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### Title

ELECTRON TRANSFER CHEMISTRY OF  $(\text{Me}_5\text{C}_5)_2\text{YB}$ : CLEAVAGE OF DIORGANOPEROXIDE AND RELATED CHALCOGENIDES TO GIVE  $(\text{Me}_5\text{C}_5)_2\text{YB}(\text{ER})(\text{L})$ , WHERE E IS O, S, SE, OR TE AND L IS A LEWIS BASE; CRYSTAL STRUCTURE OF  $(\text{Me}_5\text{C}_5)_2\text{YB}(\text{ER})(\text{L})$

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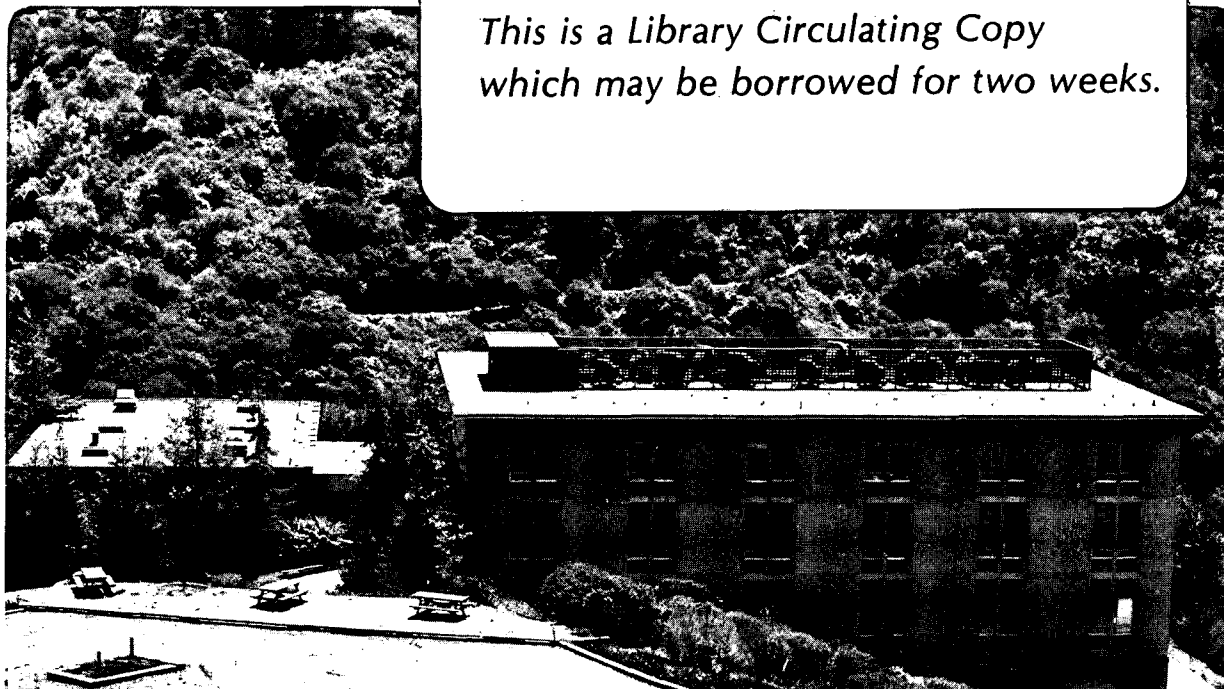
**Electron Transfer Chemistry of  $(\text{Me}_5\text{C}_5)_2\text{Yb}$ :  
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E Is O, S, Se, or Te and L Is a Lewis Base;  
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D.J. Berg, R.A. Andersen, and A. Zalkin

January 1988

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Electron Transfer Chemistry of  $(\text{Me}_5\text{C}_5)_2\text{Yb}$ : Cleavage of Diorganoperoxide and Related Chalcogenides to give  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{ER})(\text{L})$  Where E is O, S, Se, or Te and L is a Lewis Base; Crystal Structure of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$

David J. Berg, Richard A. Andersen,<sup>\*</sup> and Allan Zalkin

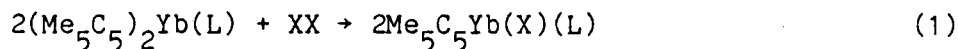
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Abstract

