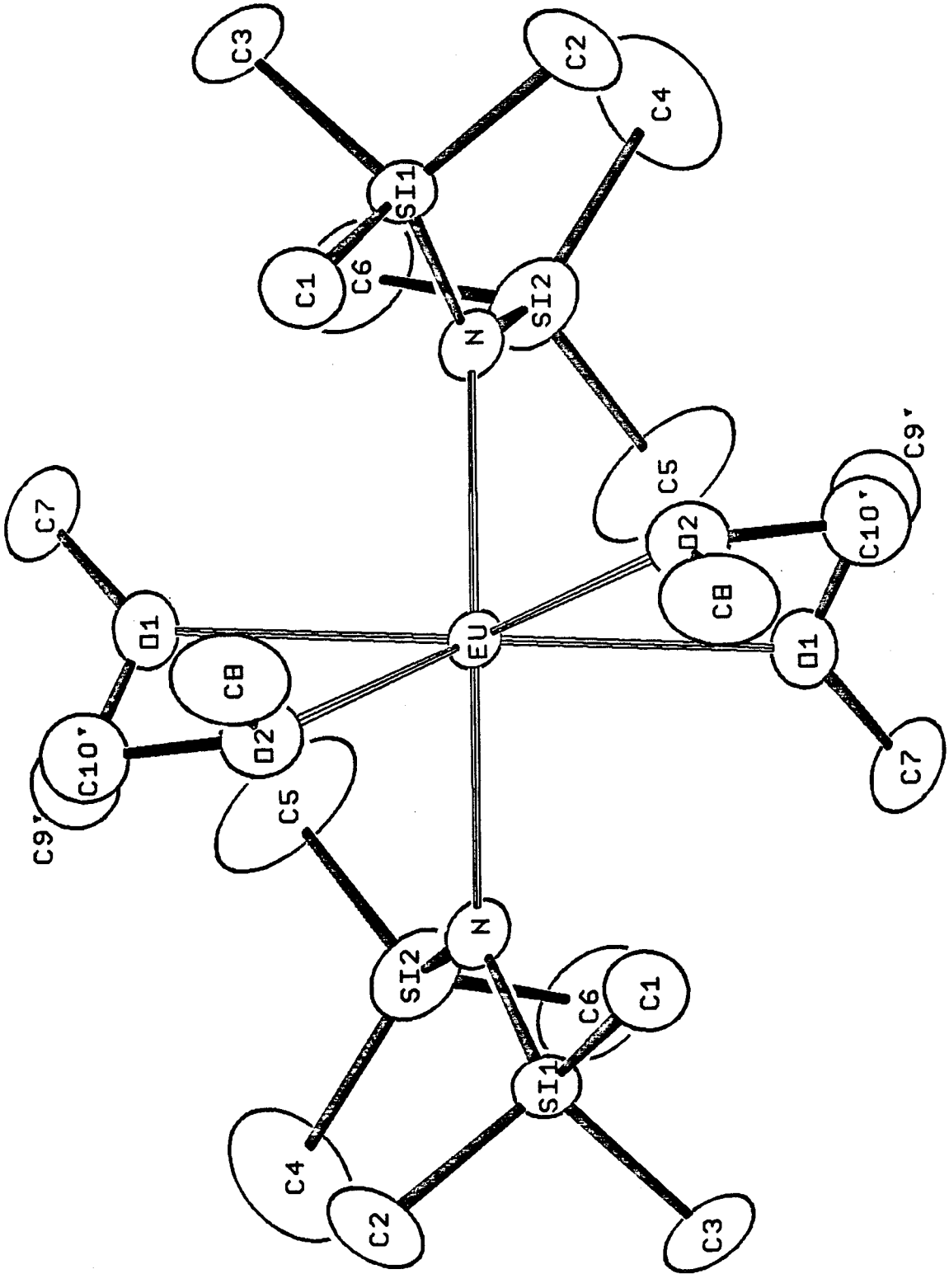


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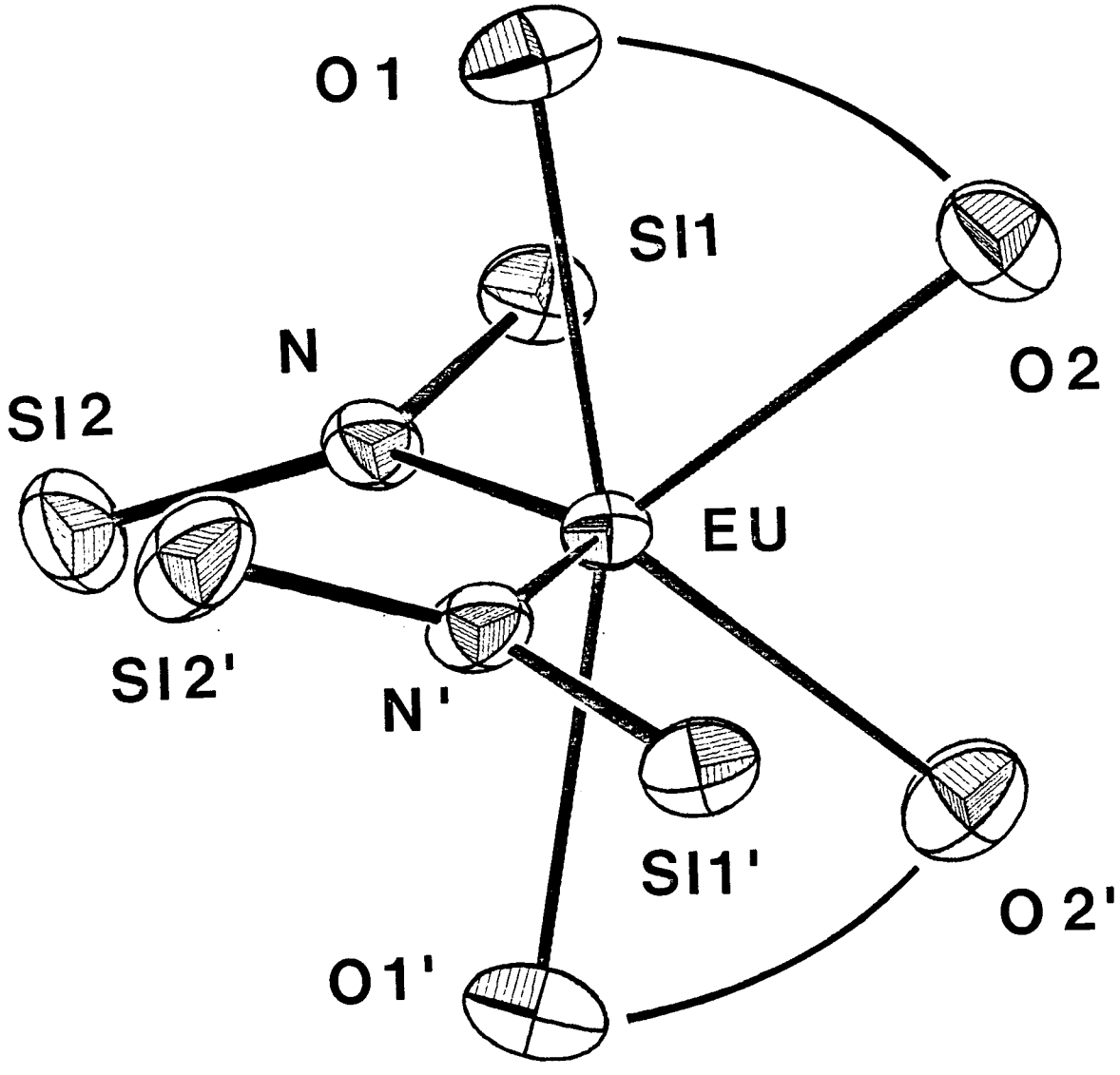
Figure 3. ORTEP view of the coordination sphere about europium in $Eu[N(SiMe_3)_2]_2(dme)_2$.



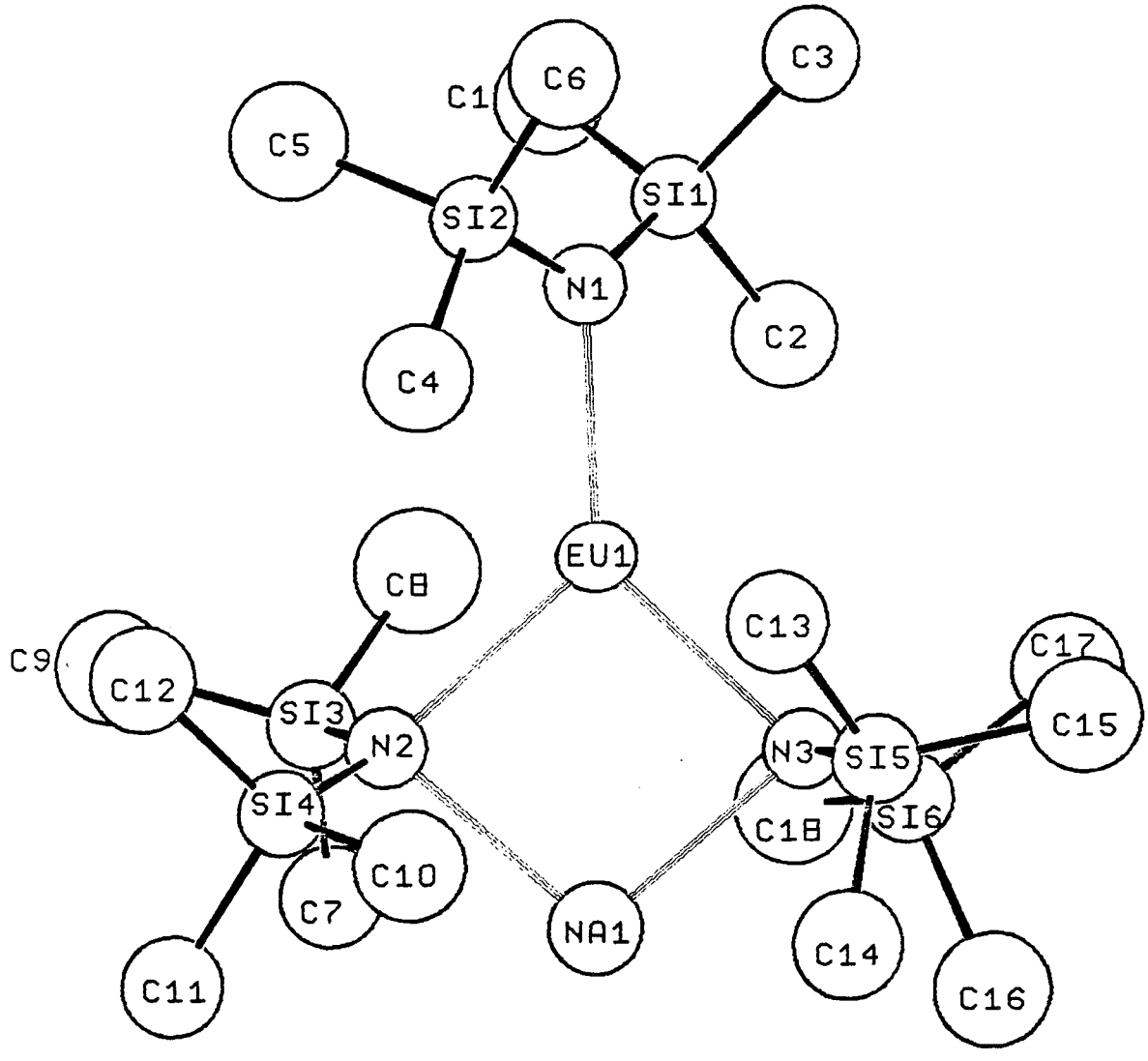
XBL 803-8765

complexes of the type M(bidentate)$_2$(unidentate)$_2$, the unidentate ligands are pulled together when the bidentate ligands have small normalized bites [3]. Kepert defines the normalized bite of a chelating ligand as the distance between donor atoms in the chelate group divided by the metal-donor atom distance. It is the bidentate nature of the 1,2-dimethoxyethane ligands that prevents the two silylamide groups from repelling each other to a greater extent. The normalized bite of the 1,2-dimethoxyethane ligands in this complex is among the smallest known, 0.98. Clearly, repulsive interactions between coordinated atoms are more important in defining this detail of the structure than the overall steric bulk of the ligands.

Bond angles and distances in the planar bis(trimethylsilyl)amide ligands are comparable to those found in other structures [4-8]. The europium(II)-nitrogen bond distance is 2.53 Å, the first such bond length determined, whereas the europium(III)-nitrogen bond length in Eu[N(SiMe$_3$)$_2$]$_3$ is 2.26 Å. The difference of 0.27 Å is due mostly to the change in bond length with oxidation state, estimated as 0.23 Å from the ionic radii listed by Shannon [9]. The europium(II)-oxygen bond lengths in this structure are 2.638 and 2.756 Å, and Kepert has shown that such a difference may accompany the bending distortion discussed above. These europium(II)-oxygen distances are in good agreement with those reported in the $EuCl_2 \cdot 2H_2O$ structure [10], which range from 2.69 to 2.74 Å.

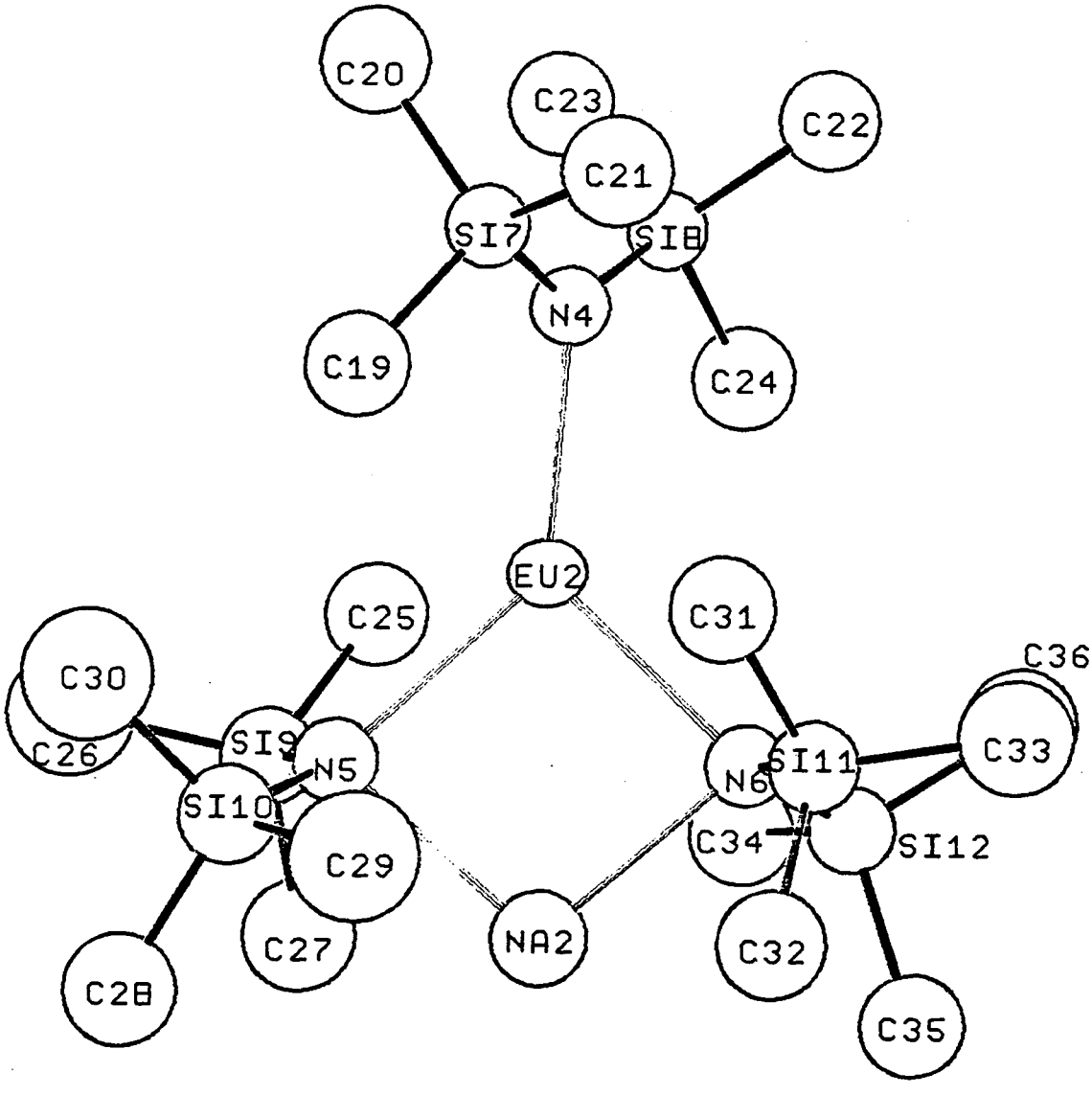
The reaction of europium diiodide with two molar equivalents of sodium bis(trimethylsilyl)amide in diethyl ether does not lead to a

Figure 4. ORTEP view of first $NaEu[N(SiMe_3)_2]_3$ molecule.



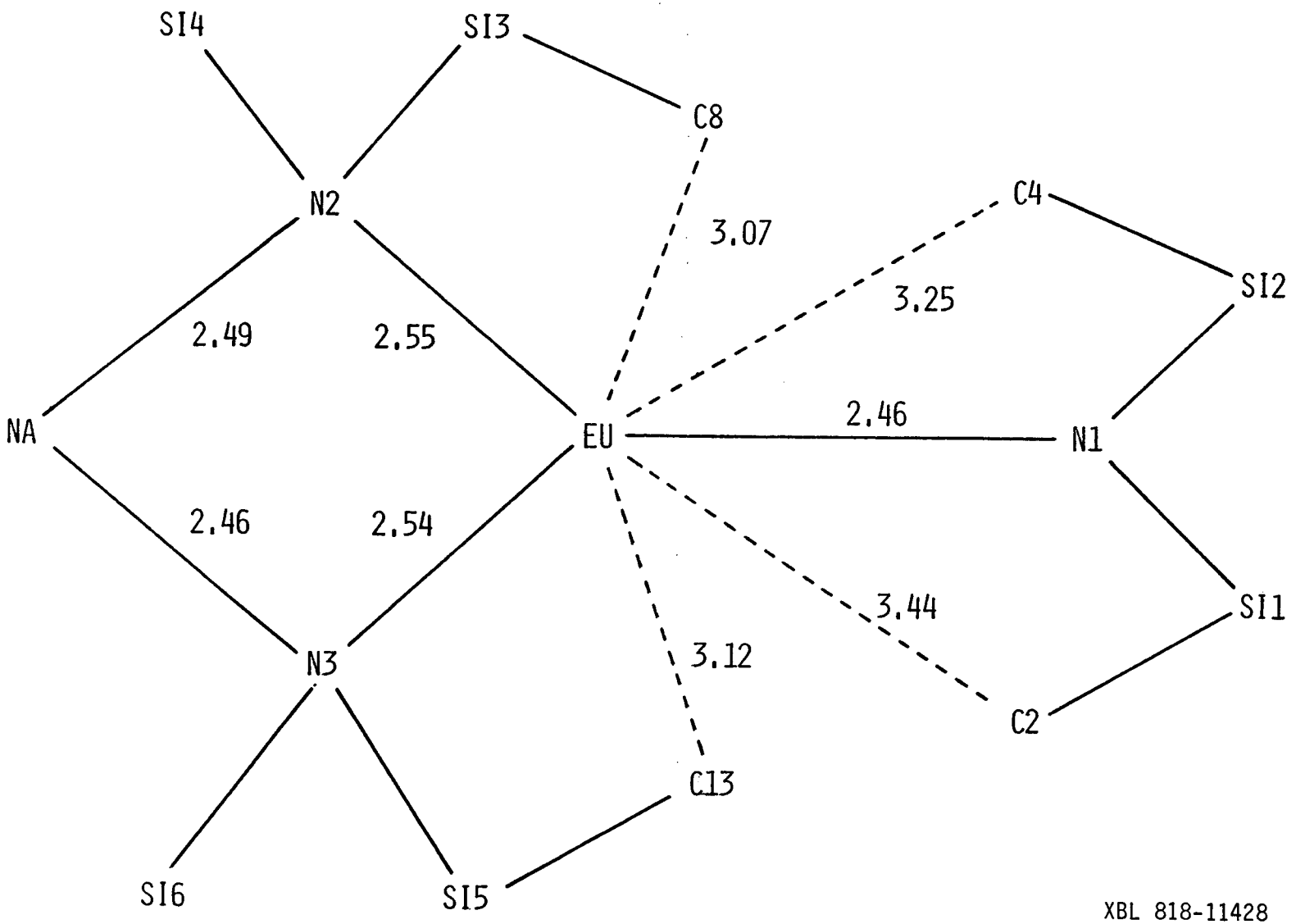
XBL 818-11434

Figure 5. ORTEP view of second $NaEu[N(SiMe_3)_2]_3$ molecule.



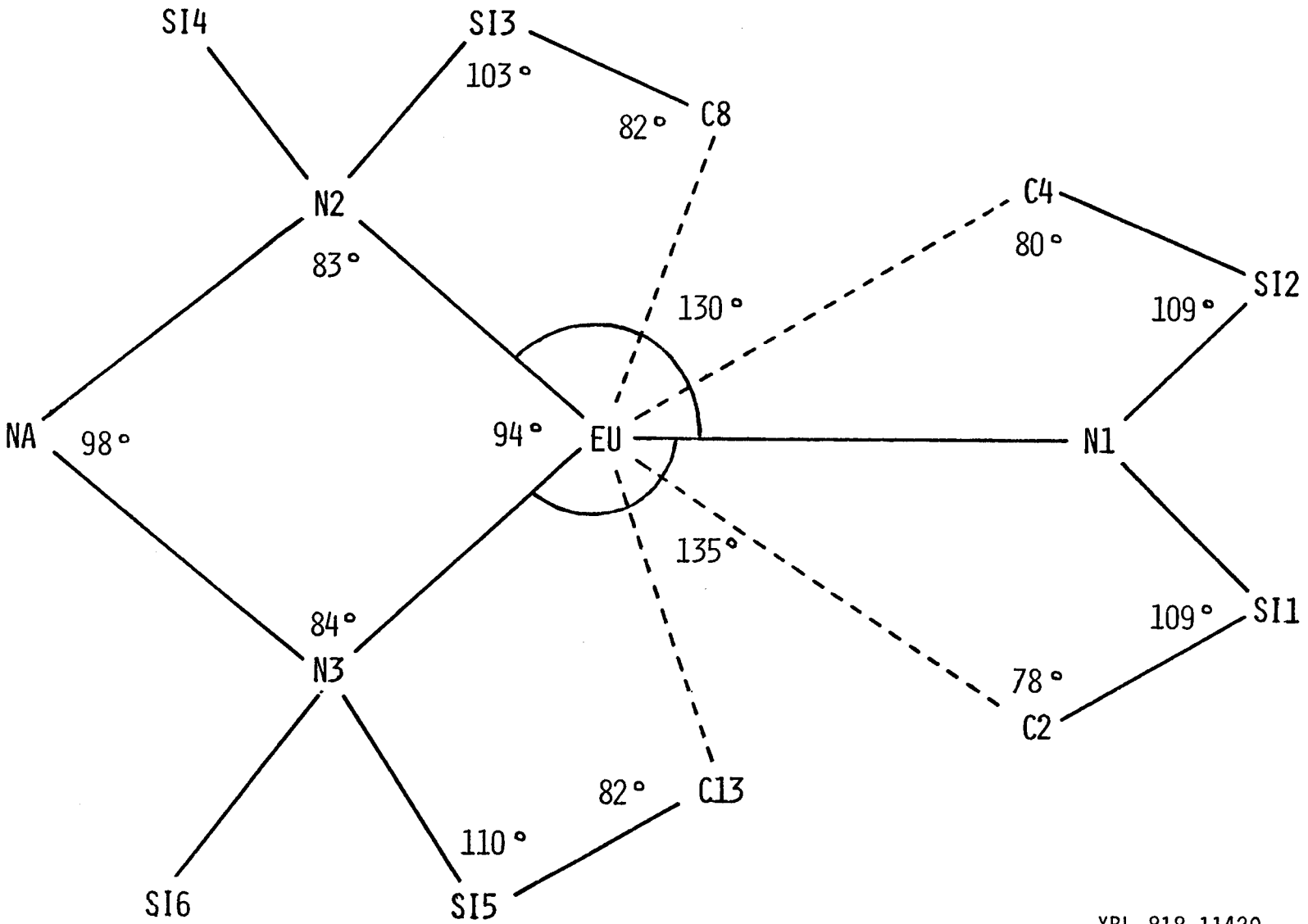
XBL 818-11433

Figure 6. Some bond distances in the molecule $NaEu[N(SiMe_3)_2]_3$.



XBL 818-11428

Figure 7. Some bond angles calculated for $NaEu[N(SiMe_3)_2]_3$.



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complex with coordinated ether, but to the anionic $NaEu[N(SiMe_3)_2]_3$ complex. This yellow, crystalline material is soluble in diethyl ether, pentane and toluene, from which it may be crystallized. The isolation of this compound from diethyl ether solutions suggests that the bis(trimethylsilyl)amide anion is a better base toward $Eu[N(SiMe_3)_2]_2$ than diethyl ether, though a weaker base than tetrahydrofuran or 1,2-dimethoxyethane.

The compound that crystallizes from pentane or diethyl ether exhibits physical properties that differ somewhat from the product that is obtained from toluene (see Experimental Section). The two species probably differ only in assuming a different space group upon crystallization, as the unit cell volume of the product crystallized from pentane (3454 $Å^3$) is nearly one-half the unit cell volume of the compound crystallized from toluene (6996 $Å^3$). Numerous attempts were made to collect suitable X-ray data with crystals obtained by slow cooling of a pentane solution. Although consistent problems with twinning prohibited collection of a full data set, unit cell parameters were obtained (a = 9.90, b = 12.35 and c = 28.85 Å; $\alpha = 99.5°$, $\beta = 91.8°$ and $\gamma = 95.8°$), along with determination of the space group ($P\bar{1}$) [11].

Fortunately, crystals of $NaEu[N(SiMe_3)_2)_2]_3$ obtained from toluene were of good quality (space group $P2_1/n$, Z = 8) [12]. There are two crystallographically unique molecules in the unit cell; ORTEP drawings for both are presented in Figures 4 and 5. Bond distances and angles, presented in figures 6 and 7, reveal some rather peculiar

structural features. The sodium atom is bonded to two bis(trimethylsilyl)amido groups, with the two nitrogen atoms bridging sodium and europium, giving the nitrogens a pseudotetrahedral environment. The third silylamide ligand is planar at the nitrogen atom. This accounts for the two $\nu(NSi_2)$ stretching frequencies observed at 1240 and 1206 cm^{-1} in the infrared spectrum. Correspondingly, the four-coordinate nitrogen atoms are further from europium (2.55 and 2.54 Å) than the three-coordinate nitrogen atom (2.46 Å). The NaN_2EuN coordination plane is very close to planar, resulting in N-Eu-N angles that sum to 359°.

A most surprising feature of the structure are the four short europium-carbon(methyl) contacts (3.07, 3.12, 3.25 and 3.44 Å) shown as dotted lines in Figure 5. Since the van der Waals radius of a methyl group is 2.0 Å [13], and the atomic radius of europium 2.42 Å (as calculated from europium metal [14]), it appears that these distances represent bonding interactions. These interactions would seem to arise from donation of electron density from the methyl groups to the electropositive and coordinatively unsaturated europium metal center. If the methyl groups are acting as ligands in this fashion, the effective ionic radius of the europium(II) center should reflect this. The effective ionic radius of a bis(trimethylsilyl)amide ligand, 1.47(3) Å, is well established from a number of X-ray structure determinations [15]. Subtracting this value from the one europium-(three coordinate)nitrogen bond distance, one obtains 0.99 Å for the ionic radius of the europium(II) ion. Shannon [9] suggests a value of

1.20 Å for the ionic radius of seven-coordinate europium(II). A value for the ionic radius of europium(II) in three-coordination can be calculated from the equation:

$$\frac{R_{II}}{R_I} = \left(\frac{CN_{II}}{CN_I}\right)^{1/(n-1)}$$

where R is the interionic distance and CN is the coordination number of the complex [15]. Using a Born exponent (n) of 12, and the six-coordinate interionic distance of 2.53 Å obtained from the structure of $Eu[N(SiMe_3)_2](dme)_2$, an interionic distance of 2.38 Å, or an effective europium(II) radius of 0.91 Å, is obtained. The observed europium(II) ionic radius therefore lies between the values expected for three- and seven-coordinate europium(II), suggesting that the methyl groups do play a role in determining the ionic radius of europium.

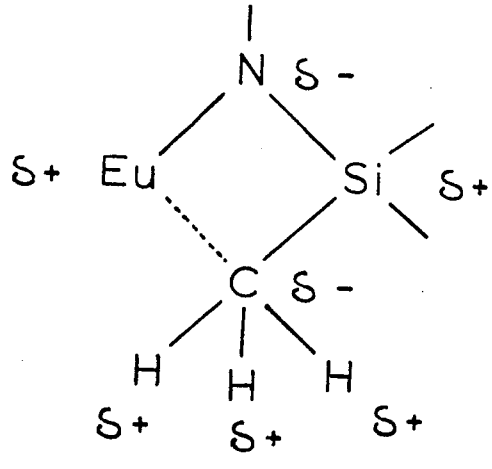
It is of interest to determine the type of interaction that gives rise to the small europium-carbon separations, particularly in light of recent interest in hydrocarbon activation by transition metals [16-19]. Previous examples of bonding between trivalent lanthanides and formally neutral hydrocarbon fragments have been structurally characterized. In the compound $[Nd(C_5H_4Me)_3]_4$, in which each neodymium atom is pentahapto-bound to three monomethylcyclopentadienyl ligands, the tetramer is formed by monohapto interactions between the metal atom and a C_5H_4Me ligand from another $Nd(C_5H_4Me)_3$ fragment [20]. The latter neodymium-carbon separations are 2.98 and

2.99 Å. Similarly, $SmCp_3$ [21] and the polymeric $ScCp_3$ [22] exhibit this secondary, metal-η^1-C_5H_5 interaction.

It is not clear from these examples, or from the structure of $NaEu[N(SiMe_3)_2]_3$, whether the metal atoms are interacting through a hydrogen atom or directly with the carbon atom. This question has been addressed for the isostructural, methyl-bridged dimers $[Cp_2MMe]_2$ (M = Yb or Y) in which direct, back-side interactions of the metals with the methyl carbon atom was differentiated from M···H-C(H_2)-M bonding by location of the hydrogen atoms in the crystal structure of the yttrium compound [23]. The structure shows all three hydrogens of the methyl groups to be pointed away from, and not interacting with, the metal atoms. Although the hydrogen atoms in $Cp_2Yb(\mu\text{-}Me)_2AlMe_2$ [24] were not located, the bridge-bonding appears to be similar to that observed in $[Cp_2MMe]_2$ (M = Yb or Y); the bridging angles at the methyl carbon atoms are 87° in $[Cp_2YbMe]_2$, 88° in $[Cp_2YMe]_2$ and 83 and 78° in $Cp_2Yb(\mu\text{-}Me)_2AlMe_2$. The crystal structure of $[AlMe_3]_3$, in which the hydrogen atoms were located, also shows direct metal-carbon interactions, and an Al-C(methyl)-Al bond angle of 76° [25].

This latter observation, i.e., that M-Me-M' angles appear to be constrained to ca. 80°, suggests a possible bonding model for $NaEu[N(SiMe_3)_2]_3$. The observed Eu-C(methyl)-Si angles are 78, 80, 82 and 82°, implying that the europium-methyl interactions can be viewed in terms of methyl groups that asymmetrically bridge the more electropositive europium and silicon atoms. This view of the structure

is consistent with expected charge distributions in the molecule, and with direct europium-carbon, rather than europium-hydrogen interactions:



The methyl groups, being bound to the electropositive silicon atoms, are rather carbanionic in character. Furthermore, considering the bonding between europium and its ligands to be highly ionic, the silylamide group probably carries close to a full negative charge, which may be partially delocalized onto the methyl carbon atoms. Therefore, one can view the europium-carbon attraction as being highly electrostatic in nature.

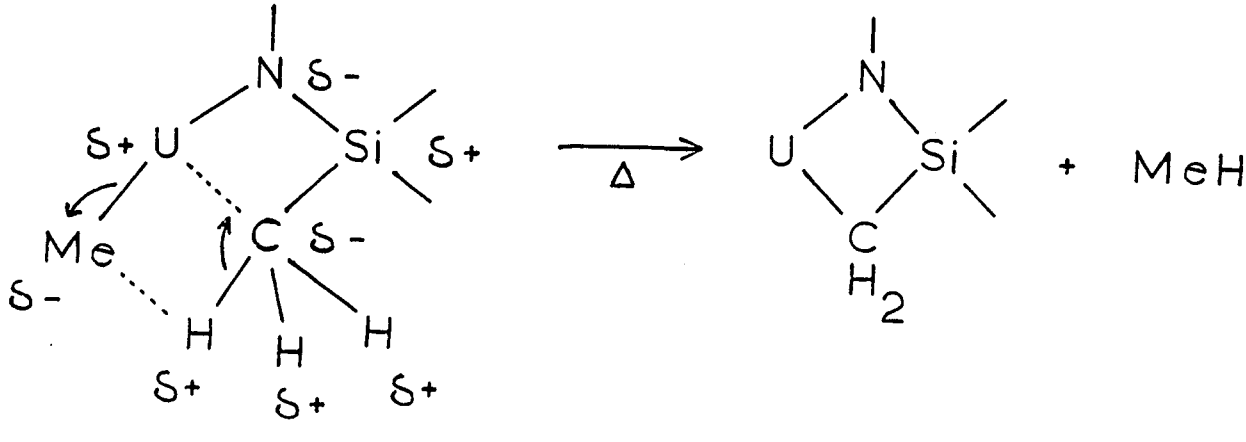
This model for the metal-carbon interaction in $NaEu[N(SiMe_3)_2]_3$ may help shed light on the role of uranium(IV) in activating the methyl groups of a bis(trimethylsilyl)amide ligand. The uranium(IV) compound $[(Me_3Si)_2N]_3UX$ (X = H or Me) has been shown to give rise to the heteroatom metallocycle

$[(Me_3Si)_2N]_2\overline{UN(SiMe_3)SiMe_2CH_2}$ [26-28] via the reactions:

$$[(Me_3Si)_2N]_3UH \rightleftharpoons [(Me_3Si)_2N]_2\overline{UN(SiMe_3)SiMe_2CH_2} + H_2$$

$$[(Me_3Si)_2N]_3UMe \xrightarrow{150^\circ} [(Me_3Si)_2N_2\overline{UN(SiMe_3)SiMe_2CH_2} + MeH$$

This transformation appears to proceed without a change in oxidation state of the metal, since metallocycle formation is also observed in analogous thorium(IV), zirconium(IV), and hafnium(IV) systems [26,29], for which an oxidative addition process is highly unlikely. A metal-carbon interaction of the type observed in $NaEu[N(SiMe_3)_2]_3$ could lead to a concerted elimination of methane (or hydrogen), if analogous bond polarizations are induced:



A possible confirmation of this scheme would be reaction of the $NaEu[N(SiMe_3)_2]_3$ compound with a methyl carbanion source (a strong base), such as methyl lithium, to yield methane and a metallocycle of the type $Li\{[(Me_3Si)_2N]\overline{EuN(SiMe_3)SiMe_2CH_2}\}$.

Bis(trimethylsilyl)amido Ytterbium(II) Complexes

The reactions between ytterbium diiodide and sodium bis(trimethylsilyl)amide in ether solvents are not as straightforward as the analogous europium reactions. The product obtained from the reaction of ytterbium diiodide and two molar equivalents of bis(trimethylsilyl)amide in 1,2-dimethoxyethane, after extraction and crystallization with toluene, is the blue $Yb[N(SiMe_3)_2]_2(dme)_2$. This compound gives a red pentane solution, from which the red $Yb[N(SiMe_3)_2]_2(dme)$ can be crystallized. These results suggest the solvent-dependent equilibrium:

$$Yb[N(SiMe_3)_2]_2(dme)_2 \rightleftharpoons Yb[N(SiMe_3)_2]_2(dme) + dme$$

The crystallization of a mono(dme) complex from pentane, rather than a bis(dme) complex, as is the case with the europium(II) silylamide, is a reflection of the smaller ionic radius of ytterbium(II) in six-coordination (1.02 vs. 1.17 Å for europium(II) [9]). In the mass spectrum, molecular ions were observed for both $Yb[N(SiMe_3)_2]_2(dme)_2$ and $Yb[N(SiMe_3)_2]_2(dme)$.

The divalent $Yb[N(SiMe_3)_2]_2(dme)_2$ can be oxidized to the yellow, trivalent $Yb[N(SiMe_3)_2]_2I(dme)$ by reaction with silver iodide in toluene. This reaction therefore represents the only known route to a bis(silylamide)monohalide derivative of a lanthanide. In an attempt to prepare a bis(silylamide)methyl complex of ytterbium(III), methyl lithium was added to a pentane solution of $Yb[N(SiMe_3)_2]_2I(dme)$. Unfortunately, the only product isolated from this reaction was $LiN(SiMe_3)_2$.

A bis(diethyl ether) complex, $Yb[N(SiMe_3)_2]_2(OEt_2)_2$, can be obtained by the reaction of ytterbium diiodide with one or two equivalents of sodium bis(trimethylsilyl)amide, followed by crystallization from diethyl ether. This is in contrast to the analogous reaction between europium diiodide and sodium bis(trimethylsilyl)amide, from which only $NaEu[N(SiMe_3)_2]_3$ was obtained from diethyl ether. As the Lewis acidity of $Yb[N(SiMe_3)_2]_2$ is probably very similar to that of $Eu[N(SiMe_3)_2]_2$, this difference most likely reflects the smaller ionic radius of ytterbium(II).

The $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ is thermochroic, being yellow at -70°C and orange at room temperature. The bonding between the ytterbium and the diethyl ether ligands is strong enough for observation of the parent ion (as an M-3 peak) in the mass spectrum. The mono(diethyl ether) complex is observed as an M-1 peak (567), and as is typical, the base-free ion appears as an M-1 peak (493). The coordinated diethyl ether seems to dissociate readily in aliphatic or aromatic hydrocarbons, in which $Yb[(N(SiMe_3)_2]_2(OEt_2)_2$

produces a red solution, since the diethyl ether is easily removed from the complex by heating to 80°C in toluene.

When the residue from the reaction between ytterbium diiodide and bis(trimethylsilyl)amide is extracted with toluene, the red sodium salt $NaYb[N(SiMe_3)_2]_3$ is obtained. This is possibly due to the tendency of coordinated diethyl ether to dissociate from $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ in toluene, producing the coordinatively unsaturated $Yb[N(SiMe_3)_2]_2$, which, in the presence of sodium iodide, disproportionates to $NaYb[N(SiMe_3)_2]_3$ and YbI_2. The sodium salt $NaYb[N(SiMe_3)_2]_3$ is more readily crystallized from pentane, from which well-formed needles are obtained. The compound is not isostructural with $NaEu[N(SiMe_3)_2]_3$, but crystallizes in space group Pbca, with Z = 8 [11]. The unit cell volume (7174 $Å^3$), however, closely resembles that of the europium analogue (6996 $Å^3$). Refinement of X-ray data for a crystal structure determination is now in progress [30].

A tetrahydrofuran complex, obtained by reaction of ytterbium diiodide and sodium bis(trimethylsilyl)amide in tetrahydrofuran, or by addition of tetrahydrofuran to $Yb[N(SiMe_3)_2]_2(OEt_2)_2$, proved somewhat difficult to characterize rigorously. From elemental analyses and ^1H NMR integrated intensities, the stoichiometry of the compound appeared to correspond approximately to $Yb[N(SiMe_3)_2]_2(tnf)_{2.5}$, though the stoichiometry varied slightly from sample to sample. This orange complex did not give a tetrahydrofuran complex in the mass spectrum, the highest mass peak observed corresponding to $Yb[N(SiMe_3)_2]_2$.

The nitrile t-BuCN readily displaces diethyl ether from $Yb[N(SiMe_3)_2]_2(OEt_2)_2$. The dark red complex obtained, $Yb[N(SiMe_3)_2]_2(NCBu^t)_3$, has a $\nu(C\equiv N)$ stretching frequency of 2254 cm^{-1} in its infrared spectrum.

The diethyl ether complex also reacts with phenylacetylene to yield the known divalent phenylacetylide $Yb(C\equiv CPh)_2$ [31].

Phosphine Complexes

The 4f-metals behave as rather hard Lewis acids in coordination complexes. Much of the organometallic chemistry of these metals is strongly influenced by strong bonding to Lewis bases, many times with bases that are generally involved in the preparative chemistry, such as solvent molecules and halide ions. Lanthanide complexes are also known to form a variety of donor comlexes with, for example, ethers, amines, cyanides and isocyanides. In spite of this, only one example of a lanthanide phosphine coordination complex, the black $YbCp_3(PPh_3)$, has been claimed [32]. This raises a question as to whether phosphines can function as good donor ligands to the lanthanides.

Based on the reported heats of formation for donor complexes of the hard Lewis acids H^+ [33], BMe_3 [34] and $GaMe_3$ [35], it seemed that phosphine coordination to a lanthanide might not only be energetically feasible, but just as favorable as coordination of nitrogen or oxygen bases (see Table I). It has recently been shown that phosphine complexes of the tetravalent actinide metals can be readily prepared [36]. Therefore, it seemed reasonable to expect to observe lanthanide phosphine complexes as stable, isolable species.

Table I. Thermochemical data for formation of some acid-base complexes.

Basicity Towards H^+ (gas phase) [33]

	$-\Delta H$ (kcal mol^{-1})
Me_3N	222
Me_3P	223
Et_2O	197
THF	196

$MMe_3 + L \rightleftharpoons MMe_3 \cdot L$ (gas phase) [34,35]

M	L	$-\Delta H$ (kcal mol^{-1})
B	Me_3N	17.6
	Me_3P	16.5
Ga	Me_3N	0
	Me_3P	18
	Me_2O	10

The preparation of pentane-soluble complexes of $Ln[N(SiMe_3)_2]_2$ (Ln = Eu or Yb) with the relatively weak donor ligands $N(SiMe_3)_2^-$ and OEt_2 would appear to offer potential routes to phosphine complexes of $Ln[N(SiMe_3)_2]_2$ *via* displacement reactions.

This is indeed the case, as sodium bis(trimethylsilyl)amide is readily displaced from the complex $NaEu[N(SiMe_3)_2]_3$ by 1,2-dimethylphosphinoethane(dmpe) or tri(n-butyl)phosphine in pentane to yield the orange complexes $Eu[N(SiMe_3)_2]_2(dmpe)_{1.5}$ and $Eu[N(SiMe_3)_2]_2(PBu^n_3)_2$, respectively. The presence of the phosphine ligands in these complexes was confirmed by hydrolysis experiments, in which the free phosphines generated were identified by their ^1H and $^{31}P\{^1H\}$ NMR spectra. The complex $Eu[N(SiMe_3)_2]_2(PBu^n_3)_2$ has an effective magnetic moment of 7.4 B.M. at 30°C in benzene, as determined by Evans' method. The species $Eu[N(SiMe_3)_2]_2(dmpe)$ was observed in the mass spectrum of $Eu[N(SiMe_3)_2]_2(dmpe)_{1.5}$ (at m/e = 623). The bis[tri(n-butyl)phosphine] complex did not give a molecular ion in the mass spectrum.

The diethyl ether complex, $Yb[N(SiMe_3)_2]_2(OEt_2)_2$, also serves as a useful starting material for the preparation of phosphine coordination complexes. Reaction with 1,2-dimethylphosphinoethane in pentane produces the purple $Yb[N(SiMe_3)_2]_2(dmpe)$. This compound exhibits normal, diamagnetic shifts in the ^1H and $^{13}C\{^1H\}$ NMR spectra. The $^{31}P\{^1H\}$ NMR spectrum contains a single resonance due to coordinated dmpe, at δ -40.9. The coordination chemical shift is therefore 8.5 ppm downfield from the free ligand [37]. A molecular ion, at m/e 644, was observed in the mass spectrum.

A crystal structure of this compound has been determined [12]. An ORTEP view of $Yb[N(SiMe_3)_2]_2(dmpe)$, which crystallizes in space group F2dd, with Z = 8, is shown in Figure 8. The two silylamide ligands are related by a twofold axis that passes through the C1-C1' bond and ytterbium. Figures 9 and 10 present some of the distances and angles, respectively, observed in the molecule.

As in $NaEu[N(SiMe_3)_2]_3$, short metal-carbon(methyl) contacts (3.04 Å) are observed. A number of the observed structural parameters in the silylamide ligand reflect distortions that result from the interaction. The Si1-C5 distance of 1.90 Å has been lengthened relative to the other Si1-C(methyl) distances of 1.86 and 1.87 Å. Likewise, the N-Si1 distance (1.69 Å) is greater than the N-Si2 distance (1.67 Å). Constriction of the Yb-N-Si1 and N-Si1-C5 angles is also apparent. Constraint of the thermal motion in C5 has allowed location of the hydrogen atoms in the C5 methyl groups. These hydrogens are seen to assume nearly tetrahedral positions about the carbon atom, and do not appear to be interacting with the ytterbium atom. This is consistent with a direct ytterbium-carbon interaction.