The divalent metallocenes of ytterbium,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  or  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{NH}_3)_2$ , react with molecules of the type REER to give the trivalent ytterbium complexes,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{ER})(\text{L})$  where L is  $\text{OEt}_2$  or  $\text{NH}_3$ , E is S, Se, or Te, and R is a phenyl or substituted phenyl group. The ammonia complexes are easier to characterize than the diethyl ether complexes since the latter complexes lose ether in the solid state and give unsatisfactory microanalytical data whereas the ammonia complexes give satisfactory elemental analyses. In addition, the line width of the  $\text{Me}_5\text{C}_5$  protons in the  $^1\text{H}$  NMR spectra of the diethyl ether complexes is ca. 500 Hz whereas the line width at half-height is ca. 50 Hz for the ammonia complexes, consistent with the notion that the barrier to chemical exchange is higher for the ammonia complexes. The peroxides,  $\text{ROOR}$  where R is  $\text{Me}_3\text{C}$  or  $\text{Me}_3\text{Si}$ , give the alkoxides,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OR})(\text{NH}_3)$  and  $\text{Et}_2\text{NC}(\text{S})\text{SS}(\text{S})\text{CNEt}_2$  gives the known  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S}_2\text{CNEt}_2)$ . In contrast, dialkyldithiophosphinates give  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S}_2\text{PR}_2)$  and  $\text{R}_2\text{PPR}_2$  where R is Me or Et. The synthetic routes developed in this work are the best methods currently available for synthesis of these trivalent species. The crystal structure of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$  has been done. The crystals are orthorhombic,  $\text{P}2_12_12_1$ , with  $a = 11.823(3)$ ,  $b = 25.917(6)$ ,  $c = 8.539(2)\text{\AA}$ ,  $V = 2616.5\text{\AA}^3$ . For  $Z = 4$ , the calculated density is  $1.69\text{ gcm}^{-3}$ . The structure was refined by full-matrix least squares to a conventional R-factor of 0.046 [4991 data,  $F^2 > \sigma(F^2)$ ]. The Yb-Te distance is  $3.039(1)\text{\AA}$  and the Yb-Te-C(Ph) angle is  $113.0(3)^\circ$ .

The divalent ytterbium metallocene,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ , reacts with a wide variety of transition metal carbonyls and substituted metal carbonyls with single metal-metal bonds as shown



in Eq. 1, where X is  $\text{Co}(\text{CO})_4$ ,<sup>1a</sup>  $\text{Mn}(\text{CO})_5$ ,<sup>1b</sup>  $\text{CpFe}(\text{CO})_2$ ,<sup>1c</sup> and  $\text{CpMo}(\text{CO})_3$ .<sup>1c</sup> The reaction in Eq. 1 involves the transfer of an electron from  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  to the lowest unoccupied molecular orbital of the dimeric transition metal carbonyl which is primarily metal-metal antibonding. The net reaction is formation of a  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{III})$  fragment which is bonded to the transition metal by way of M-CO-Yb bonds. The electron transfer process that results in oxidation of  $(\text{Me}_5\text{C}_5)_2\text{Yb}$  to  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{III})$  is an exothermic one by ca. 1.35v (ca. 30 kcal mol<sup>-1</sup>).<sup>2</sup> The use of  $(\text{Me}_5\text{C}_5)_2\text{Yb}$  as a hydrocarbon soluble source of a single electron has been extended to other transition metal cluster carbonyl systems in which metal-metal bonds are broken or formed.<sup>3</sup> We wanted to extend the reaction shown in Eq. 1 to other classes of X-X molecules, i.e., those with single X-X bonds. In this paper we show that molecules of the type REER, where R is an organic group and E is O, S, Se, or Te, can be cleaved to give compounds of the type  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{ER})(\text{L})$ , where L is a Lewis base.

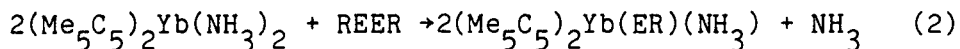
### Synthetic Studies

Two molar equivalents of the diethyl ether complex,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ , react on mixing with PhEPh, E is S, Se, or Te, in diethyl ether giving the purple (E = S, Se) or green (E = Te), trivalent

compounds  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{EPh})(\text{OEt}_2)$ , eq. 1, X = EPh. The substituted alkyl and aryl thiolates,  $\text{PhCH}_2\text{S}$ , *m*-tolylS, and *p*-tolylS were prepared similarly as was the mesitylthiolate,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S-mesityl})$ . The latter compound was the only compound prepared in this study which crystallized free of diethyl ether, a result consistent with the large size of the mesityl group relative to the others used in this study.