Phosphine coordination complexes are also formed by the reaction of $Yb[N(SiMe_3)_2]_2(OEt_2)_2$ with 1,2-dimethylphosphinomethane (dmpm) and tri(n-butyl)phosphine. The red $Yb[N(SiMe_3)_2]_2(dmpm)_2$ complex gives a temperature independent (-40 to +25°C) shift in the $^{31}P\{^1H\}$ NMR spectrum of δ - 44.7, corresponding to a downfield shift of 11.0 ppm from that of the free ligand [38]. The $^{31}P\{^1H\}$ NMR spectrum of brown-red $Yb[N(SiMe_3)_2]_2(PBu^n_3)_2$ in d_6-benzne contains a resonance at δ - 29.6, coincedent with the

Figure 8. An ORTEP drawing of $Yb[N(SiMe_3)_2]_2(dmpe)$.

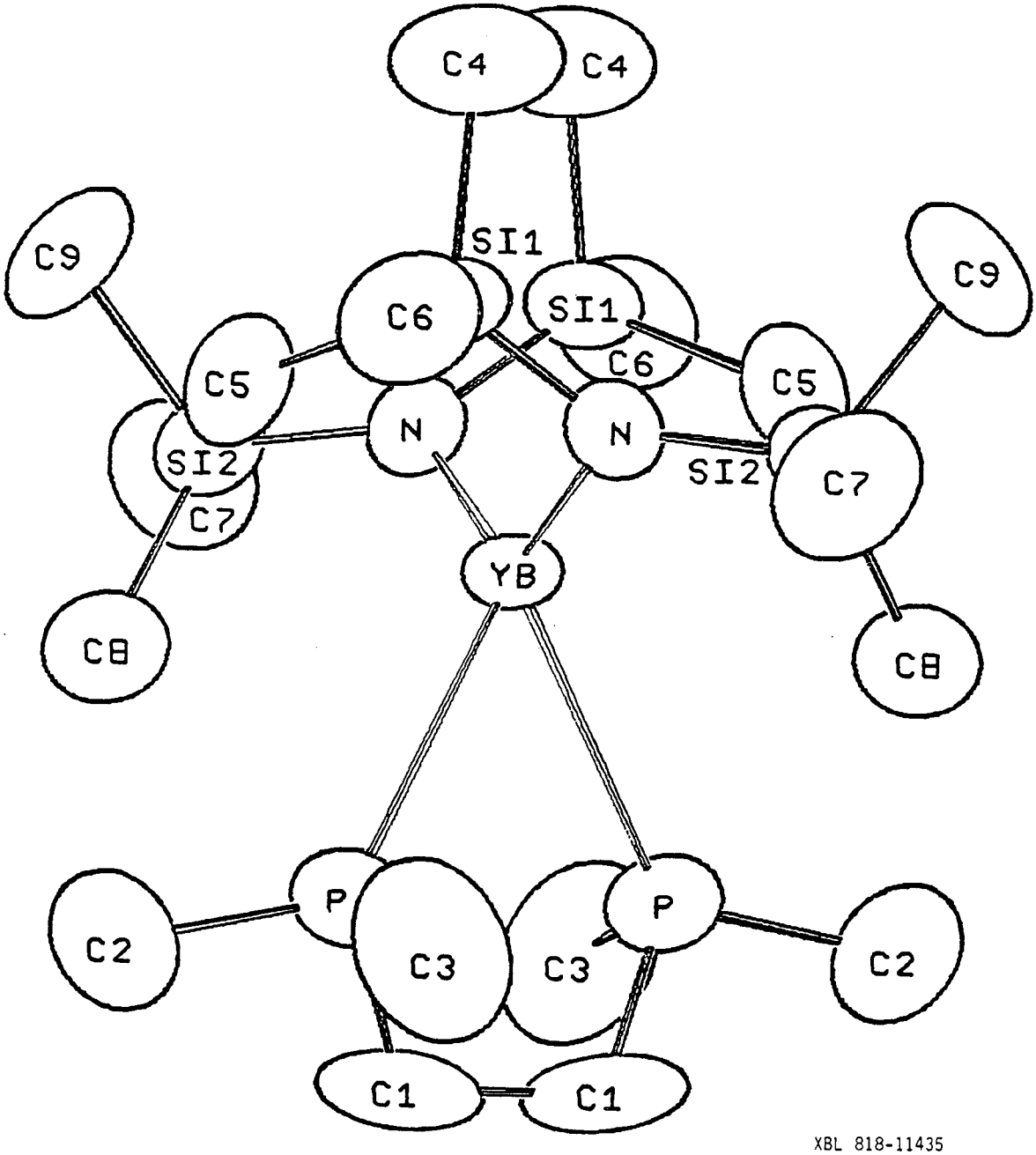


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Figure 9. Some bond distances in the complex $Yb[N(SiMe_3)_2]_2(dmpe)$.

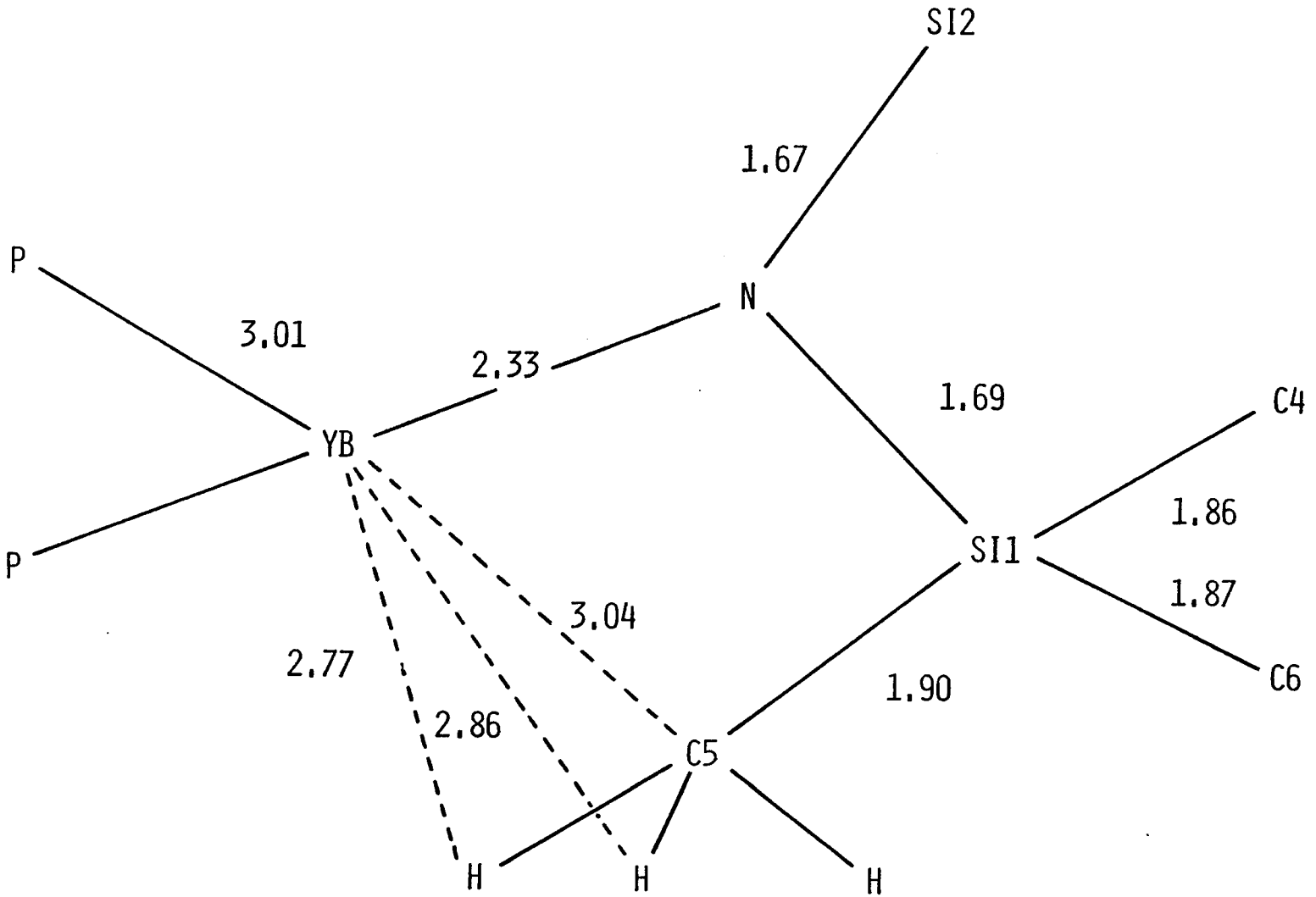

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Figure 10. Some bond angles in the complex $Yb[N(SiMe_3)_2]_2(dmpe)$.

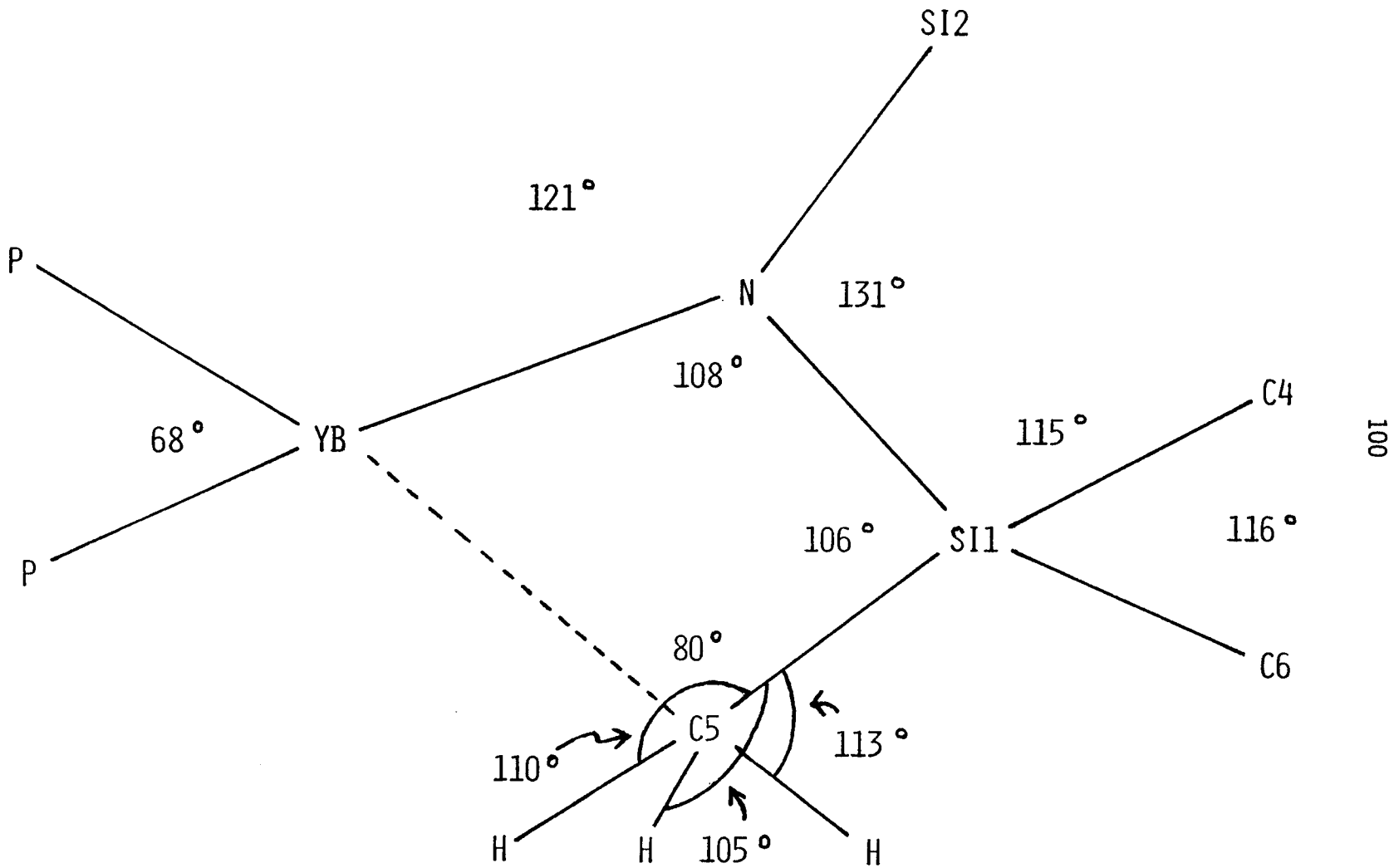

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Table II. Some physical properties of the $Ln[N(SiMe_3)_2]_2$-phosphine complexes.

Compound	Color	m.p., °C	$^{31}P\{^1H\}$[a]	Δ[b]
$Eu[N(SiMe_3)_2]_2(dmpe)_{1.5}$	orange	94–95	---	---
$Eu[N(SiMe_3)_2]_2(PBu^n_3)_2$	orange	48–49	---	---
$Yb[N(SiMe_3)_2]_2(dmpe)$	purple	195–197	-40.9	8.5
$Yb[N(SiMe_3)_2]_2(dmpm)_2$	red	60–61	-44.7	11.0
$Yb[N(SiMe_3)_2]_2(PBu^n_3)_2$	brown-red	46–48	-29.6	0
$Yb[N(SiMe_3)_2]_2(diphos)$	red	206–209	---	---

a All values in ppm (δ) vs. 85 percent H_3PO_4

b Downfield shift in ppm from free ligand value.

chemical shift observed for free tri(n-butyl)phosphine [39]. This latter observation suggests a very weak interaction between tri(n-butyl)phosphine and the $Yb[N(SiMe_3)_2]_2$ fragment, or an extensive dissociation of the phosphine in solution.

The chelating phosphine 1,2-diphenylphosphinoethane (diphos) reacts with the sodium salt $NaYb[N(SiMe_3)_2]_3$ in pentane to precipitate the red $Yb[N(SiMe_3)_2]_2$(diphos), which is only sparingly soluble in aromatic hydrocarbons. Some physical properties of the phosphine complexes reported here are listed in Table II.

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CHAPTER 4

TRIVALENT PENTAMETHYLCYCLOPENTADIENYL LANTHANIDE COMPLEXES

As a result of difficulties encountered in trying to prepare the monochlorobisamide species, $Ln[N(SiMe_3)_2]_2Cl$, pentamethylcyclopentadienide (C_5Me_5), anotner sterically demanding ligand, was used. The known chemistry of this ligand with other large metals suggests that only two C_5Me_5 units can be substituted about the metal atom. Therefore, preparation of $(C_5Me_5)_2LnCl$ derivatives appeared to be straightforward. In the analogous bis(cyclopentadienyl) compounds ($[(C_5H_5)_2Ln(\mu\text{-}Cl)]_2$ in benzene and $(C_5H_5)_2LnCl(thf)$ in tetrahydrofuran),[1] the metal is formally eight-coordinate, being bound to two cyclopentadienyl groups (three coordinate ligands) and two other donor ligands.

Ytterbium trichloride reacts with two equivalents of LiC_5Me_5 in tetrahydrofuran, and after crystallization from diethyl ether, violet $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ is obtained as the only product. Though species analogous to the bis(cyclopentadienyl) compounds are not obtained, the coordination number of eight is maintained. Presumably, the steric bulk of the C_5Me_5 ligands prevents formation of the chloro-bridged dimer. The diethyl ether in this anionic complex can be displaced by N,N,N',N'-tetramethylethylenediamine, giving $[Li(tmed)][(C_5Me_5)_2YbCl_2]$. Anionic complexes of samarium and neodymium, $[Li(tmed)][(C_5Me_5)_2SmCl_2]$, $[Li(OEt_2)_2][(C_5Me_5)_2NdCl_2]$ and $[Li(tmed)_2][(C_5Me_5)_2NdCl_2]$ were prepared in a similar manner.

The solid-state structure of $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2)][2]$ shows the diethyl ether ligands coordinated to lithium with the chlorides bridging ytterbium and lithium. This structure, which is also exhibited by the anionic complexes $[Li(OEt_2)_2][(C_5Me_5)_2YbI_2]$ and $[Li(OEt_2)_2][(C_5H_4SiMePh_2)_2YbCl_2]$ [2], is probably maintained in all the above ionic species, except $[Li(tmed)_2][(C_5Me_5)_2NdCl_2]$. The stoichiometry of this compound suggests separated ion pairs, as in $[n\text{-}Bu_4N][(C_5Me_5)_2YbCl_2]$ (see below). This difference in structure probably reflects subtle changes in coordination energies and/or lattice energies in going from samarium and ytterbium to the larger neodymium ion.

Isolation of anionic organometallic species has precedent in lanthanide chemistry; other examples include $[Li(thf)_2][Yb(C_5H_4SiMe_3)_2Cl_2]$, $[Li(thf)_4][Yb(CH(SiMe_3)_2)_3Cl]$ and $[Li(thf)_4][Yb(CH_2SiMe_3)_4]$, reported by Lappert et. al. [3]. Factors that influence relative stabilities for the neutral and anionic complexes are not clear [3], but the stability of the anionic derivatives is most likely related to the strong affinity of these hard metal acids for high coordination numbers and hard donor ligands. By forming organolithium adducts, these metals are therefore able to stabilize species that can be considered as intermediates in alkyl-halide exchange reactions [2].

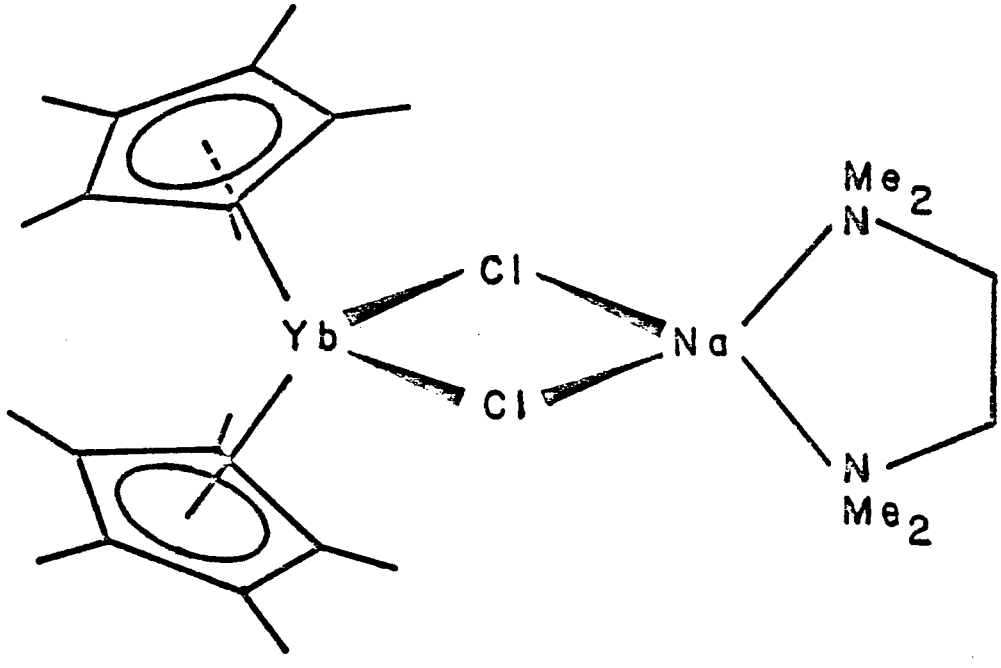
In an attempt to destabilize the anionic structure, NaC_5Me_5 was used as a reagent. Two equivalents of NaC_5Me_5 react with $YbCl_3$ to give two products, the anionic $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ (33 percent) and $(C_5Me_5)_2YbCl(thf)$ (42 percent), isolated by fractional crystallization from diethyl ether. Thus, elimination of NaCl is more facile than LiCl elimination under similar conditions.

When extraction and crystallization are carried out with toluene, $(C_5Me_5)_2YbCl(thf)$ is obtained as the only product. The coordinated tetrahydrofuran in this molecule is readily identified by infrared absorptions at 1014 and 862 cm^{-1}. The $(C_5Me_5)_2YbCl(thf)$ was prepared independently from the divalent $Yb(C_5Me_5)_2(thf)$ and CH_2Cl_2 or $YbCl_3$ (see Chapter 6). It can also be prepared from $(C_5Me_5)_2YbCl_2AlCl_2$ and tetrahydrofuran [2].

The salt $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ yields the complex $[Na(tmed)][(C_5Me_5)_2YbCl_2]$ upon reaction with N,N,N',N'-tetramethylethylenediamine. Data for a crystal structure determination were collected on crystals of this complex, but it could not be refined properly [4]. A disorder in the hydrocarbon ligands allowed only the heavy atoms (Yb, Cl and Na) to be located. These atoms form the bridged structure I (Figure 1), analogous to $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$. The magnetic susceptibility of $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ follows Curie-Weiss behavior from 4 to 45 K, the effective magnetic moment being 3.91 B.M. (θ = - 3.7K and C = 1.90); the magnetic moment of $(C_5Me_5)_2YbCl(thf)$ at 28°C (Evans' method) is 4.20 B.M.

The $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ can be converted quantitatively to the neutral, trivalent, tetrahydrofuran complex by stirring it in toluene with a small amount of tetrahydrofuran present. This observation suggests that in the reaction of NaC_5Me_5 with $YbCl_3$, the salt $[Na(thf)_2][(C_5Me_5)_2YbCl_2]$ is formed initially, which then eliminates NaCl in solvents less polar than

Figure 1. Structure of $[Na(tmed)][(C_5Me_5)_2YbCl_2]$.



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tetrahydrofuran. The analogous lithium salts appear to be much more stable with respect to loss of LiCl, since they do not undergo this disproportionation in toluene-tetrahydrofuran mixtures.

Attempts to obtain the base-free species, $(C_5Me_5)_2YbCl$, by sublimation of the tetrahydrofuran or anionic complexes failed (see Experimental Section). However, $(C_5Me_5)_2YbCl$ is observed as the highest mass peak in the mass spectrum of $(C_5Me_5)_2YbCl(thf)$. The tetrahydrofuran in this complex may be displaced by nitrogen bases; pyridine and diethyl amine yield $(C_5Me_5)_2YbCl(py)$ and $(C_5Me_5)_2YbCl(NHEt_2)$, respectively. However, diisopropyl amine does not displace tetrahydrofuran from $(C_5Me_5)_2YbCl(thf)$. Crystals of $(C_5Me_5)_2YbCl(thf)$ were unsuitable for a single-crystal X-ray analysis due to twinning, and $(C_5Me_5)_2YbCl(py)$ appeared to have a stacking disorder [4].

The reaction between neodymium trichloride and two equivalents of NaC_5Me_5 in tetrahydrofuran also yields two products after crystallization from diethyl ether, blue $[Na(OEt_2)_2][(C_5Me_5)_2NdCl_2]$ and green $(C_5Me_5)_2NdCl(thf)$. The latter complex has the same infrared spectrum as $(C_5Me_5)_2YbCl(thf)$. The $(C_5Me_5)_2NdCl(thf)$ is obtained as the only product if extraction and crystallization are carried out with pentane. The only product isolated from samarium trichloride and NaC_5Me_5 under similar conditions was $[Na(OEt_2)][(C_5Me_5)_2SmCl_2]$. The sodium salts of neodymium and samarium, which give identical infrared spectra, differ from $[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ in containing less diethyl ether and in not eliminating NaCl upon stirring in toluene in the presence

of tetrahydrofuran. The tmed complex $[Na(tmed)][(C_5Me_5)_2SmCl_2]$, however, does appear to be isostructural with the ytterbium analogue (by ir).

The mono-ring complex, $[Na(OEt_2)_2][(C_5Me_5)NdCl_3]$, which is simply a $NaC_5Me_5(OEt_2)_2$-adduct of $NdCl_3$, can be isolated from one molar equivalent of NaC_5Me_5 and $NdCl_3$ in tetrahydrofuran, followed by crystallization from diethyl ether. All the above chloride species and some of their physical properties are listed in Table 1.

It was of interest to explore the utility of the $[(C_5Me_5)_2YbCl_2]^-$ and $(C_5Me_5)_2YbCl(thf)$ species as starting materials for the preparation of more reactive $(C_5Me_5)_2YbX$ (X = alkyl, hydride, borohydride, amide, etc.) derivatives. The neutral, base-free systems are of interest, since these coordinatively unsaturated species are expected to exhibit an extensive reaction chemistry and to lead to compounds of unusual structural types. These compounds might also serve as routes to base-free divalent compounds, if reduction in a non-coordinating solvent can be effected. However, the lanthanide metals in these systems are quite tenacious in maintaining an eight-coordinate environment.

Watson has shown that reactions of $[(C_5Me_5)_2YbCl_2]^-$ with MeLi lead to $[(C_5Me_5)_2Yb(Me)Cl]^-$, $[(C_5Me_5)_2YbMe_2]^-$, and $(C_5Me_5)_2YbMe(thf)$, depending upon reaction conditions [5]. The Grignard reagent, PhMgBr, reacts with $(C_5Me_5)_2YbCl(py)$ to give $(C_5Me_5)_2YbClBrMgPh(py)$. This compound probably has a

Table I. Some Physical Properties of the Pentamethylcyclopentadienyl Chloride Compounds

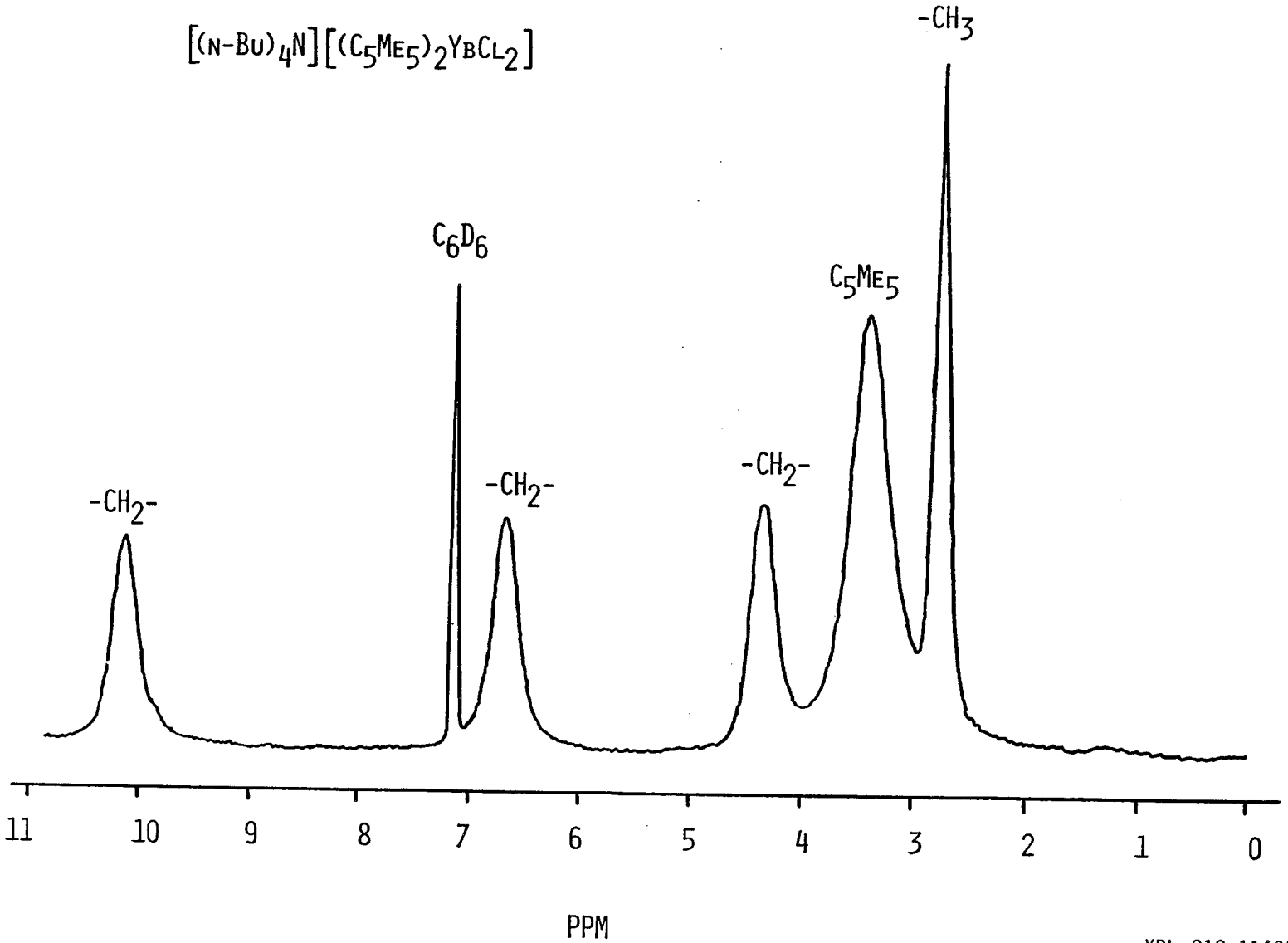
Compound	Melting or Decomposition Point (°C)	Color
$[Na(OEt_2)_2][(C_5Me_5)NdCl_3)$	125 dec	blue
$[Li(OEt_2)_2][(C_5Me_5)_2NdCl_2]$	114 dec	blue
$[Li(tmed)_2][(C_5Me_5)_2NdCl_2]$	> 300	blue
$[Na(OEt_2)][(C_5Me_5)_2NdCl_2]$	> 300	blue
$(C_5Me_5)_2NdCl(thf)$	220-223	green
$[Li(tmed)][(C_5Me_5)_2SmCL_2]$	200 dec	yellow
$[Na(OEt_2)][(C_5Me_5)_2SmCl_2]$	> 300	orange
$[Na(tmed)][(C_5Me_5)_2SmCl_2]$	> 300	yellow
$[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$	130 dec	violet
$[Li(tmed)][(C_5Me_5)_2YbCl_2)$	255 dec	violet
$[Na(OEt_2)_2][(C_5Me_5)_2YbCl_2]$	280 dec	violet
$[Na(tmed)][(C_5Me_5)_2YbCl_2]$	120 dec	violet
$[n\text{-}Bu_4N][(C_5Me_5)_2YbCl_2]$	204-205	purple
$(C_5Me_5)_2YbCl(thf)$	221-223	violet
$(C_5Me_5)_2YbCl(py)$	270-272	purple
$(C_5Me_5)_2YbCl(NHEt_2)$	181 dec	purple

structure similar to I, with the halide ligands bridging the ytterbium and magnesium atoms. Reaction of $[n\text{-}Bu_4N][BH_4]$ with $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ in toluene did not lead to a borohydride derivative, but to $[n\text{-}Bu_4N][(C_5Me_5)_2YbCl_2]$, the stoichiometry of which can be derived from the ^1H NMR spectrum. Broadened, shifted singlets were observed at δ 10.17 (8H), 6.75 (8H), 4.45 (8H), 3.52 (30H) and 2.85 (12H) (Figure 2).

The simplest approach to preparing neutral, seven-coordinate $(C_5Me_5)_2LnX$ is to incorporate an X group that is bulky enough to prevent coordination of another base. The silylamides $(C_5Me_5)_2LnN(SiMe_3)_2$, where Ln is Nd or Yb, have been prepared from $[Li(OEt_2)_2][(C_5Me_5)_2NdCl_2]$ and $(C_5Me_5)_2YbCl(py)$, respectively, with sodium bis(trimethylsilyl)amide. These compounds have infrared spectra identical to the related monomeric uranium(III) derivative, $(C_5Me_5)_2UN(SiMe_3)_2$ [6]. In an attempt to prepare the base-free divalent compound, $Yb(C_5Me_5)_2$, $(C_5Me_5)_2YbN(SiMe_3)_2$ was refluxed with sodium amalgam in toluene, but no reduction was observed. In an attempt to prepare the amide complex $(C_5Me_5)_2YbNEt_2$, $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ was reacted with $LiNEt_2$ in diethyl ether. A small amount of insoluble material was formed, and most of the $[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ remained unreacted (see Experimental Section).

Use of chelating, four-electron donor ligands could yield neutral, base-free complexes which are still eight-coordinate. Such compounds might then be useful in preparing base-free divalent complexes by

Figure 2. ^{1}H NMR spectrum of $[n\text{-}Bu_4N][(C_5Me_5)_2YbCl_2]$.



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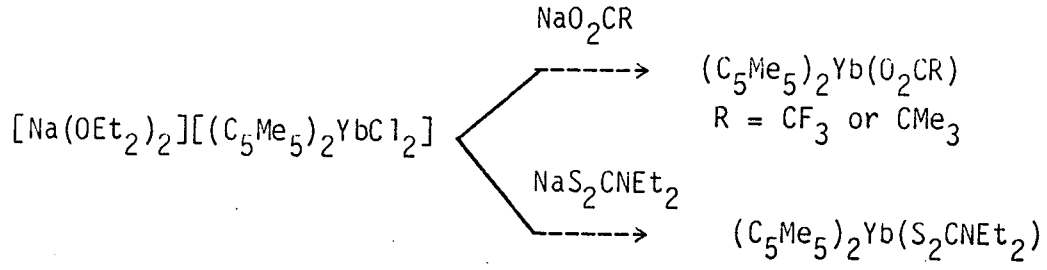
reduction in a non-coordinating solvent. Since carboxylate (RCO_2^-) ligands have been effectively utilized as leaving groups in transition metal chemistry, they seemed ideally suited. Another chelating ligand, diethyldithiocarbamate ($Et_2NCS_2^-$) is electronically similar, but contains the softer sulfur atoms as donors. Derivatives of both of these ligands were prepared as shown:



The analogous neodymium dithiocarbamate, $(C_5Me_5)_2Nd(S_2CNEt_2)$, was prepared similarly. The physical properties of these compounds are described in the experimental secton.

Because two donor atoms are present, RCO_2^- and $Et_2NCS_2^-$ yield ether-free complexes. Unfortunately the ytterbium(III) species could not be reduced with sodium-amalgam in refluxing toluene. Dubeck has reported $(C_5H_5)_2Ln(O_2CR)$ derivatives [1], which are dimeric in solution, with bridging carboxylates. The $(C_5Me_5)_2Yb(O_2CCMe_3)$ gives dimeric fragments in the mass spectrum, suggesting that it is associated in a similar fashion.

The similarity in the magnetic behavior of $(C_5Me_5)_2Yb(O_2CCMe_3)$ and $(C_5Me_5)_2Yb(S_2CNEt_2)$ at low temperature suggests that the magnetic properties of the ytterbium ions in these complexes are not greatly effected by the change from carboxylate to dithiocarbamate

ligand. The effective magnetic moments (5-45K) of 3.29 and 3.39 B.M., respectively, are close in value to those of other ytterbium(III) complexes in this temperature range (cf. $Yb[N(SIMe_3)_2]_3$, 3.10 B.M. and $[(C_5H_5)_3Yb]_2$(pyrazine) [7], 3.48 B.M.).

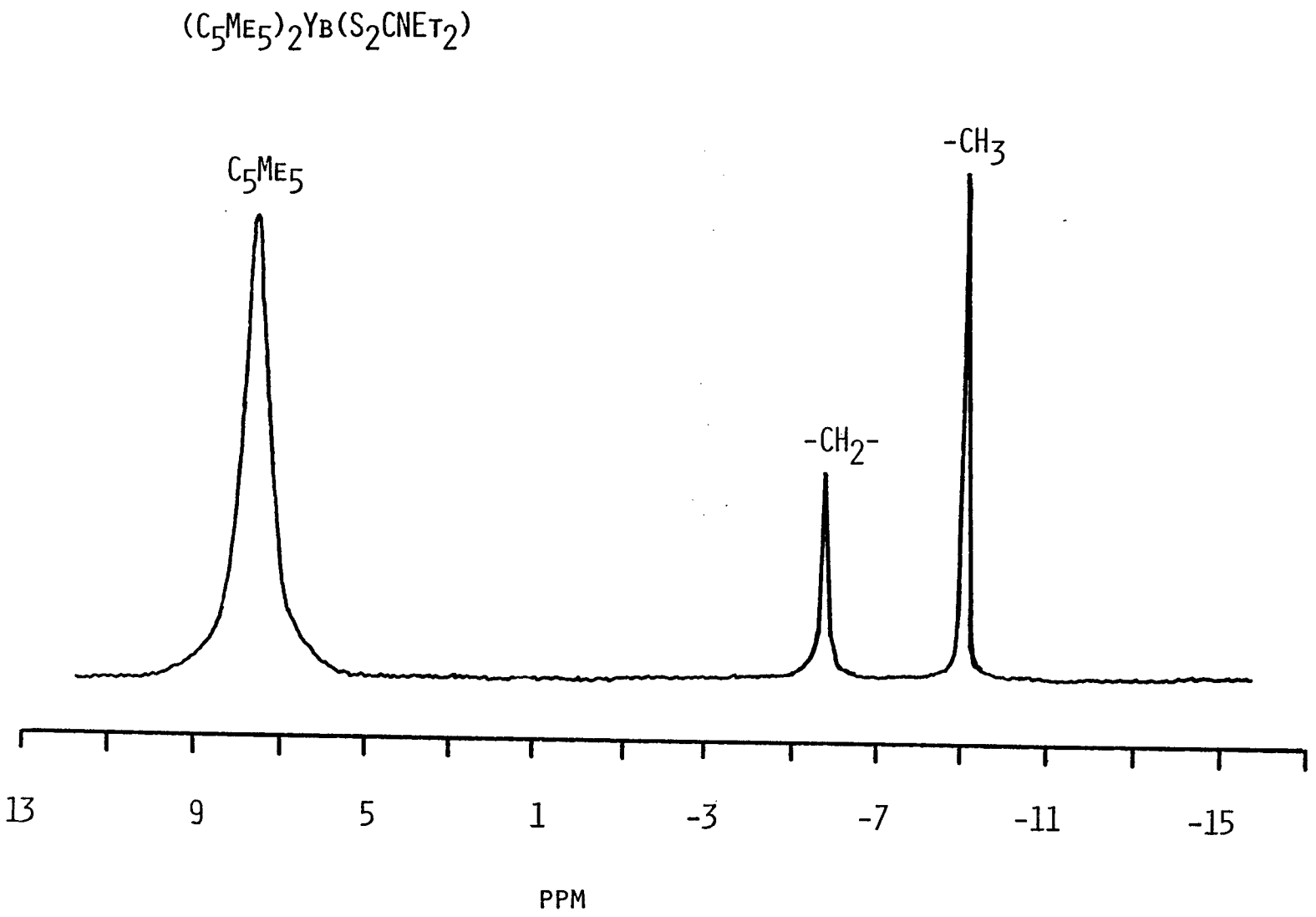
Figure 3, which shows the ^1H NMR spectrum of $(C_5Me_5)_2Yb(S_2CNEt_2)$, illustrates the usefulness of NMR data in characterizing these paramagnetic complexes. Though proton-proton coupling is lost due to line broadening, the integrated intensities confirm the stoichiometry of the complex.

Because little is known about the properties of sulfur-based ligands in molecular lanthanide systems, an X-ray crystal structure determination of $(C_5Me_5)_2Yb(S_2CNEt_2)$ was also undertaken [8]. Crystal structures have appeared for $Na[La(S_2CNEt_2)_4]$ [9] and $Ln[S_2P(C_6H_{11})_2]_3$, where Ln is Sm, Pr, Dy and Lu [10,11].

Figure 4 shows the ytterbium atom bonded to two pentamethylcyclopentadienyl rings and to the two sulfur atoms of the diethyldithiocarbamate ligand. The diethyldithiocarbamate ligand is disordered; the atoms N, C(12A), C(13A), C(12B), and C(13B) are in general positions with half of the molecules in the conformation shown, and half in the conformation that would result from a 180° rotation about the two-fold axis. The $(C_5Me_5)_2Yb$ fragment has perfect C_2 symmetry.

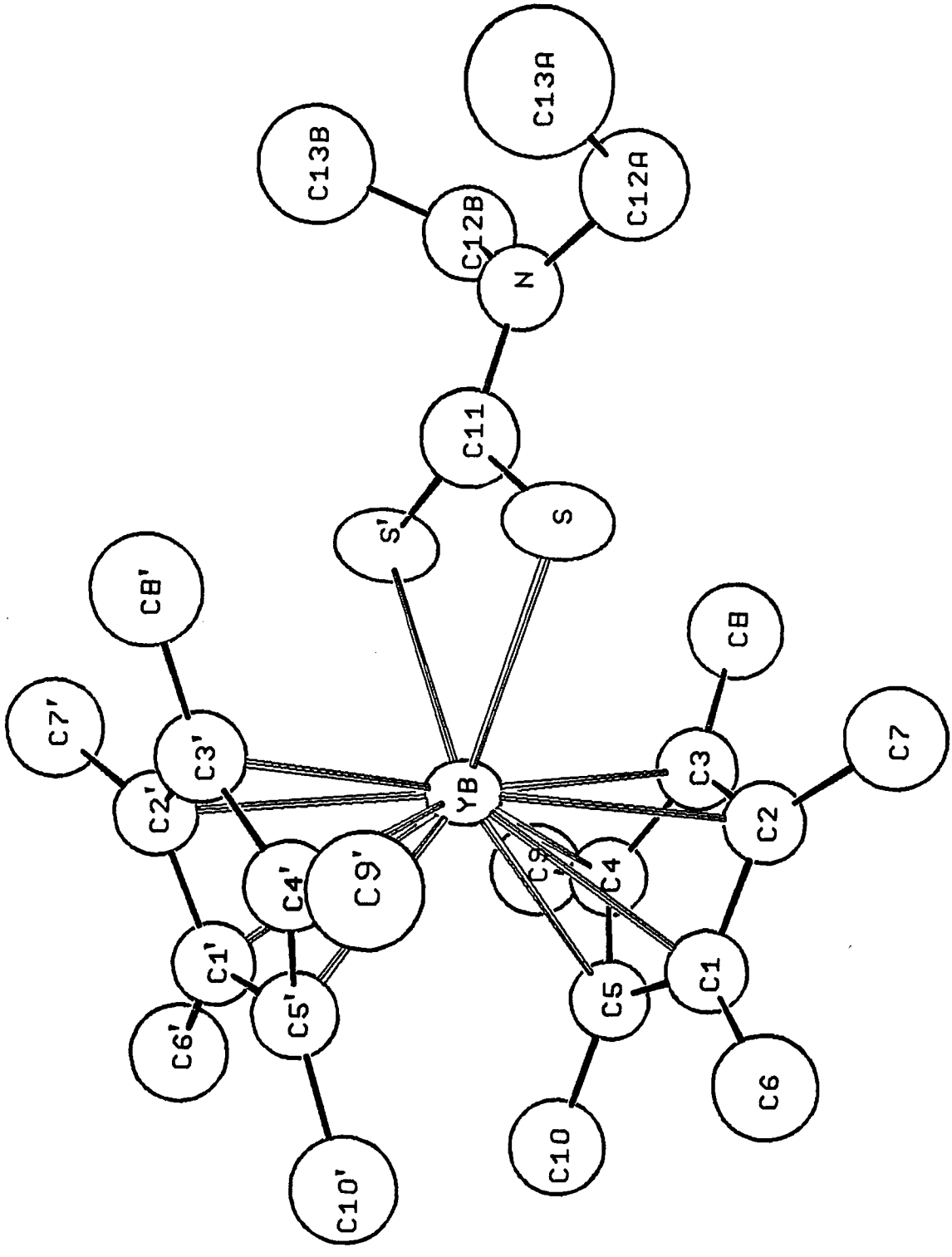
The ytterbium-carbon distances average 2.63 ± 0.03 Å and the ytterbium-sulfur distance is 2.70 Å. The metal atom is 2.33 Å from the mean plane defined by the C(1)-C(5) ring. The five methyl carbon atoms of the C_5Me_5 group are all bent out of the mean plane away from

Figure 3. ^{1}H NMR spectrum of $(C_5Me_5)_2 Yb(S_2CNEt_2)$.



XBL 818-11424

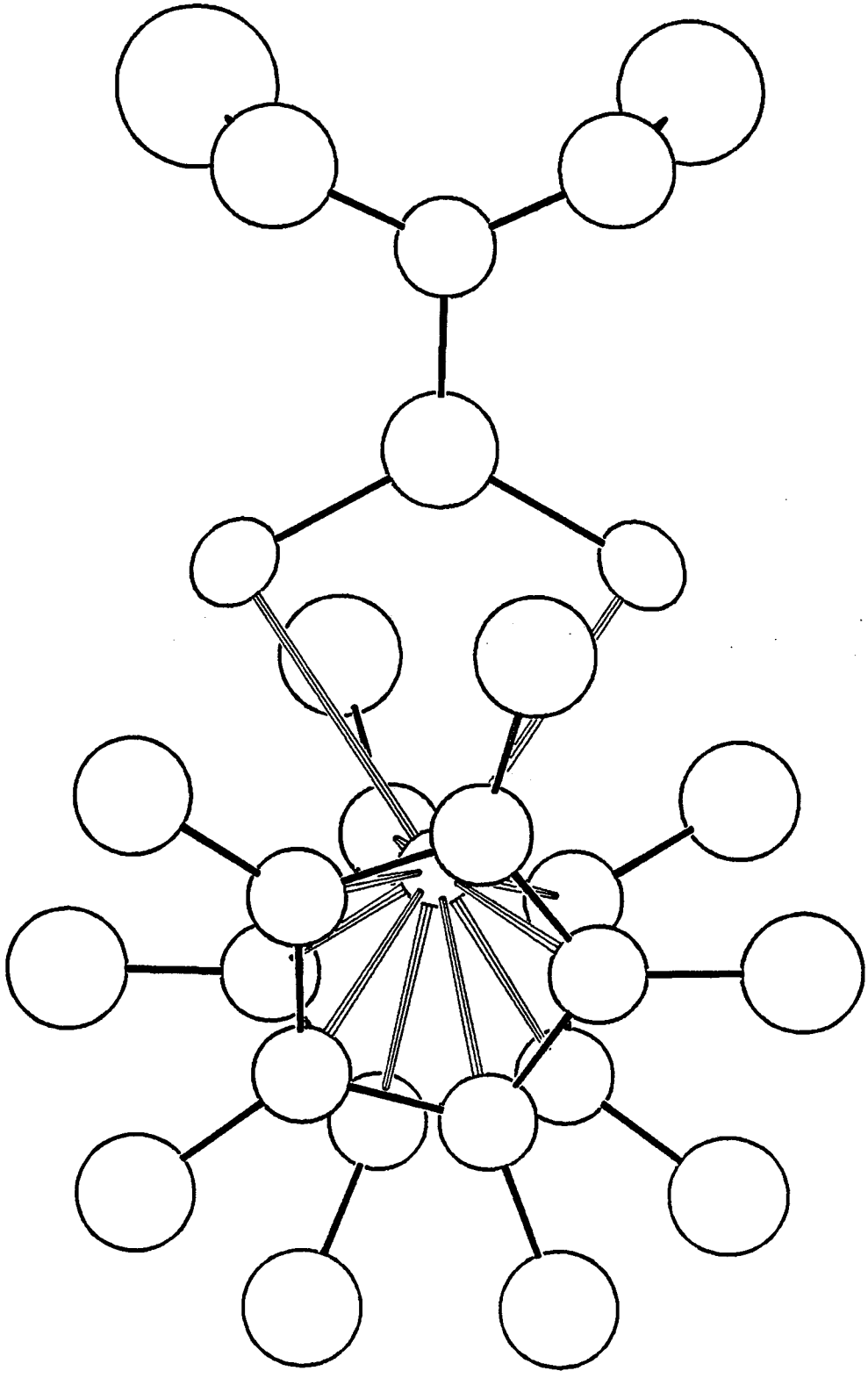
Figure 4. ORTEP drawing of $(C_5Me_5)_2$ $Yb(S_2CNEt_2)$.