The diethyl ether complexes are rather difficult to characterize since elemental analyses of all of them give low values (C,H) in combustion microanalysis. Hydrolysis of the compounds with  $\text{D}_2\text{O}$  in benzene solution shows that one equivalent of diethyl ether is present, except in the case of the mesitylthiolate, since the integrated intensity of the resonances in the  $^1\text{H}$  NMR spectrum of the hydrolyzed material shows that the ratio of  $\text{Et}_2\text{O}:\text{Me}_5\text{C}_5\text{D}$  is 1:2. Diethyl ether is lost in the mass spectrum, since the highest mass peak of all of the diethyl ether complexes is  $[\text{M-OEt}_2]^+$ . The  $^1\text{H}$  NMR spectra of the paramagnetic complexes do not show resonances due to diethyl ether, from +100 to -85°C, though the resonances for the Yb-ER and Yb- $\text{C}_5\text{Me}_5$  portions are observed. The line width, in contrast to the usual line width of the  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{III})$  fragment of ca. 30-50 Hz at half height, is an order of magnitude broader in the diethyl ether complexes, presumably due to chemical exchange processes on the NMR time scale. All these observations suggest that diethyl ether is not coordinated particularly strongly in these complexes.

In order to overcome these difficulties we have prepared the ammonia complexes, since ammonia is a better base to  $(\text{Me}_5\text{C}_5)_2\text{Yb}$  than is diethyl ether.<sup>4</sup> The ammonia complexes are readily prepared in high yield by the reaction shown in Eq. 2, where R is Ph and



E is S, Se, or Te and R is Me and E is S. This synthetic route is more convenient than displacing the coordinated diethyl ether in  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{ER})(\text{OEt}_2)$  by addition of excess ammonia. In all cases the ammonia complexes give satisfactory combustion microanalytical data though, in those cases that were examined,  $(\text{M-NH}_3)^+$  molecular ions are observed in the mass spectra. The line widths in the  $^1\text{H}$  NMR spectra are normal, i.e., ca. 30-50 Hz, though resonances due to ammonia are not observed. Further, the ammonia complexes are nicely crystalline and an X-ray structure of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SPh})(\text{NH}_3)$  has been described<sup>5</sup> and that of the tellurium analogue is described below.

Cleavage of sulfur-sulfur bonds in RSSR compounds by metals is not new since sodium amalgam gives NaSR and  $\text{Fe}_3(\text{CO})_{12}$  gives  $\text{Fe}_2(\text{CO})_6(\mu\text{-SR})_2$ , to quote two classic examples.<sup>6</sup> The reduction potential of PhSeSePh ( $E_{1/2} = -1.20\text{v}$  vs. SCE)<sup>7a</sup> and PhTeTePh ( $-1.06\text{v}$ )<sup>7b</sup> is less than that of PhSSPh ( $-1.70\text{v}$ )<sup>7a</sup>, and it is not surprising that  $(\text{Me}_5\text{C}_5)_2\text{Yb}$  cleaves the E-E bonds in these compounds. This is the first time that lanthanide compounds have been used to cleave E-E bonds in REER compounds. Only two lanthanide thiolate complexes have been prepared

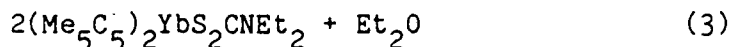
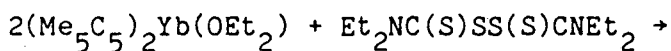
$[(\text{Me}_3\text{Si})_2\text{N}]_4\text{Gd}_2(\mu\text{SCMe}_3)_2$  from reaction of  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{GdCl}$  and  $\text{LiSCMe}_3$  or  $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Gd}$  and  $\text{Me}_3\text{CSH}$ <sup>8a</sup> and  $(\text{Me}_5\text{C}_5)_2\text{Lu}(\text{SCMe}_3)_2\text{Li}(\text{thf})_2$  from reaction of  $(\text{Me}_5\text{C}_5)_2\text{LuMe}_2\text{Li}(\text{thf})_2$  and  $\text{Me}_3\text{CSH}$ .<sup>8b</sup>