C13A
C13B
C12A
C12B
N
C11
S'
S
C8'
C7'
C3'
C2'
C4'
C9'
C1'
C5'
C6'
C10'
YB
C8
C7
C3
C2
C4
C5
C1
C6
C10

XBL 812-8216

ytterbium; the distances from the planes for these methyl carbon atoms are 0.18, 0.19, 0.07 and 0.34 Å for atoms C(6)-C(10). The pentamethylcyclopentadienyl rings are in a staggered conformation with respect to each other (see Figure 5).

Figure 5. ORTEP view of $(C_5Me_5)_2$ $Yb(S_2CNEt_2)$ down the ring center-ring center vector.



XBL 816-10260

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CHAPTER 5

DIVALENT PENTAMETHYLCYCLOPENTADIENYL LANTHANIDE COMPLEXES

Ether Complexes

In contrast to the trichlorides of neodymium, samarium and ytterbium, europium trichloride does not yield a trivalent compound upon reaction with two equivalents of NaC_5Me_5 in tetrahydrofuran. The product isolated after crystallization from toluene is the red, divalent $Eu(C_5Me_5)_2(thf)$. Thus, NaC_5Me_5 appears to be a reducing agent towards $EuCl_3$. In support of this, reaction of $EuCl_3$ with three equivalents of NaC_5Me_5 in tetrahydrofuran generates the europium(II) compound in higher yield (65–70 percent). The reduction of europium(III) to europium(II) by the $C_5Me_5^-$ anion is not all that surprising, considering the small Eu(III)/Eu(II) reduction potential (ca. - 0.4 V, as estimated from spectroscopic data [1]). The less reducing parent anion, $C_5H_5^-$, is known to reduce Ta(V) to Ta(IV) [2], Ti(IV) to Ti(III) [3] and Re(V) to Re(III) [4].

It is interesting to note that the tris(cyclopentadienyl) compound $EuCp_3$ was not reported in the original description of other tris-(cyclopentadienyl)lanthanide complexes, which were purified by sublimation [5]. The apparent decomposition of this compound upon attempted vacuum sublimation is most likely related to the stability of the divalent oxidation state. This compound was later isolated as a monotetrahydrofuranate adduct by crystallization from tetrahydrofuran [6]. The tris(monomethylcyclopentadienyl) complex, $Eu(C_5H_4Me)_3(thf)$, is also readily prepared [7].

These observations suggest an increase in the reducing power of the cyclopentadienyl group upon substitution of hydrogens for electron-donating methyl groups. The He(I) and He(II) photoelectron spectra of substituted ferrocenes shows that this inductive effect of the methyl groups causes the first ionization energy from the ligand to drop by ca. 0.2 eV in going from $Fe(\eta\text{-}C_5H_5)_2$ to $Fe(\eta\text{-}C_5H_4Me)_2$, and by ca. 1.0 eV in going from $Fe(\eta\text{-}C_5H_5)_2$ to $Fe(\eta\text{-}C_5Me_5)_2$ [8].

The divalent complex $Eu(C_5Me_5)_2(thf)$ is quite soluble in aromatic hydrocarbons and sparingly soluble in aliphatic hydrocarbons. From diethyl ether, it crystallizes with one molar equivalent of diethyl ether to give $Eu(C_5Me_5)_2(thf)(OEt_2)$. The diethyl ether can be removed by recrystallization from toluene, suggesting that it is weakly bound or simply present as solvent of crystallization.

The oxidation state of europium was confirmed by a low temperature magnetic susceptiblity study, which shows that $Eu(C_5Me_5)_2(thf)(OEt_2)$ follows Curie behavior from 5-50K, with μ_{eff} = 7.99 B.M. and C = 7.91. This magnetic behavior is that expected for the $^8S_{7/2}$ ground state term of $4f^7$ ions [9].

The related ytterbium(II) complex, $Yb(C_5Me_5)_2(thf)$, can be obtained from ytterbium dichloride and two molar equivalents of NaC_5Me_5 in refluxing tetrahydrofuran. This complex is red and diamagnetic, as expected for a closed-shell $4f^{14}$ electron configuration ($^1S_0$). Accordingly, normal, diamagnetic ^1H and $^{13}C\{^1H\}$ nuclear magnetic resonance parameters are observed. The proton chemical shift attributed to the C_5Me_5 ligand is temperature

dependent, ranging from 1.98 ppm at 80°C to 2.18 ppm at -50°C. The tetrahydrofuran resonances are also temperature dependent. Between +80 and -50°C the center of the multiplet due to the α-protons ranges from 4.02 to 3.30 ppm, and those due to the β-protons range from 1.81 to 1.32 ppm.

The $^{13}C\{^{1}H\}$ NMR resonances for the C_5Me_5 ligand of some divalent ytterbium compounds are listed in Table I, along with those of other diamagnetic pentamethylcyclopentadienyl complexes. It is to be noted that the observed shifts of the ytterbium(II) derivatives are comparable to those observed in compounds of the more electropositive metals.

A good correlation between aromatic carbon-13 chemical shifts and electron populations in aromatic systems has been established [10,11]. An increase in the π-electron density at a carbon atom will result in a downfield shift of that carbon atom, by ca. 180 ppm per unit charge density for benzene rings [12]. Therefore, the observed shifts of the C_5Me_5 ring carbons may be a measure of the amount of electron density that a C_5Me_5 ring is donating to a metal. Such a correlation has been attempted for carbon-13 shifts in cyclooctatetraene derivatives of thorium [13]. It appears that more charge density is localized on the C_5Me_5 rings for the early transition metals than for ytterbium(II), despite the strongly reducing character of ytterbium(II) (vide infra). Also, it appears that the C_5Me_5 anion donates more electron density to the later transition metals than to ytterbium(II).

Table I. $^{13}C\{^{1}H\}$ NMR data for diamagnetic C_5Me_5 Compounds.[a]

Compound	Ring C	Methyl C	Solvent	Reference
$Na[(C_5Me_5)_2Mn]$	72	8.5	d_8-tnf	b
$(C_5Me_5)_2Fe$	78	9.6	d_6-PnH	b
$[(C_5Me_5)_2Co]PF_6$	93	6.3	d_6-Me_2CO	b
$(C_5Me_5)_2Rh(S_2CNMe_2)_2$	97	9.3	$CDCl_3$	c
$[Rh_4H_4(C_5Me_5)_4]^{2+}$	102	12.1	d_6-Me_2CO	d
$[(C_5Me_5)_2V(CO)_2]PF_6$	107	9.3	d_6-Me_2CO	b
$(C_5Me_5)_2Yb(thf)$	111	11.5	d_8-PhMe	this work
$(C_5Me_5)_2Yb(MeOC_2H_3)$	112	11.5	d_6-PhH	this work
$(C_5Me_5)_2Yb(dmpm)$	112	12.0	d_6-PhH	this work
$(C_5Me_5)Ta(CHCMe_3)(CH_2CMe_3)_2$	114	12.1	d_6-PhH	e
$(C_5Me_5)_2Zr(H)(OCHNbCp_2)$	116	7.8	d_6-PhH	f
$(C_5Me_5)_2TiMe_2$	119	17.8	d_8-PhMe	g
$(C_5Me_5)Ta(CH_2CMe_3)_2Cl_2$	124	12.8	d_6-PhH	e

a) All values in ppm (δ) vs. tetramethylsilane

b) Robbins, J. L. Ph.D. Thesis, University of California, Berkeley, 1981.
c) Robertson, D. and Stephenson, T., J.C.S. Dalton, 1978, 486.
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The $Yb(C_5Me_5)_2(thf)$ forms a hemi-toluene solvate, $Yb(C_5Me_5)_2(thf)$ 1/2PhMe, upon crystallization from toluene. Crystals of this compound are monoclinic ($P2_1/n$) with Z = 4 [14]. An ORTEP diagram (Figure 1) shows the ytterbium atom bonded to two η^5-C_5Me_5 ligands and the oxygen atom of tetrahydrofuran. The $Yb(C_5Me_5)_2(thf)$ molecule has approximate C_2 symmetry about the ytterbium-oxygen bond. The toluene molecules are disordered between two positions in the lattice [14].

The coordination about ytterbium is very close to planar, with a C_5Me_5 centroid-Yb-C_5Me_5 centroid angle of 143.5(3)° and centroid-Yb-O angles of 107.73(3)° and 108.8(3)°. The close approach of the C_5Me_5 rings results in severe displacements of methyl carbons C9, C16, and C17 from the planes of their respective C_5 rings (0.18, 0.14 and 0.21 Å, respectively). Other methyl carbon displacements range from 0.03 to 0.11 Å. Figure 2 is a projection of the two C_5Me_5 rings down the ring centroid-ring centroid vector, showing the staggered conformation of the rings.

The average ytterbium-carbon bond length (2.66 ± 0.02 Å) less the ionic radius of ytterbium(II) in seven coordination (counting C_5Me_5 as a three-coordinate ligand) of 1.08 Å [15] yields 1.58 Å for the effective ionic radius of the pentamethylcyclopentadienide group. This value is similar to those observed for other lanthanide and actinide cyclopentadienide compounds (1.64 ± 0.04 Å) in which the metal-ring bonding is considered to be primarily ionic [16]. The ytterbium-oxygen distance, 2.412(5) Å, less the ytterbium(II) ionic radius gives 1.33 Å as the ionic radius of a three-coordinate oxygen atom. A value of 1.36 Å has been suggested by Shannon [15].

Figure 1. ORTEP diagram of $Yb(C_5Me_5)_2(thf)$.

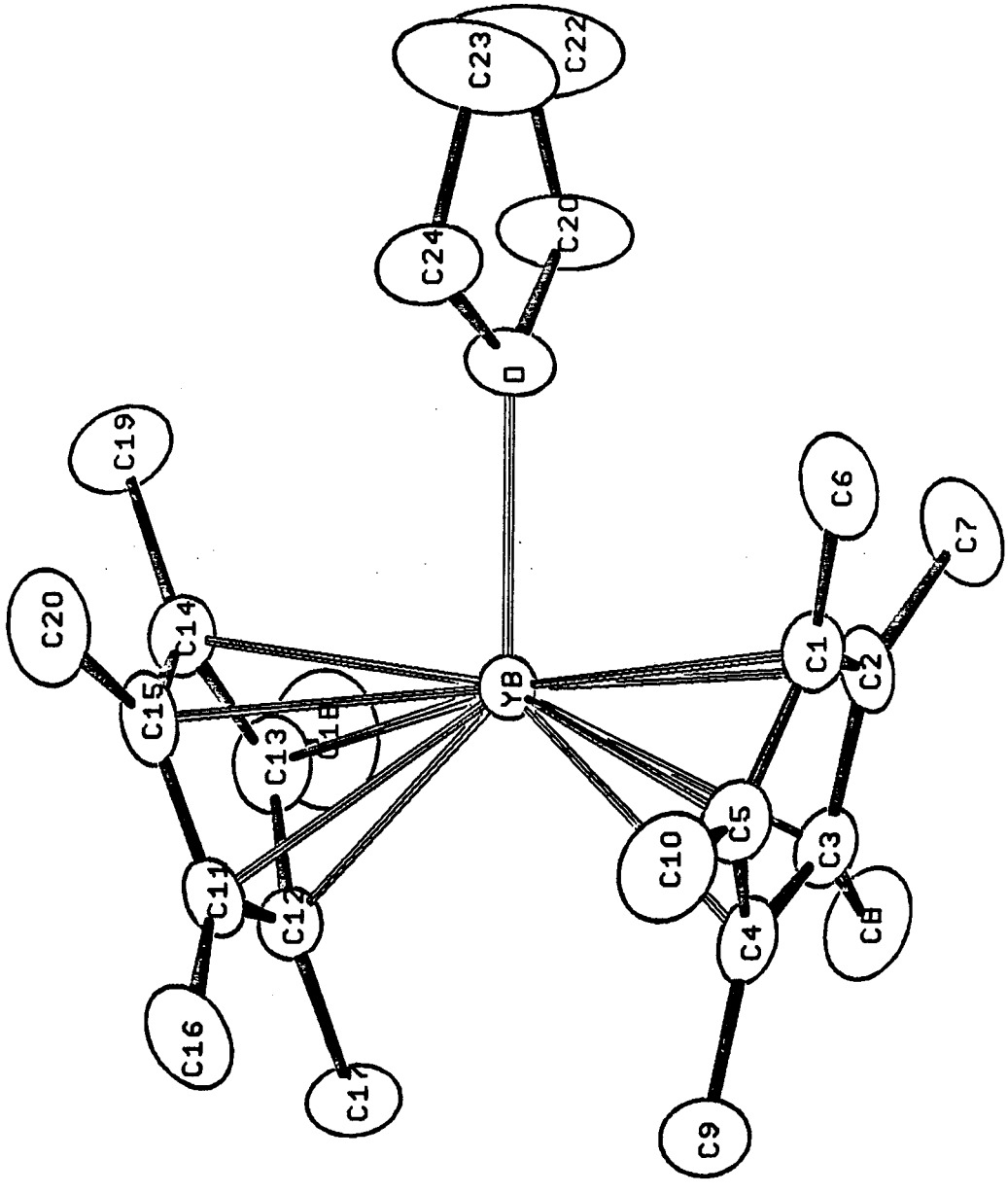

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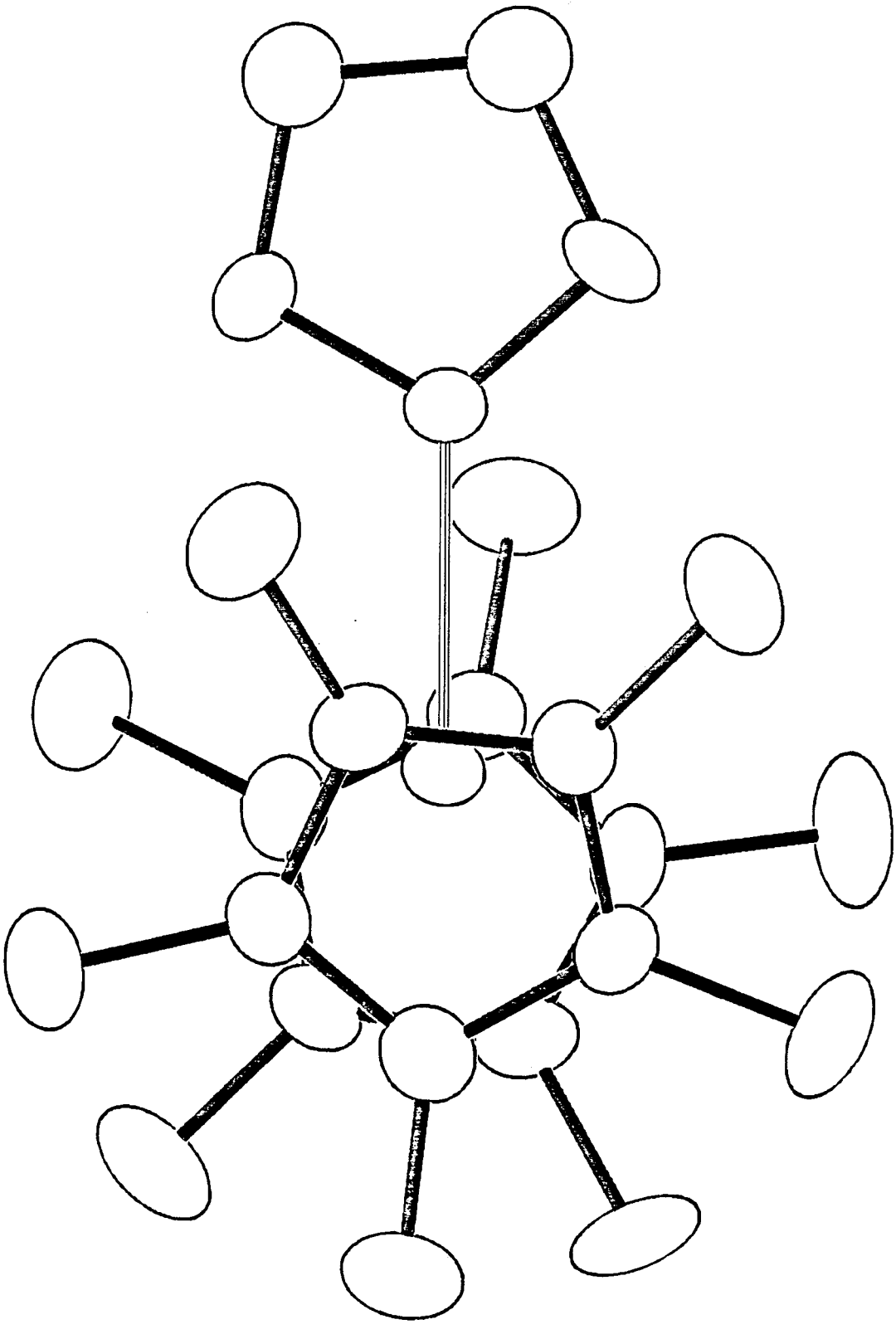
Figure 2. A view of $(C_5Me_5)_2Yb(thf)$ down the ring centroid-ring centroid vector, showing the staggered conformation of the C_5Me_5 rings.



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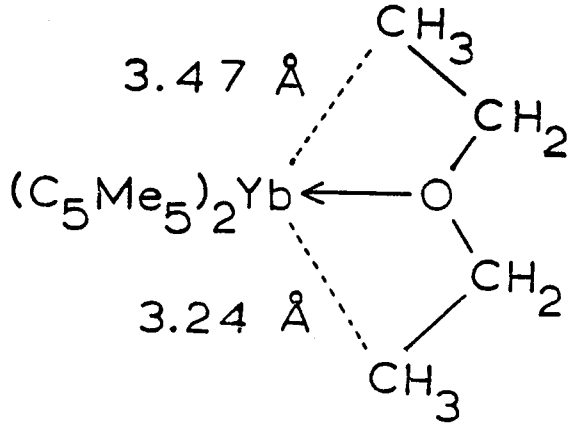
Under less forcing conditions one can obtain the diethyl ether complex $Yb(C_5Me_5)_2(OEt_2)$ by the room temperature reaction of ytterbium diiodide and two equivalents of NaC_5Me_5 in diethyl ether. This complex is bright green and diamagnetic. The red europium(II) analogue, $Eu(C_5Me_5)_2(OEt_2)$, can be prepared in a similar manner.

The crystal structure of $Yb(C_5Me_5)_2(OEt_2)$ [17], by Watson and Harlow, shows the low-valent, coordinatively-unsaturated ytterbium center interacting with the methyl groups of the diethyl ether ligand. This interaction, which is most likely analogous to the metal-carbon interactions observed in $Yb[N(SiMe_3)_2]_2(dmpe)$ and $NaEu[N(SiMe_3)_2]_3$, results in rather short ytterbium-methyl carbon contacts as shown:



This unusual bonding mode for diethyl ether may be responsible for the dramatic difference in color between $Yb(C_5Me_5)_2(thf)$ (red) and $Yb(C_5Me_5)_2(OEt_2)$ (green).

Tetrahydrofuran is a better base towards $Yb(C_5Me_5)_2$ than diethyl ether, since tetrahydrofuran displaces diethyl ether almost quantitatively from $Yb(C_5Me_5)_2(OEt_2)$. Some lability of the tetrahydrofuran ligand can be observed in the presence of excess diethyl ether, since upon recrystallization of $Yb(C_5Me_5)_2(thf)$ from diethyl ether, small yields (ca. 10 percent) of $Yb(C_5Me_5)_2(OEt_2)$ are obtained.

Attempts to remove the ether ligands from the above compounds to give the base-free complex have failed. The $Eu(C_5Me_5)_2(thf)$ compound gives small amounts of an orange sublimate at ca. 145°C and 10^{-2} mm Hg. This impure orange sublimate could not be purified by fractional crystallization. The $Yb(C_5Me_5)_2(thf)$ compound gave an orange sublimate at 125°C/10^{-2} mm Hg in ca. 40 percent yield. This material, which was impure (m.p. 122-140°C), gave peaks in the infrared spectrum at 3692 and 3648 cm^{-1} (possibly due to an -OH group); the presence of tetrahydrofuran was indicated by absorptions at 1020 and 890 cm^{-1}. The same material, which could not be fully characterized due to the small quantity obtained, is also formed by refluxing $Yb(C_5Me_5)_2(thf)$ in p-xylene. The diethyl ether complex, $Yb(C_5Me_5)_2(OEt_2)$, decomposes without subliming at ca. 120°C and 10^{-2} mm Hg. The fact that the bis(cyclopentadienyl) complexes of europium(II) and ytterbium(II) can be sublimed under

vacuum at 400-420°C [18] suggests that the C_5Me_5 derivatives, which have a lower coordination number and a more electron-rich metal, have a lower energy decomposition pathway, possibly via reaction with the ether ligands.

Apparently, reactions of the tetrahydrofuran compounds with Lewis acids do not result in simple transfer of the tetrahydrofuran ligand to the added Lewis acids. The reaction of $Yb(C_5Me_5)_2(thf)$ with $AlCl_3$ or BBr_3 gave a red solid (containing halide) that was insoluble in pentane, toluene and diethyl ether. A mixture of products that could not be purified was obtained by the reaction of $Eu(C_5Me_5)_2(thf)$ with $AlMe_3$.

A methyl vinyl ether complex, $Yb(C_5Me_5)_2(MeOC_2H_3)$ was prepared from YbI_2, NaC_5Me_5 and methyl vinyl ether in toluene. The green color of this compound suggests a ytterbium-carbon interaction of the type observed for $Yb(C_5Me_5)_2(OEt_2)$. Methyl vinyl ether appears to be a better donor than diethyl ether toward $Yb(C_5Me_5)_2$, since $Yb(C_5Me_5)_2(MeOC_2H_3)$ can be crystallized unchanged from diethyl ether. Methyl vinyl ether is displaced, however, by tetrahydrofuran and pyridine.

Addition of $OPPh_3$ to $Yb(C_5Me_5)_2(OEt_2)$ in diethyl ether, followed by crystallization of the precipitate from tetrahydrofuran-dietnyl ether gives purple $Yb(C_5Me_5)_2(thf)(OPPh_3)$. The tetrahydrofuran is lost in the mass spectrometer, since only $Yb(C_5Me_5)_2(OPPh_3)$ was observed in the mass spectrum.

The preparation of these coordination complexes establishes the utility of the bulky C_5Me_5 ligand in preparing a new class of monomeric, hydrocarbon-soluble divalent complexes. Though the divalent ionic radii are greater than the trivalent radii for a given coordination number, the divalent C_5Me_5 compounds often form seven-coordinate complexes, in contrast to the trivalent C_5Me_5 derivatives, which are typically eight-coordinate. This suggests that the lower oxidation state results in a softer, more electron-rich metal center that may exhibit reaction chemistry that has not been observed in lanthanide systems. We are now in a position to study the chemistry of these reduced metal species in non-coordinating hydrocarbon solvents.

Amine Complexes

Aromatic amines displace tetrahydrofuran or diethyl ether from the europium(II) and ytterbium(II) complexes to yield the eight-coordinate compounds listed in Table II. These compounds are very intensely colored, and except for $Yb(C_5Me_5)_2(bipy)$, are only sparingly soluble in non-coordinating hydrocarbons. Solution properties are therefore difficult to study. However, normal, diamagnetic ^1H NMR shifts are observed for $Yb(C_5Me_5)_2(py)_2$ and $Yb(C_5Me_5)_2(p\text{-}Me_2NC_5H_5N)_2$ at room temperature.

Diamagnetic NMR shifts are not observed for $Yb(C_5Me_5)_2(bipy)$. The resonance for the C_5Me_5 protons in the ^1H NMR spectrum was shifted ca. 2 ppm downfield to δ 4.11 ($\nu_{1/2}$ = 9 Hz). The proton chemical shifts for the bipyridine ligand could not be assigned, but broadened peaks were observed at δ 25.82, 5.24 and -13.11. The two

Table II. Aromatic Amine Complexes of $Eu(C_5Me_5)_2$ and $Yb(C_5Me_5)_2$

Compound	Color	Melting Point
$Eu(C_5Me_5)_2(bipy)$	brown	> 300°C
$Yb(C_5Me_5)_2(bipy)$	brown	> 300°C
$Yb(C_5Me_5)_2(py)_2$	green	208–210°C
$Yb(C_5Me_5)_2(p\text{-}Me_2NC_5H_5N)_2$	blue	241–242°C

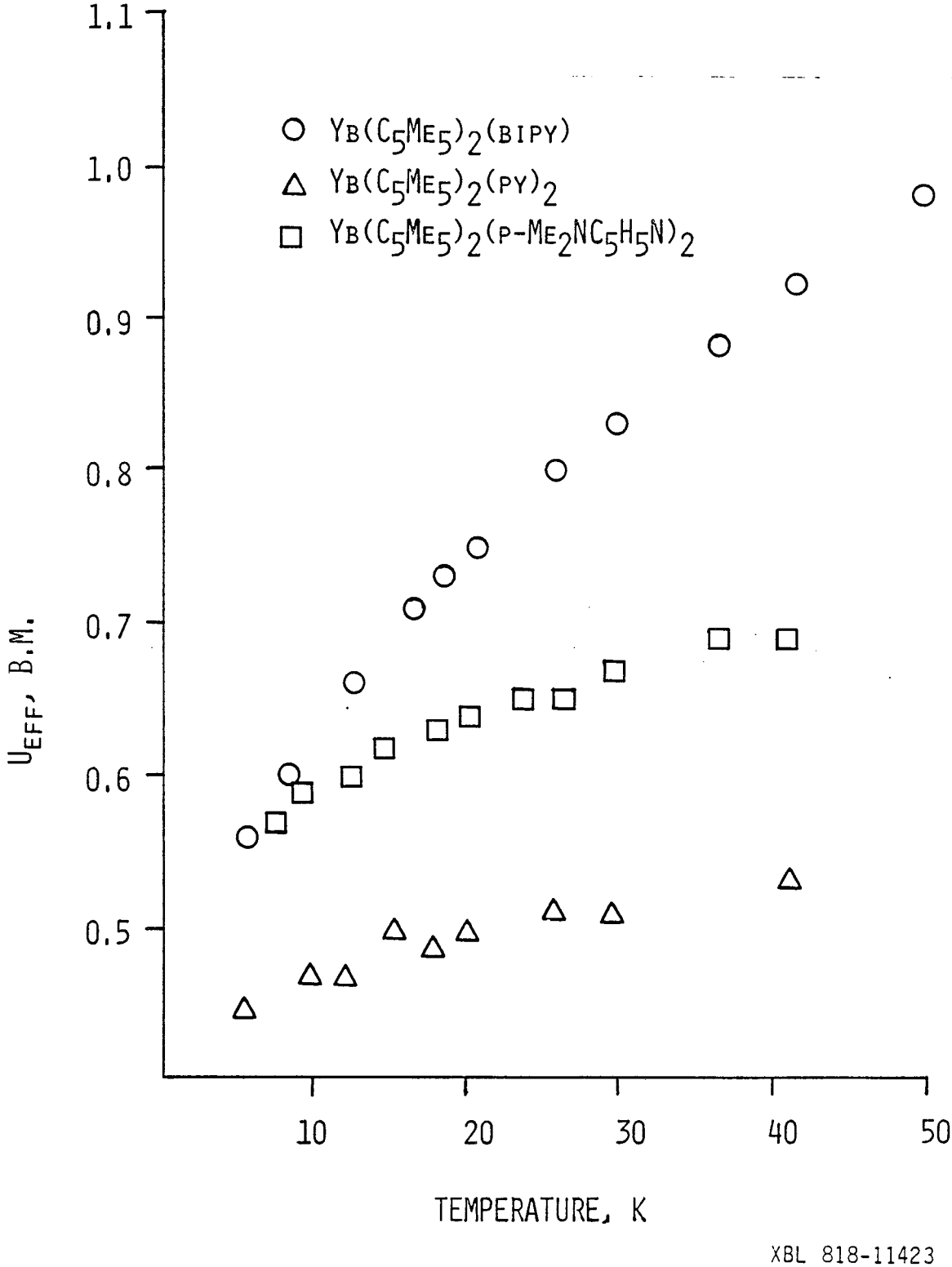
resonances due to the C_5Me_5 group were the only resonances observed in the $^{13}C\{^1H\}$ spectrum. The ring and methyl carbon resonances, which were assigned from the coupled spectrum, were shifted upfield to -42.2 and -3.35 ppm, respectively.

These NMR data suggest that $Yb(C_5Me_5)_2(bipy)$ is paramagnetic. This is substantiated by the effective magnetic moment, 2.4 B.M. (30°C, C_6H_6), measured by the Evans method. This moment is much lower than the value of ca. 4.5 B.M. expected for ytterbium(III) at 30°C [9]. The most straightforward explanation for the magnetic behavior is that the reducing ytterbium(II) ion has transferred some electron density to the π-system of the bipyridine ligand. If bipy accepts an electron to generate the bipy radical anion, $bipy^{\cdot-}$, two unpaired electrons would result--one on the metal (now ytterbium(III), f^{13}) and one on bipy . The two unpaired electrons must then be interacting antiferromagnetically, since the observed moment is much less than that expected for two unpaired electrons. This type of intramolecular antiferromagnetic exchange has been postulated for the compounds $Yb(bipy)_4$ (μ_{eff} = 2.79 B.M. at 34°C), $Yb(o\text{-phen})_4$ (μ_{eff} = 2.78 B.M. at 34°C) and $Eu(bipy)_4$ (μ_{eff} = 5.74 B.M. at 34°C) [19]. As with these binary compounds, a simple bonding explanation for $Yb(C_5Me_5)_2(bipy)$ is not possible, since the valence 4f electrons are well-shielded from ligand orbitals by the $5S^25p^6$ shell. It is difficult to ascertain whether promotion of a 4f electron to a 5d orbital to generate a more covalent bonding interaction with the unpaired bipy electron is energetically feasible. A similar situation exists for $Cp_2Ti(bipy)$,

in which weak paramagnetism can be explained in terms of a thermally accessible triplet system, $Cp_2Ti(III)(bipy^{\cdot-})$ [20]. This triplet state lies just above a singlet ground state in energy, so that both states contribute to observed magnetic moments at temperatures above -196°C. Values reported for the reduction of free bipyridine range from -1.30 to -1.87 V, depending on the solvent [25]. Since the oxidation potential of Yb(II) is only about 1.1 V, it appears as though coordination of bipyridine to the Yb(II) ion must promote the electron transfer.

The low-temperature susceptibility data for $Yb(C_5Me_5)_2(bipy)$, $Yb(C_5Me_5)_2(py)_2$ and $Yb(C_5Me_5)_2(p\text{-}Me_2NC_5H_5N)_2$, plotted as μ_{eff} vs. temperature, are presented in Figure 3. All three compounds show very weak paramagnetism, with effective magnetic moments ranging from 0.56 to 0.98 B.M. for $Yb(C_5Me_5)_2(bipy)$, 0.45 to 0.53 B.M. for $Yb(C_5Me_5)_2(py)_2$ and 0.57 to 0.69 B.M. for $Yb(C_5Me_5)_2(p\text{-}Me_2NC_5H_5N)_2$. Unfortunately, the errors in these values are very large (25-50 percent), since the values measured approach the sensitivity of the magnetometer. Therefore, the observed magnetic behavior might be due to small amounts of trivalent impurities. However, this seems unlikely, since the $Yb(C_5Me_5)_2(thf)$ complex, of comparable air-sensitivity, showed the expected negative values for diamagnetism over the same temperature range, when manipulations and measurements were conducted in a similar manner. The europium(II) complex $Eu(C_5Me_5)_2(bipy)$ shows perfectly normal magnetic behavior from 5-60K, following Curie behavior with an effective moment of 7.73 B.M. (C = 7.41).

Figure 3. Effective magnetic moments a a function of temperature for $Yb(C_5Me_5)_2(bipy)$, $Yb(C_5Me_5)_2(py)_2$ and $Yb(C_5Me_5)_2$-$(p\text{-}Me_2NC_5H_5N)_2$.



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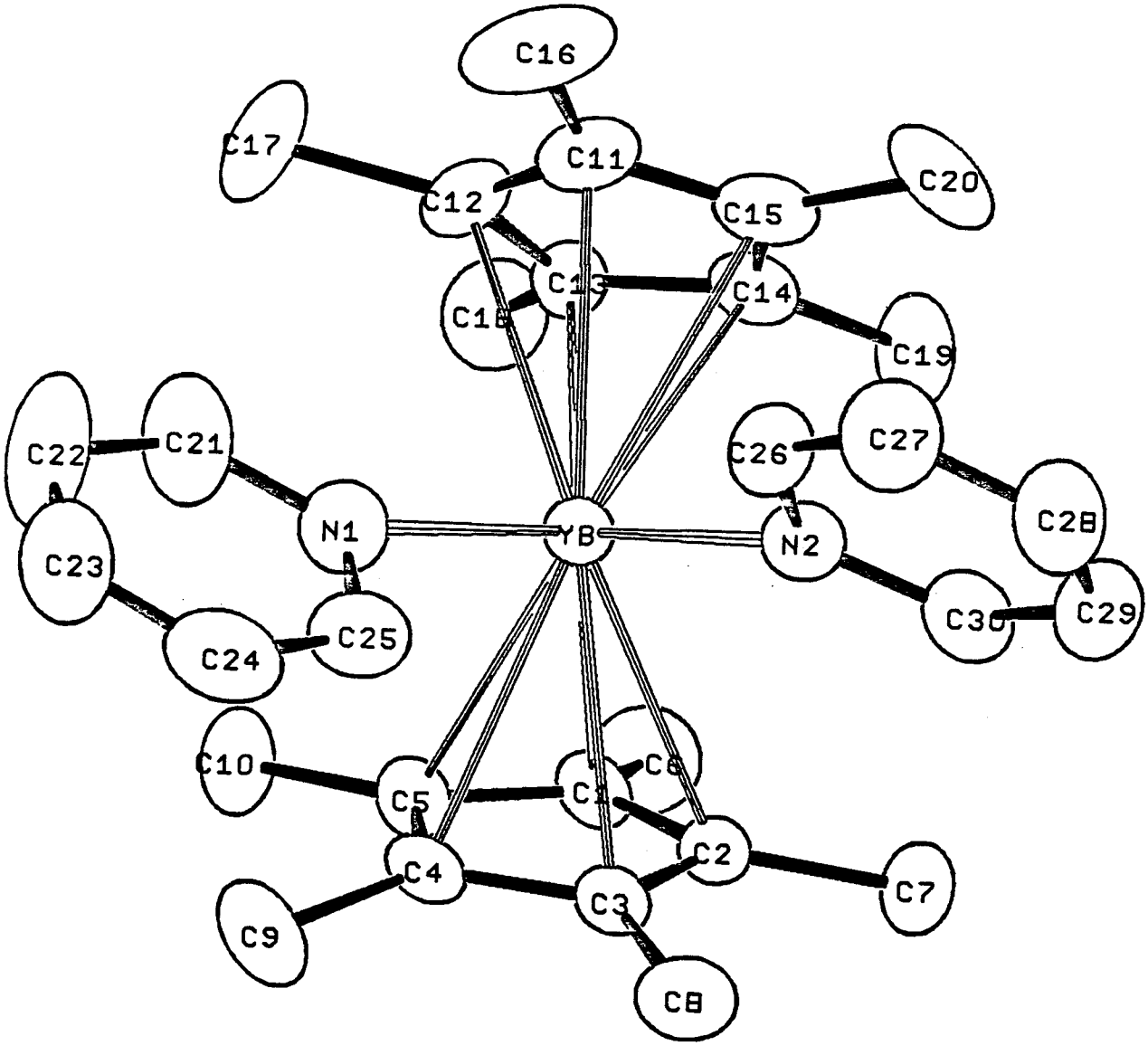
A more complete description of the electronic structure of these aromatic amine coordination complexes must wait for more detailed measurements of their electronic properties. Of most importance are a more accurate μ_{eff} vs. temperature study over a wide temperature range, epr investigations and a single crystal X-ray structure determination. These studies are now in progress [21].

Whatever is responsible for the observed moments, it seems clear that the ytterbium(II) center is pushing electron density onto the heterocycle, nitrogen ligand. This raises the possibility of interactions of the base-free complex, $Yb(C_5Me_5)_2$, with softer ligands giving weaker donor but stronger acceptor properties (i.e., CO, olefins and acetylenes), and, in light of the tendency of ytterbium(II) to coordinate hydrocarbons, the potential use of $Yb(C_5Me_5)_2$ in activating such ligands. The $Yb(C_5Me_5)_2$ unit seems to be exhibiting dual properties in terms of its electron affinity. It is clearly quite electron-donating toward some substrates, as will be discussed further in Chapter 6, and in this sense electron rich. However, its strong affinity for hard Lewis bases, such as diethyl ether and tetrahydrofuran, make it appear electron poor, and willing to accept electron density.

An X-ray structure has been determined for $Yb(C_5Me_5)_2(py)_2$ [22]. This compound crystallizes from toluene as well-separated monomeric units in the monoclinic system $P2_1/c$, with $Z = 4$. Figure 4 shows the distorted tetrahedral array of the ligands about ytterbium, with approximate C_2 symmetry. The angles about the coordination sphere are: N(1)-Yb-N(2) = 82.5(2)°, N(1)-Yb-C_5Me_5 centroid(1) =

Figure 4. ORTEP view of $Yb(C_5Me_5)_2(py)$.



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103.6(2)°, N(1)-Yb-C_5Me_5 centroid(2) = 111.5(3)° and centroid(1)-Yb-centroid(2) = 107.7(3)°.

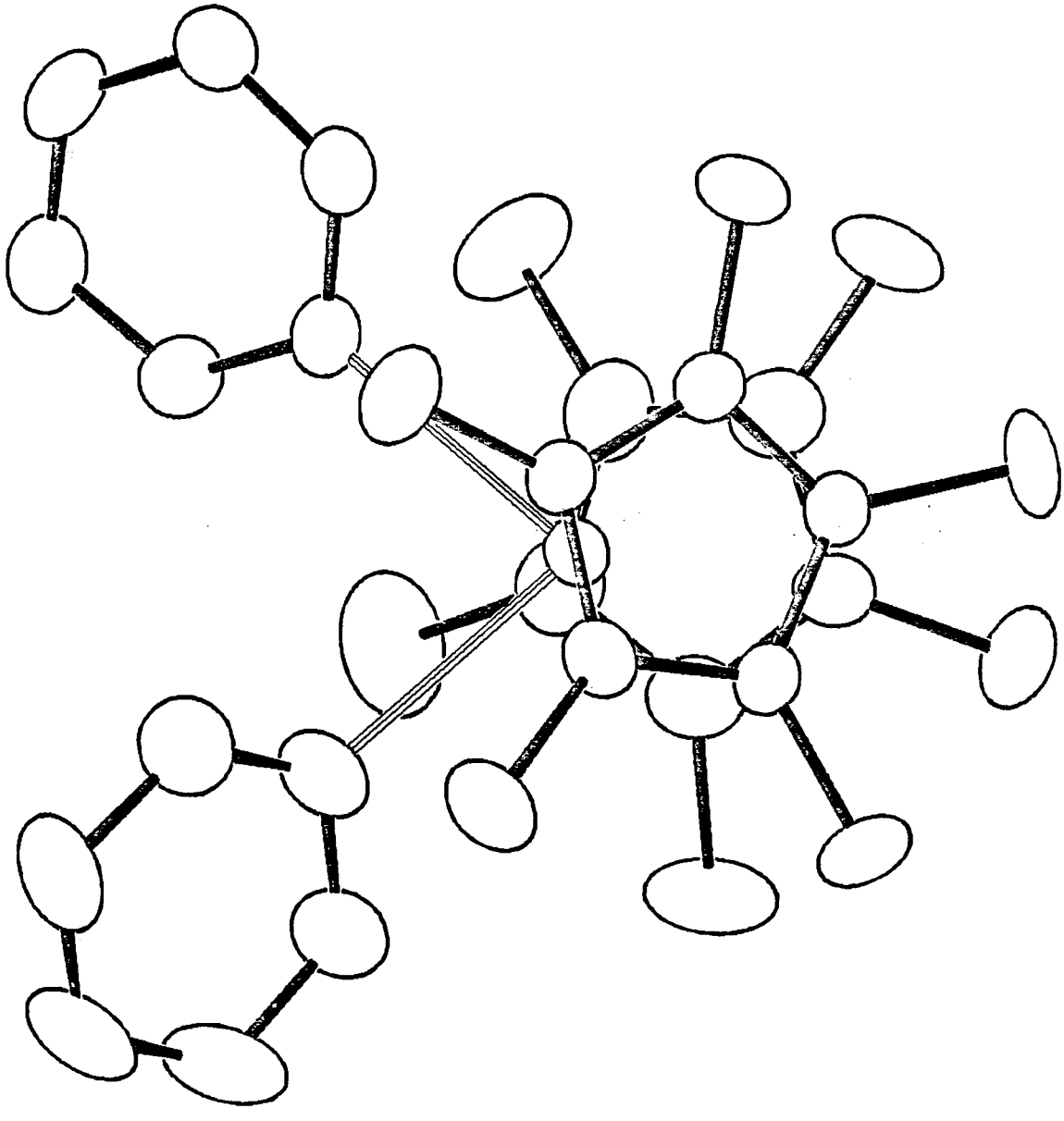
The average ytterbium-carbon distance is 2.74 ± 0.04 Å, somewhat longer than the corresponding distance in $Yb(C_5Me_5)_2(thf)$ (2.66 ± 0.02 Å) due to the increase in coordination number. The Yb-N(1) and Yb-N(2) distances are 2.586(7) and 2.544(6) Å, respectively. If one subtracts the ionic radius of eight-coordinate ytterbium(II), 1.14 Å [15], from the Yb-N distances, one obtains 1.45 and 1.40 Å for the ionic radii of the pyridine nitrogen atoms. A value of 1.40 Å can be calculated from the structure of the eight-coordinate bis(pyridine) tris(2,2,6,6-tetramethylheptane-3,5-dionato) europium(III) [23]. The bond distances therefore reflect ionic coordination about a ytterbium(II) center. Bond distances within the pyridine and C_5Me_5 rings are also normal.

The displacements of the methyl carbon atoms from the planes of their respective C_5 rings are greater than in $Yb(C_5Me_5)_2(thf)$, ranging from 0.13 to 0.31 Å. This is a result of more steric crowding in $Yb(C_5Me_5)_2(py)_2$, which has a higher coordination number. A view of the staggered C_5Me_5 rings is shown in Figure 5.

Phosphine Complexes

In toluene, the divalent $Ln(C_5Me_5)_2(OEt_2)$ species do not form isolable phosphine coordination complexes with the monodentate phosphines PMe_3 or $P(n\text{-}Bu)_3$, or with the bidentate 1,2-diphenylphosphinoethane. The chelating phosphines 1,2-dimethylphosphinoethane (dmpe) and 1,2-dimethylphosphinomethane (dmpm), however, do give isoluble complexes. Reaction of the diethyl ether complexes with one

Figure 5. View of $Yb(C_5Me_5)_2(py)_2$ down the centers of the C_5Me_5 rings.



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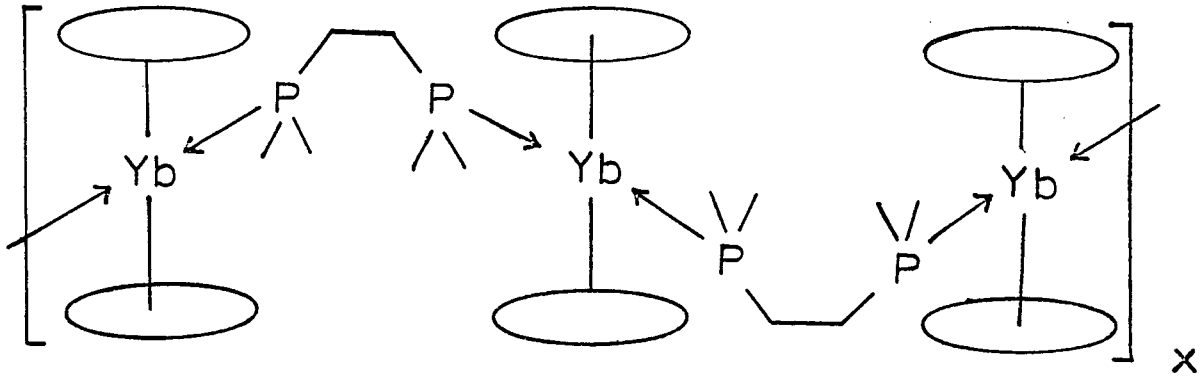
molar equivalent of dmpe in toluene results in precipitation of an insoluble substance having the stoichiometry $Ln(C_5Me_5)_2(dmpe)$, where Ln = Eu or Yb. Hydrolysis of the europium derivative in benzene gives a 2:1 mixture of pentamethylcyclopentadiene and dmpe (by ^1H NMR). The $^{31}P\{^1H\}$ NMR spectrum of the hydrolysate shows that free dmpe is the only phosphine-containing product. The europium and ytterbium compounds have identical infrared spectra and similar melting points, suggesting similar structures. Their exceedingly low solubilities in hydrocarbons indicates a polymeric structure such as:



The dmpe complexes are slightly soluble in diethyl ether, from which microcrystalline samples may be obtained. Addition of tetrahydrofuran results in immediate formation of the $Ln(C_5Me_5)_2(thf)$.

Addition of dmpm to $Ln(C_5Me_5)_2(OEt_2)$ (Ln = Eu, Yb) in toluene results in formation of the red $Eu(C_5Me_5)_2(dmpm)$ or the dark green $Yb(C_5Me_5)_2(dmpm)$. These complexes appear to be isostructural since they have superimposable infrareds and indentical melting points. They are soluble in toluene, from which they can be

crystallized, though attempts to crystallize the dmpm complexes from diethyl ether yielded only the diethyl ether complexes. Therefore, in the presence of excess ether, the dmpm ligand is completely exchanged.

Normal, diamagnetic chemical shifts are observed in the ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of $Yb(C_5Me_5)_2(dmpm)$. Coordination of dmpm to ytterbium results in a downfield shift of ca. 16 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum, from δ -55.7 [24] for the free ligand to δ - 39.6. None of the chelating phosphine complexes of $Eu(C_5Me_5)_2$ or $Yb(C_5Me_5)_2$ gave molecular ions in their mass spectra.

In forming coordination complexes with the divalent $Ln(C_5Me_5)_2$ (Ln = Eu, Yb), chelating alkyl phosphines appear to act as better bases toward $Ln(C_5Me_5)_2$ than does diethyl ether. In contrast to the divalent $Ln[N(SiMe_3)_2]_2$ units, the $Ln(C_5Me_5)_2$ do not form complexes with $P(n\text{-}Bu)_3$ from their diethyl ether complexes. Ligand exchange reactions indicate the following ordering of basicities toward $Yb(C_5Me_5)_2$: bipyridine, pyridine > tetrahydrofuran > methyl vinyl ether, dmpe, dmpm > diethyl ether.

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CHAPTER 6

REACTION CHEMISTRY OF THE DIVALENT PENTAMETHYLCYCLOPENTADIENYL LANTHANIDES

Reactions with Lewis and Protic Acids

Having prepared toluene-soluble, monomeric derivatives of ytterbium(II) and europium(II), we could begin to explore the simple reaction chemistry of these low-valent compounds. In toluene, the ytterbium(II) diethyl ether complex, $Yb(C_5Me_5)_2(OEt_2)$, does not react with the unsaturated molecules carbon monoxide (15 atm), propene (2 atm) or diphenylacetylene (1:1 in refluxing toluene). There is also no observable reaction between $Yb(C_5Me_5)_2(OEt_2)$ and D_2 (16 atm) in toluene. This may mean that these molecules simply do not compete well with diethyl ether for a coordination site at ytterbium. As we have seen, tri(n-butyl)phosphine, a stronger donor than carbon monoxide, an olefin or an alkyne, does not displace diethyl ether from $Yb(C_5Me_5)_2(OEt_2)$ (see Chapter 5).

The ether complex $Yb(C_5Me_5)_2(OEt_2)$ reacts with sodium bis(trimethylsilyl)amide to form a simple coordination complex, $[Na(OEt_2)][Yb(C_5Me_5)_2N(SiMe_3)_2]$, after crystallization from diethyl ether. This green sodium salt is completely insoluble in toluene, but can be crystallized from diethyl ether. The presence of only one molar equivalent of diethyl ether suggests that the sodium ion may be coordinated to the nitrogen atom of the $N(SiMe_3)_2$ ligand and/or a methyl group (cf. $NaEu[N(SiMe_3)_2]_3$, Chapter 3). The amine, $HN(SiMe_3)_2$, does not react with $Yb(C_5Me_5)_2(OEt_2)$ in tetrahydrofuran nor in refluxing toluene.

Dornberger, et. al. have shown that one cyclopentadienyl ligand can be removed from $YbCp_3$ and $SmCp_3$ by protonation with NH_4Cl to yield the chloro-species $YbCp_2Cl$ and $SmCp_2Cl$, respectively [1]. Fischer and Bielany have shown that this type of reaction is more general in using a variety of protic acids HX to obtain the mixed-ligand species $[Cp_{3-n}LnX_n]_x$ [2]. Of particular interest are reactions in which the acids used were weaker than cyclopentadiene (pKa $\approx$ 15). Thus, ammonia (pKa $\approx$ 33) was used to obtain $[Cp_2YbNH_2]_x$, and terminal alkynes (pKa $\approx$ 20-21) yielded $[Cp_2LnC_2R]_x$. The latter reaction seems to contradict the claims that $SmCp_3$ only catalyzes the trimerization of phenylacetylene [3], and that $NdCp_3$ induces a small paramagnetic shift in the ^1H NMR spectrum of phenylacetylene due to formation of the adduct $Cp_3Nd{\cdot}HC_2Ph$ [4].

Since the inductive effect of the methyl groups should increase the basicity of the pentamethylcyclopentadienide anion relative to that of the cyclopentadienide anion, it appeared that protonation of the C_5Me_5 ligands in lanthanide compounds would be even more favorable. Upon reaction of $Yb(C_5Me_5)_2(thf)$ with one molar equivalent of NH_4Cl in tetrahydrofuran, a yellow solid precipitated, which gave an elemental analysis consistent with the formulation $YbCl_2(thf)_2$. Only absorptions due to tetrahydrofuran were observed in the infrared spectrum. The known mono-tetrahydrofuran complex $YbCl_2(thf)$ is also yellow [5]. The $Yb(C_5Me_5)_2(thf)$ starting material was isolated from the tetrahydrofuran solution. The yields of $YbCl_2(thf)_2$ and starting material indicate that the NH_4Cl reacted with only one-half

an equivalent of $Yb(C_5Me_5)_2(thf)$. Some unsuccessful reactions of $Yb(C_5Me_5)_2(OEt_2)$ and $Eu(C_5Me_5)_2(thf)$ with organic acids are described in the experimental section (Chapter 2).

One molar equivalent of phenylacetylene reacts with the ether complex $Yb(C_5Me_5)_2(OEt_2)$ to give a red, pentane-soluble compound of stoichiometry $[Yb(C_5Me_5)C_2Ph)]_x$. The presence of the alkynyl ligand is indicated by an infrared absorption, $\nu(C\equiv C)$, at 2040 cm^{-1}. This compound is undoubtedly associated since the mass spectrum contains peaks due to $Yb_2(C_5Me_5)_3(C_2Ph)_2$, $Yb_2(C_5Me_5)_2(C_2Ph)_2$, $Yb_2(C_5Me_5)(C_2Ph)_2$, $Yb_2(C_5Me_5)(C_2Ph)$ and $Yb(C_5Me_5)(C_2Ph)$ ions.

The ^1H NMR spectrum of $[Yb(C_5Me_5)(C_2Ph)]_x$ also shows the presence of C_5Me_5 and phenylacetylide in a 1:1 molar ratio. However, the resonances have been shifted downfield and broadened (see Experimental Section), implying the presence of a paramagnetic molecule. It is very difficult to rationalize this observation, except to suggest the presence of another small-mass ligand that could account for a trivalent oxidation state, such as hydrogen or oxygen. However, this would seem to be inconsistent with the mass spectral results. Clearly further work is required to clarify the molecular structure of this unusual complex.

It is interesting tnat this compound is isolated ether-free. The alkynyl ligand, which probably bridges ytterbium centers through one carbon atom, or in a $\sigma-\pi$ fashion (cf. $[CuC_2Ph]_x$ [6]), is a better donor ligand than diethyl ether. A more dramatic example of the base strength of an alkynyl group as a ligand toward ytterbium(II) is found

in the base-free $[Yb(C_2Ph)_2]_x$, which can be crystallized from tetrahydrofuran [7]. We have seen that neutral, sp^3-hybridized carbon atoms can serve as donor ligands to divalent europium and ytterbium (Chapters 3 and 5). It is not surprising, then, that the more electronegative sp-hybridized carbon atoms will form stronger bonds to a lanthanide metal. The compounds Cp_2LnC_2R (Ln = Gd, Ho, Er and Yb [8]; R = Ph and Ln = Er; R = Ph and t-Bu [9]) and $CpHo(C_2Ph)$ [8], are probably associated as well. The mode of bridge-bonding in all of the above lanthanide alkynyl complexes is similar, since the $\nu(C\equiv C)$ stretching frequencies fall in the same region, 2040-2050 cm^{-1}.

Reactions with Oxidizing Agents

In dichloromethane, the divalent compound $Yb(C_5Me_5)_2(thf)$ is readily oxidized to the mono-chloro species $Yb(C_5Me_5)_2Cl(thf)$. Formally, this reaction represents transfer of a chlorine radical, $Cl^{\bullet}$, from dichloromethane to ytterbium(II) in a one-electron oxidative addition. In contrast, the europium(II) compound $Eu(C_5Me_5)_2(thf)$ does not react with dichloromethane. This is consistent with the greater stability of the divalent oxidation state for europium.

A more convenient route to the mono-chloro species $Yb(C_5Me_5)_2Cl(thf)$ is by reaction of $Yb(C_5Me_5)_2(thf)$ with one molar equivalent of ytterbium trichloride in toluene. This type of reaction has also provided a route to a trivalent complex of 1,2-dimethylphosphinomethane, $Yb(C_5Me_5)_2Cl(dmpm)$, by the reaction of $Yb(C_5Me_5)_2(dmpm)$ with $YbCl_3$ in toluene. This purple,

crystalline compound has an effective magnetic moment of 4.4 B.M. (by Evans' method). It is of interest to determine the mode of coordination of dmpm to the $Yb(C_5Me_5)_2Cl$ unit, as the nine-coordinate complex would seem to be severely sterically hindered. A single-crystal X-ray diffraction study is in progress [10].

If general, one-electron oxidative additions to ytterbium(II) could provide routes to numerous trivalent derivatives. It is reasonable to expect formation of ytterbium-carbon bonds by oxidative addition of an organic radical to ytterbium(II). However, the compounds $HCPh_3$ and $HgPh_2$, both potential sources of radicals, did not react with $Yb(C_5Me_5)_2(OEt_2)$ in refluxing toluene.

One-electron oxidative additions can also be carried out with silver(I) salts. In toluene, silver iodide reacts with $Yb(C_5Me_5)_2(thf)$ to give the purple, mono-iodo complex $Yb(C_5Me_5)_2I(thf)$. The infrared spectrum of this compound is identical to that for $Yb(C_5Me_5)_2Cl(thf)$, except for the presence of a metal-chlorine stretching frequency at 253 cm^{-1} in the spectrum of the latter compound.

Adding one molar equivalent of silver trifluoroacetate in toluene to $Yb(C_5Me_5)_2(OEt_2)$ generates the trivalent $[Yb(C_5Me_5)_2(O_2CCF_3)]_2$, which was also prepared from $[Yb(C_5Me_5)_2Cl_2]^-$ and NaO_2CCF_3 (see Chapter 4).

A one-electron oxidation of $Yb(C_5Me_5)_2(dme)$ to the cationic complex $[Yb(C_5Me_5)_2(dme)][PF_6]$ with $[FeCp_2][PF_6]$ has been reported by Watson [11].

Attempts to oxidize the divalent $Eu(C_5Me_5)_2(thf)$ did not lead to isolation of a trivalent product, but to loss of the C_5Me_5 rings. Reaction of $Eu(C_5Me_5)_2(thf)(OEt_2)$ with one-half molar equivalent of I_2 in diethyl ether led to isolation of $EuI_2(thf)_2$ after crystallization from tetrahydrofuran. Allyl bromide or trimethylchlorosilane (one molar equivalent) react with $Eu(C_5Me_5)_2(thf)(OEt_2)$ to generate yellow insoluble precipitates. The reaction with allyl bromide proceeded through a blue species (in diethyl ether) that persisted for approximately 20 minutes at room temperature. Approximately one-half of the $Eu(C_5Me_5)_2(thf)(OEt_2)$ starting material was isolated from these reaction mixtures. The yellow precipitates show only bands due to tetrahydrofuran in the infrared spectrum, and contain halide ($AgNO_3$ test). Therefore, they are most likely $EuBr_2(thf)_x$ and $EuCl_2(thf)_x$, respectively.

In a similar fashion, silver trifluoroacetate (one molar equivalent) reacts with $Eu(C_5Me_5)_2(thf)(OEt_2)$ to give a tetrahydrofuran-soluble product that contains no C_5Me_5 ligands (by infrared spectroscopy), and gives an elemental analysis consistent with $Eu(CO_2CCF_3)_2(thf)_2$.

The 1:1 reactions of $Eu(C_5Me_5)_2(thf)(OEt_2)$ with $CHCl_3$ or $EuCl_3$ led to blue solutions which deposited green, insoluble solids after approximately 5 minutes. If the reaction with $CHCl_3$ is carried out at 0°C for 10 minutes, a blue solid may be isolated by removal of the diethyl ether solvent under reduced pressure. Minute quantities of this blue compound were crystallized from pentane at -10°C. The

blue prisms contained chlorine (by $AgNO_3$ test). Unfortunately, the small quantites isolated precludes proper characterization.

The blue species that results from attempted oxidation of $Eu(C_5Me_5)_2(thf)(OEt_2)$ appear to be rather unstable compounds, possibly a divalent $Eu(C_5Me_5)Cl$ or a trivalent $Eu(C_5Me_5)_2Cl$ species, which disproportionates or decomposes to other products. Since the only products isolated from these attempted oxidations are divalent, it would appear that the europium(III) oxidation state is unstable in the presence of the pentamethylcyclopentadienide anion. In support of this, a mono-ring derivative of stoichiometry $[Eu(C_5Me_5)(thf)_3][PF_6]$ can be obtained from the reaction of $Eu(C_5Me_5)_2(thf)(OEt_2)$ with $[FeCp_2][PF_6]$. Therefore, rather than oxidize the divalent metal species to a trivalent compound, as in the case for ytterbium, an electron is transferred from the C_5Me_5 anion to $[FeCp_2][PF_6]$, generating ferrocene. The oxidation state of $[Eu(C_5Me_5)(thf)_3][PF_6]$ was established by a low-temperature (5-40 K) magnetic susceptibility study, which showed the compound to have an effective magnetic moment of 7.52 B.M., with C = 7.02.

Reactions with Transition Metal Carbonyl Compounds

The observation that $Yb(C_5Me_5)_2(thf)$ is readily oxidized to the trivalent species $Yb(C_5Me_5)_2Cl(thf)$ suggested that the divalent metallocene might be able to reduce low-valent transition metal compounds. Zero-valent, transition metal carbonyl compounds, being readily available, were therefore chosen as substrates. These compounds seemed to offer the possibility of reaction with the zero-valent metal center and/or a carbonyl ligand.

By varying reaction stoichiometries, it was discovered that $Yb(C_5Me_5)_2(OEt)$ reacted with $Co_2(CO)_8$ in a 2:1 molar ratio, generating a blue solid that could be crystallized from tetrahydrofuran/pentane mixtures as well-formed prisms. This compound is paramagnetic (μ_{eff} = 4.1 B.M. at 30°C in benzene, by Evans' method), indicating an oxidation from ytterbium(II) to ytterbium(III). The ^1H NMR spectrum showed a broad singlet ($\nu_{1/2}$ = 43 Hz) at δ 8.36 due to C_5Me_5 protons. The elemental analysis was consistent with the formulation $[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$, implying that the Co-Co bond had been broken by a one-electron reduction from Co(0) to Co(-I). The tetracarbonylcobaltate anion can also be generated using sodium amalgam [12] or thallium metal [13] as the reducing agent. The infrared spectrum (ν(CO) = 2023 s, 1973 w, 1939 s, 1917 s, 1823 w, 1708 w sh, and 1761 s cm^{-1}) shows significantly lowered carbonyl stretching frequencies relative to $[Et_3NH][Co(CO)_4]$ [14], which could indicate isocarbonyl bonding.

In order to elucidate the structure of this novel compound, a single crystal X-ray study was undertaken [15]. Crystals of $[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$ are triclinic, $P\bar{1}$, with Z = 2. Two views of the compound (Figures 1 and 2) show the presence of a Yb-O-C-Co isocarbonyl linkage (<Yb-O(1)-C(21) = 163.0(2)° and <Co-C(21)-O(1) = 177.8(2)°). There is a significant difference (0.05 Å) between the average C-O(terminal) bond length (1.14 ± 0.02 Å) and the C-O(iso) bond length of 1.183(3) Å. This, in addition to the lowered carbonyl stretching frequencies, implies a weakening of the

Figure 1. ORTEP drawing of $[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$.

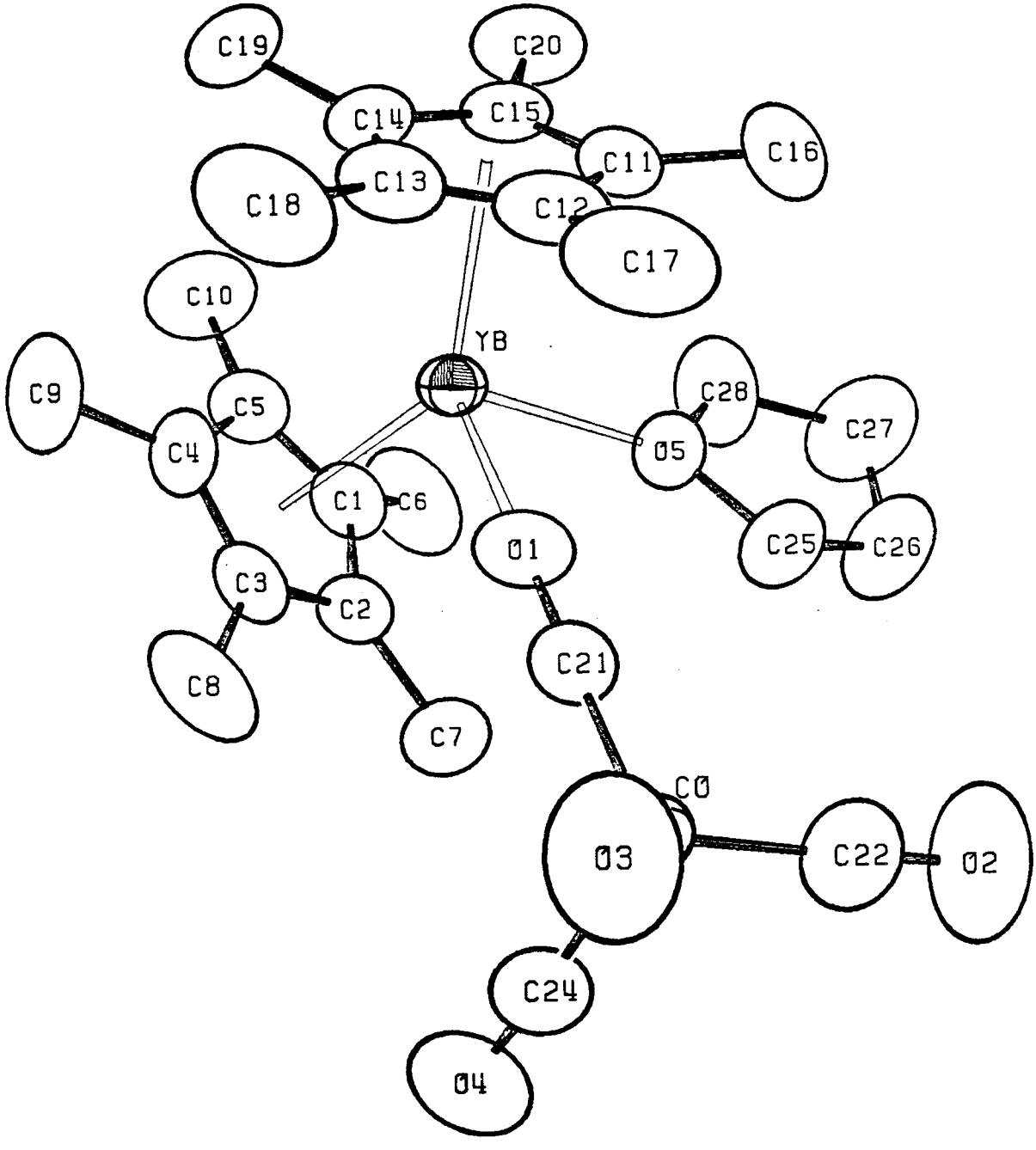
C19
C20
C14
C15
C11
C16
C18
C13
C12
C17
C10
YB
C9
C5
C28
C27
C4
05
C1
C6
C25
C26
01
C3
C2
C21
C8
C7
C0
03
C22
02
C24
04

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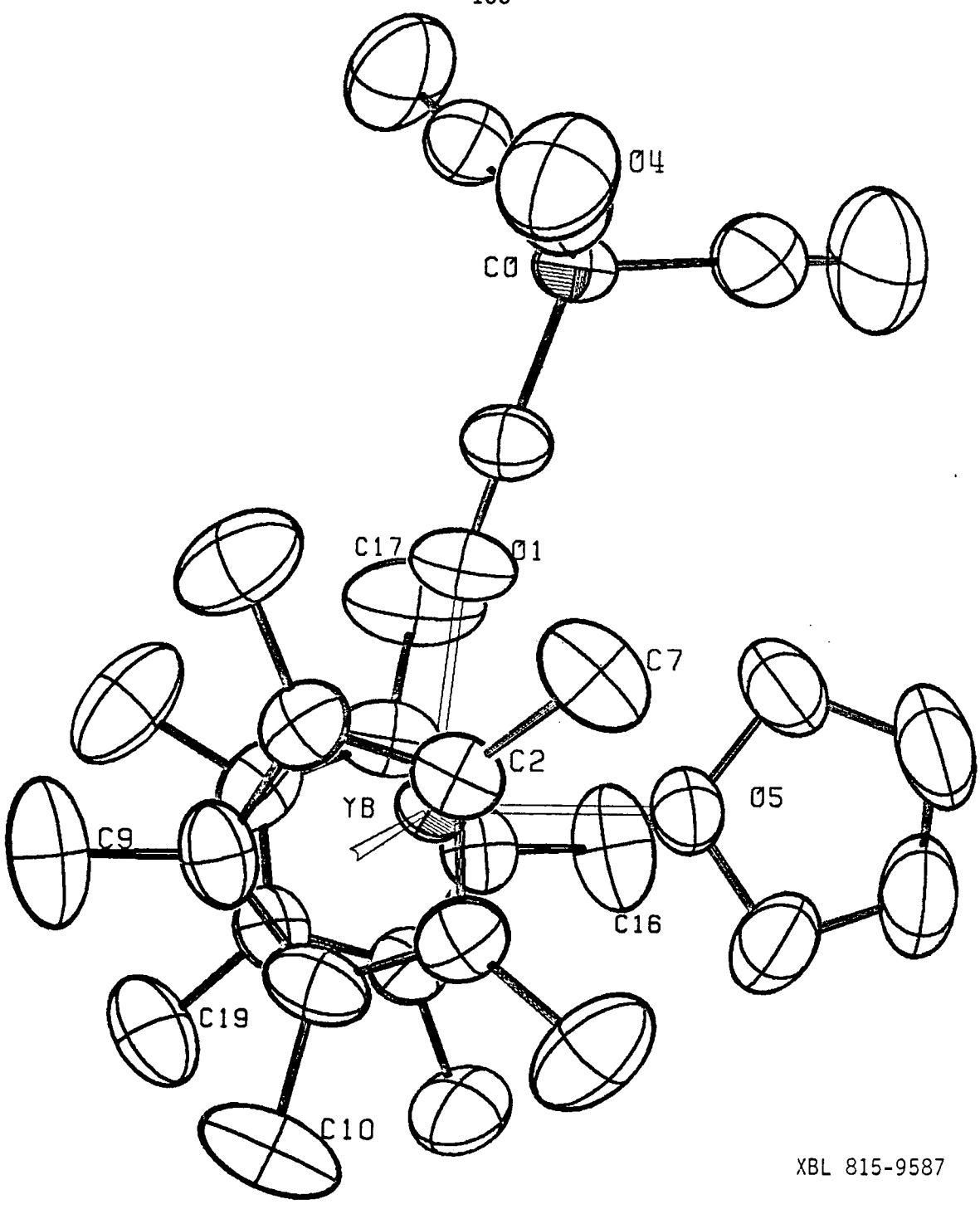
Figure 2. View of $[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$ through the C_5Me_5 ring centers.



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C-O bond upon coordination of the Lewis acid center $Yb(C_5Me_5)_2(thf)^+$. Such carbonyl 'activation' in transition metal compounds has been extensively investigated by Shriver, who has utilized group IIIA Lewis acids [16]. In concert with a lengthening of the C-O(iso) bond, the Co-C(iso) bond appears to be strengthened by this interaction; the difference between the average Co-C(terminal) bond length (1.77 ± 0.03 Å) and the Co-C(iso) bond length (1.699(3) Å) is 0.07 Å.

The ytterbium-oxygen(thf) bond (2.335(2) Å) is longer than that of the ytterbium-oxygen(CO) bond of 2.258(2) Å. This may be ascribed to the different coordination number (hybridization) of the two different types of oxygen atoms.

The average ytterbium-carbon bond length of 2.596(2) Å is similar to that found in the trivalent species $(C_5Me_5)_2Yb(S_2CNEt_2)$ (2.63(3) Å) of identical coordination number but significantly shorter than that found in the divalent species, $(C_5Me_5)_2Yb(py)_2$ (2.742(7) Å) of the same coordination number. These bond length changes are consistent with the view that the ytterbium atom in $[(C_5Me_5)_2Yb(thf)][Co(CO)_4]$ is trivalent, since Shannon suggests that the ionic radius of ytterbium(III) is ca. 0.16 Å smaller than that of ytterbium(III) [17].

The ytterbium atom is displaced 2.312(1) Å from the C(1)-C(5) ring plane, and 2.294(1) Å from the C(11)-C(15) ring plane. The displacements of the methyl carbons from their respective C_5 ring planes range from 0.31(2) to 0.66(4) Å away from ytterbium.

Other Lewis acid-transition metal isocarbonyl linkages have been structurally characterized, including $[Mg(py)_4][CpMo(CO)_3]_2$ [18],

$[(CO)_9Co_3CO]_2[CpTiCo(CO)_4]$ [19] and $[CpFe(COAlEt_3)_2]_2$ [20]. However, $[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$ is the first structurally characterized example of a lanthanide metal serving as the Lewis acid in an isocarbonyl linkage. The compound $SmCp_3$ has been shown to induce a shift of the carbonyl stretching frequencies in various binary transition metal carbonyls to lower frequency [21]. Crease and Legzdins [4] have reported the 2:1 adducts $(MeC_5H_4)Mn(CO)_3(LnCp_3)_2$, where Ln is Sm, Yb or Nd.

When crystallized from toluene, $[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$ looses tetrahydrofuran to produce $[Yb(C_5Me_5)_2][Co(CO)_4]$ (ν(CO): 2038 m, 1974 m, 1962 w sh, 1870 s, 1788 s, and 1739 s cm^{-1}). This implies that a second carbonyl ligand can readily displace tetrahydrofuran from the coordination sphere of ytterbium. This compound, as well as its thf complex, exhibit more carbonyl stretching bands than would be predicted for the lowest possible point group symmetries. A possible explanation for this observation is the existence of more than one isomer, or partial loss of thf (in nujol) in the case of the thf complex. However, note that this phenomenon is also observed for the other ytterbium-transition metal carbonyl complexes described here.

Because crystallographic and infrared data suggested an activation of the isocarbonyl C-O bond, $[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$ was exposed to hydrogen (18 atm) for 24 h in both toluene and tetrahydrofuran. However, only starting material was recovered from the reaction solutions. The reactivity of this isocarbonyl toward electrophiles and nucleophiles are of interest, but such reactions were not investigated.

Other transition metal carbonyl anions are also readily prepared from $Yb(C_5Me_5)_2(OEt_2)$. Molybdenum hexacarbonyl reacts with two molar equivalents of the divalent ytterbium compound to yield $[Yb(C_5Me_5)_2]_2[Mo(CO)_5]$. This compound can be crystallized from tetrahydrofuran without incorporation of tetrahydrofuran as a ligand, presumably because two isocarbonyl linkages per ytterbium are formed in a chelating fashion. Sodium [22] and lithium [23] salts of $Mo(CO_5)^{2-}$ have also been reported. The carbonyl stretching frequencies in $[Yb(C_5Me_5)_2]_2[Mo(CO)_5]$ are observed at 2009, 1920, 1903, 1882, 1632 and 1414(?) cm^{-1}. No reaction was observed between the divalent $Eu(C_5Me_5)_2(thf)$ and $Mo(CO)_6$ in toluene after 48 h.

In a similar fashion, $[Yb(C_5Me_5)_2(thf)]_2[Fe(CO)_4]$ can be prepared by reaction of $Fe(CO)_5$ and two molar equivalents of $Yb(C_5Me_5)_2(OEt_2)$ in toluene, followed by crystallization from tetrahydrofuran. Carbonyl stretching frequencies are observed at 2004 w, 1980 w, 1961 w, 1928 s, 1922 s, 1753 m sh, 1741 s, 1711 s, 1648 m sh and 1608 s br cm^{-1}. This blue, paramagnetic compound gives a single, broad resonance ($\nu_{1/2}$ = 144 Hz) in the ^1H NMR spectrum at δ 9.52. Reaction of $[Yb(C_5Me_5)_2(thf)]_2[Fe(CO)_4]$ with two molar equivalents of $SnPh_3Cl$ in tetrahydrofuran gives the known compound $Fe(CO)_4(SnPh_3)_2$ [24], and $Yb(C_5Me_5)_2Cl(thf)$.

The $Fe_3(CO)_{12}$ cluster may also be reduced by $Yb(C_5Me_5)_2(OEt_2)$. Reaction of two equivalents of $Yb(C_5Me_5)_2(OEt_2)$ with $Fe_3(CO)_{12}$ in toluene, or stoichiometric amounts of $Yb(C_5Me_5)_2(OEt_2)$ and $Fe_2(CO)_9$

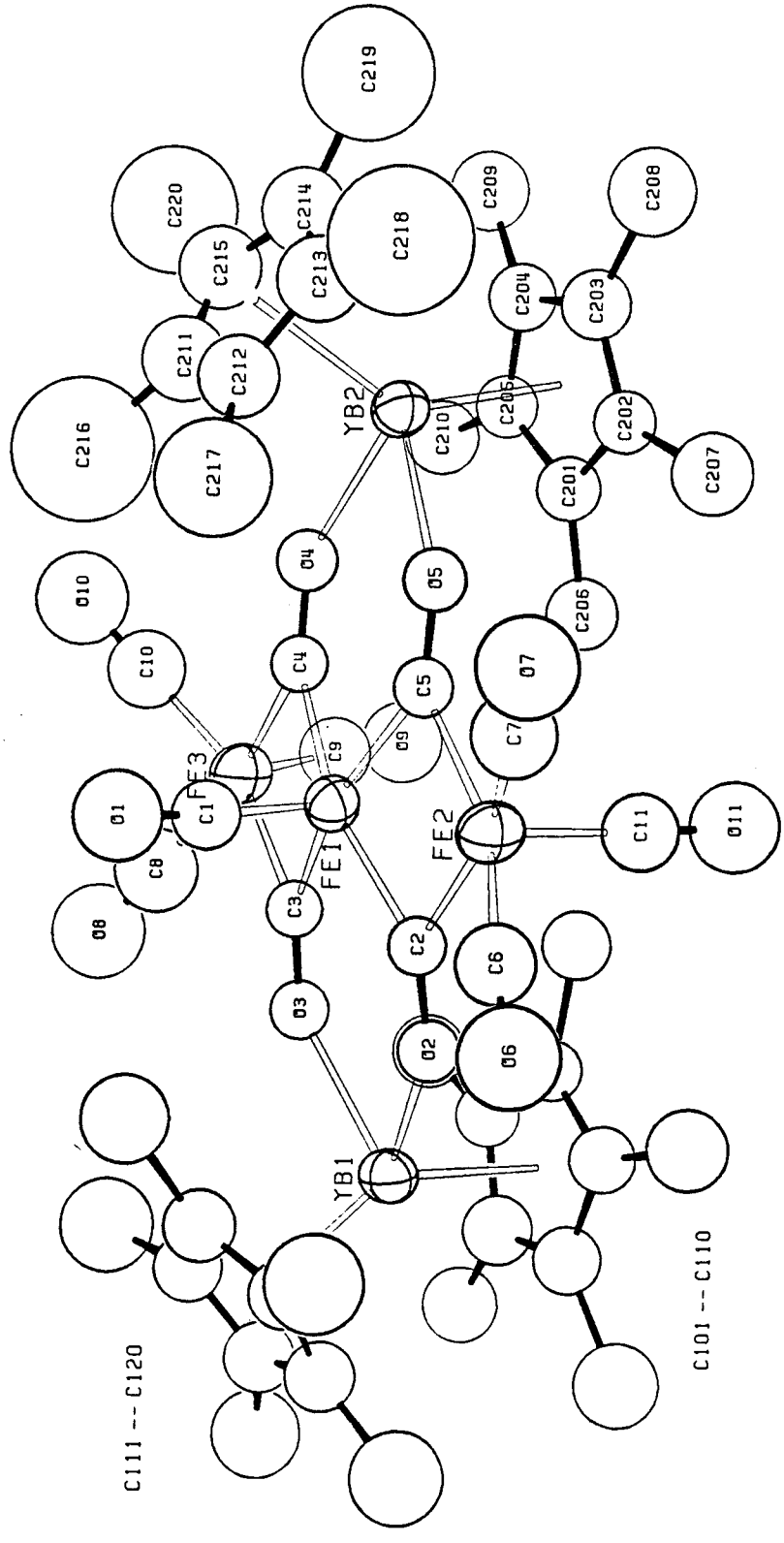
in toluene results in a dark red solution, from which violet prisms of $[Yb(C_5Me_5)_2]_2[Fe_3(CO)_{11}]$ can be crystallized. The infrared spectrum shows carbonyl stretching frequencies at 2048 w, 1998 s, 1973 s, 1667 w and 1604 s br cm^{-1}. The complex is paramagnetic (μ_{eff} = 3.91 B.M. per ytterbium; 5-60 K), and has two resonances ($\nu_{1/2}$ = 130 Hz) in the ^1H NMR spectrum at δ 8.09 and 6.11 for the inequivalent C_5Me_5 rings.

The structure was determined from an X-ray crystallographic study [25]. Of the three discrete molecules in the unit cell, two are well ordered and related by inversion (Figure 3), while the third is disordered about the center of inversion. The molecule possesses approximate C_{2V} symmetry about the Fe(1)-C(1) vector.

The two Fe-Fe distances of 2.524(1) and 2.538(1) Å are essentially identical, as are the four Yb-O distances [average 2.243(5) Å]. The average Yb-C bond length [2.573(13) Å] compares favorably with those observed in related eight-coordinate ytterbium(III) species (see below).

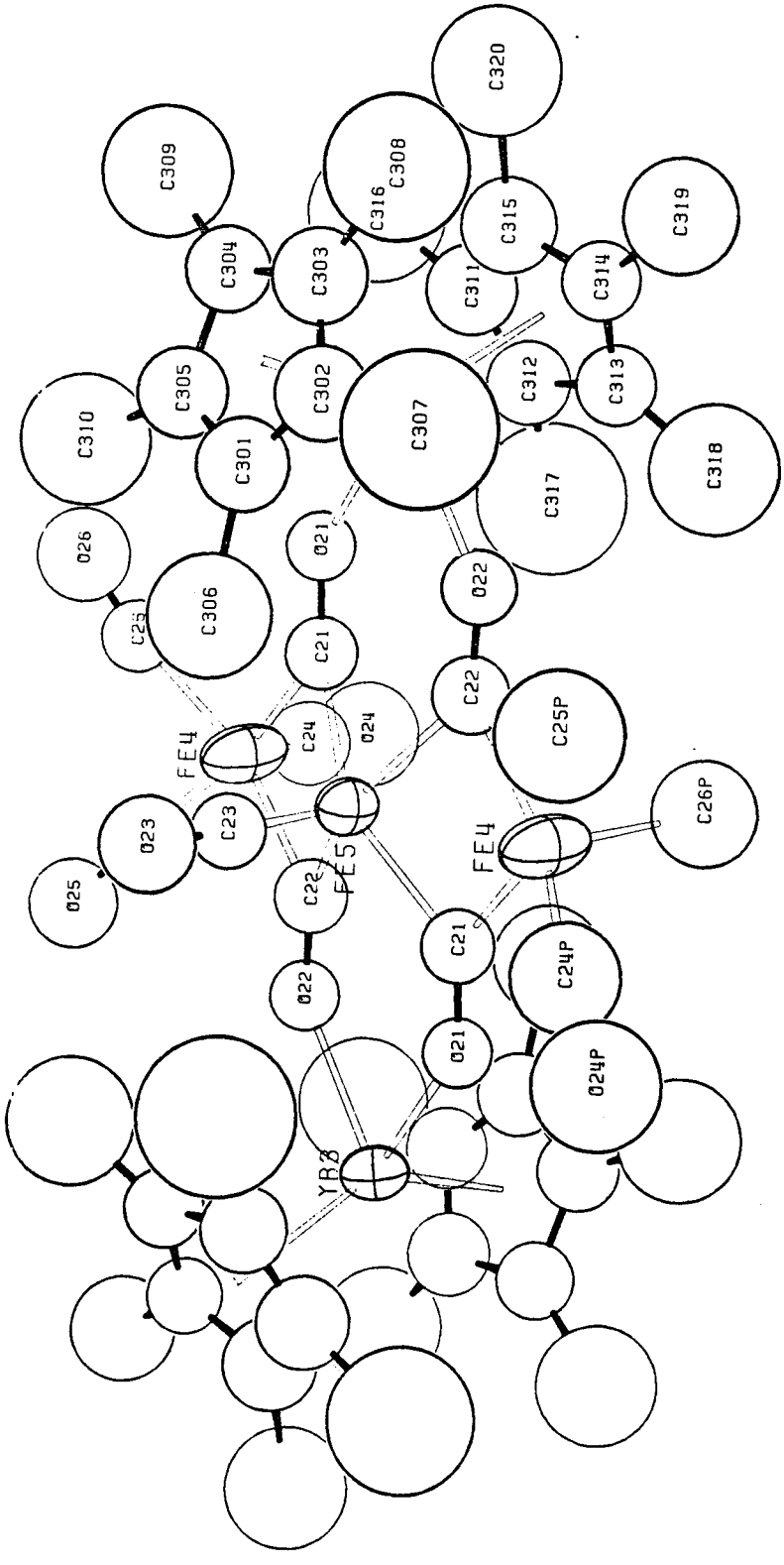
The Fe(2)-Fe(1)-Fe(3) angle is 161.8°; there is no direct interaction between Fe(2) and Fe(3). The two planes defined by the carbonyls bound to Yb(1) and Yb(2) are inclined with respect to each other with a dihedral angle of 168.1°, and bend away from the unique carbonyl ligand bonded to Fe(1). Thus, the overall shape of the cluster might be described as an inverted umbrella, the handle being the unique carbonyl bound to Fe(1). The least-squares plane defined by the bridging carbonyl carbons C(2), C(3), C(4) and C(5) is 0.36 Å below Fe(1) and above Yb(1) and Yb(2) by 0.56 and 0.48 Å, respectively.

Figure 3. ORTEP view of ordered $[Yb(C_5Me_5)_2][Fe_3(CO)_{11}]$ molecule.


C219
C220
C214
C218
C209
C208
C215
C213
C204
C203
C211
C212
C205
C202
C216
C210
C201
C207
C217
YB2
O4
O5
C206
O10
C10
C4
C5
O7
C7
C9
O9
FE3
O1
C1
C11
O11
FE1
FE2
C8
C3
C2
C6
O8
O3
O2
O6
YB1
C111 -- C120
C101 -- C110

XBL 815-9793

Figure 4. ORTEP view of disordered $[Yb(C_5Me_5)_2][Fe_3(CO)_{11}]$ molecule. Oxygen atoms bonded to C25P and C26P were not located.


C320
C309
C316
C308
C315
C319
C304
C303
C311
C314
C305
C302
C312
C313
C310
C307
C301
C317
C318
026
021
C306
022
C21
C22
C25P
C24
024
FE4
C23
C26P
023
FE5
FE4
025
C22
C21
C24P
022
021
024P
YR8

XBL 815-9795

The terminal Fe(2) and Fe(3) atoms are slightly below this plane (by 0.06 and 0.02 Å, respectively).

Although the Fe-Fe distances are similar to those found in the triiron clusters $[Fe_3(CO)_{11}]^{2-}$ [26], $[Fe_3(CO)_{11}H]^-$ [27] and $Fe_3(CO)_{12}$ [28], the familiar triangular arrangement of iron atoms is not observed. The preferred triangular geometry of the $[Fe_3(CO)_{11}]^{2-}$ cluster is clearly perturbed by the presence of the $(C_5Me_5)_2Yb(III)$ units, which have forced two more carbonyls into bridging positions. It is well known that bridging CO's are better than terminal CO's as σ-donors to hard Lewis acids and that certain Lewis acids can induce terminal-to-bridge CO shifts [29-31]. In order to act as chelating groups to both $(C_5Me_5)_2Yb(III)$ units, in which eight-coordination is favored, the $[Fe_3(CO)_{11}]^{-2}$ cluster distorts by breaking an Fe-Fe bond. This process would not require much energetically, as Fe-Fe bond strengths in carbonyl clusters have been estimated as being ca. 19 kcal/mole [32]. Although the open structure of the Fe_3 cluster core is not typical, the $[Fe_3(CO)_{11}]^{2-}$ portion of the compound is electron precise, with 48 electrons.

It is not clear now or why $Fe_2(CO)_9$ can also be used to generate $[Yb(C_5Me_5)_2]_2[Fe_3(CO)_{11}]$, but this reaction seems to imply that the product is a particularly stable ytterbium-iron isocarbonyl species. This stability may be due to the ability of $[Fe_3(CO)_{11}]^{2-}$ to form chelate rings to two ytterbiums simultaneously. The resulting 'opened' cluster would seem to have a rich

reaction chemistry. However, toluene solutions of the $[Yb(C_5Me_5)_2]_2[Fe_3(CO)_{11}]$ cluster did not react with H_2 or CO at 18 atm during a 24 h period.

Summary of Crystallographic Data

Bonding of the cyclopentadienyl group and its substituted analogues to f-block metals is thought to be predominantly ionic, i.e., there is very little electron exchange between the metal atom and the organic ligand. A structural criterion has been advanced by Raymond that is remarkably accurate in predicting f-metal to carbon bond lengths, given the simplicity and therefore utility of the model [33]. The fundamental principle of the model is that metal-carbon bond lengths are a sensitive function of the oxidation state and coordination number of a given metal ion. Subtraction of the ionic radius of a metal atom, which is a function of the oxidation state and coordination number, from the observed metal-carbon bond length gives the effective ionic radius of a cyclopentdienyl group. Though ligand-ligand repulsions also play a role in determining the metal-carbon bond length, for the f-block metals, the effective ionic radius of the cyclopentadienyl ligand is observed to be fairly constant, 1.64 ± 0.04 Å. Thus, it may be said that the bonding in these organometallic molecules is largely ionic.

In the course of these investigations into the chemistry of pentamethylcyclopentadienyl derivatives of the lanthanide metals, a number of compounds whose structures can be used to test this model have been prepared. Using the ionic radii tabulated by Shannon [17],

one can estimate the effective ionic radius of the C_5Me_5 ligand in the bis(pentamethylcyclopentadienyl)ytterbium complexes that have been structurally characterized. As shown in Table 1, these radii are consistent with the value suggested by Raymond for predominantly ionic bonding, 1.64 ± 0.04 Å. Based on these structural data alone, the bonding in ytterbium(II) and ytterbium(III) pentamethylcyclopentadienyl complexes appears to be largely ionic.

Table 1. Effective Ionic Radii (Å) of $C_5Me_5^-$ in Ytterbium Compounds.

Compound	M–C Bond Length, Å	Metal Ion Radius, Å	Effective C_5Me_5 Radius, Å
$Yb(C_5Me_5)_2(py)_2$	2.74(4)	1.14	1.60
$Yb(C_5Me_5)_2(thf)$	2.66(2)	1.08	1.58
$Yb(C_5Me_5)_2(S_2CNEt_2)$	2.63(3)	0.985	1.64
$[Yb(C_5Me_5)_2(thf)][Co(CO)_4]$	2.596(2)	0.985	1.61
$[Yb(C_5Me_5)_2]_2[Fe_3(CO)_{11}]$	2.57(1)	0.985	1.59
$[Li(OEt_2)_2][(C_5Me_5)_2YbCl_2]$ [34]	2.611(4)	0.985	1.63
$Yb(C_5Me_5)_2AlCl_4$ [34]	2.584(5)	0.985	1.60

Chapter 6 References

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