The synthetic route, Eqs. 1 or 2, is the best one that we have been able to develop for complexes of the type  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SR})(\text{L})$ . We decided to extend the synthetic method to cleavage of peroxide bonds. The alkoxides  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OR})(\text{NH}_3)$  where R is  $\text{CMe}_3$  or  $\text{SiMe}_3$  are readily



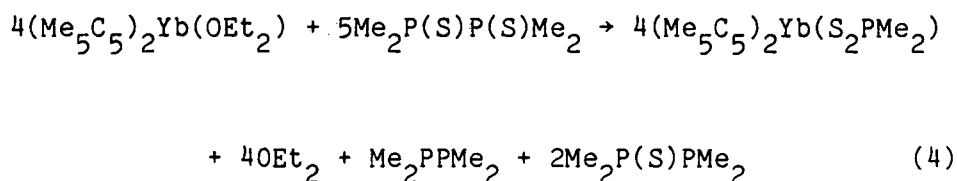
prepared from  $\text{Me}_3\text{COOCMe}_3$  or  $\text{Me}_3\text{SiOOSiMe}_3$ . Diphenyl peroxide is not stable so the phenoxide cannot be obtained from this synthetic route.<sup>9</sup> Few cyclopentadienyl lanthanide alkoxides are known and the known ones have been prepared by traditional synthetic routes of salt<sup>10a</sup> or alkane elimination.<sup>8b,10b</sup>

The scope of the non-metal to non-metal bond cleavage reaction has been examined in the following set of reactions. The diethyl ether complex,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ , reacts with tetraethyldithiuramdisulfide to give the known  $(\text{Me}_5\text{C}_5)_2\text{YbS}_2\text{CNEt}_2$ <sup>11</sup>, Eq. 3. The phosphorus-phosphorus bond in



$\text{Ph}_2\text{PPPh}_2$  cannot be cleaved by  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  since the latter is recovered unchanged after refluxing the reactants in toluene for several hours. This lack of reaction is not due to the thermodynamic instability of  $\text{M-PR}_2$  bonds as this class of compound has been prepared by alternative synthetic methods,<sup>12</sup> but is due either to steric effects or the high reduction potential of  $\text{Ph}_2\text{PPPh}_2$  ( $E_{1/2} = -2.05\text{v}$ )<sup>7c</sup> which is more negative than that of  $\text{PhSSPh}$  by ca. 0.3v. The metallocene,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ , reacts with  $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$  whose reduction potential is  $-2.48\text{v}$ ,<sup>7c</sup> but the rearrangement product  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S}_2\text{PMe}_2)$  is the only metal containing species isolated. Examination of the reaction solution by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy shows that  $\text{Me}_2\text{PPMe}_2$  and  $\text{Me}_2\text{P}(\text{S})\text{PMe}_2$  are the only other phosphorus containing species formed and the net

reaction can be written as in Eq. 4. The diethyl derivative,  $\text{Et}_2\text{P(S)P(S)Et}_2$ , behaves similarly



### $^1\text{H}$ NMR Spectra

The  $^1\text{H}$  NMR spectra of the paramagnetic diethyl ether complexes are complicated by chemical exchange processes that render the line widths of the  $\text{Me}_5\text{C}_5$  and aryl-ring resonances broader than usually observed<sup>1</sup>. In addition the resonances due to diethyl ether are not observed. Nonetheless, information is available since the chemical shift range is large and the resonances may be assigned as shown in Table I. These assignments are made by examination of the substituted derivatives. The methyl protons of the  $\text{Me}_5\text{C}_5$ -ring resonate at ca.  $\delta$ 9 and the aryl-ring hydrogens lie in the order of decreasing chemical shift,  $m > p > o$ . In the phenylselenates, phenyltellurates, and benzylthiolates we have assigned the most deshielded resonance to the meta-proton by analogy to that of the phenyl-thiolates.

In the ammonia complexes, the  $\text{Me}_5\text{C}_5$ -ring protons are shielded ca. 5ppm relative to the values in the diethyl ether complexes. In these complexes the chemical shift of the aryl-ring hydrogens lie in the order of decreasing chemical shift,  $o > m > p$ . In two cases,  $(\text{Me}_5\text{C}_5)_2\text{Yb(S-p-tolyl)(NH}_3)$  and  $(\text{Me}_5\text{C}_5)_2\text{Yb(S-m-tolyl)(OEt}_2)$  we have done a variable temperature study to show that the resonances follow the Curie law<sup>13</sup> and to show that the aryl-methyls are located under the  $\text{Me}_5\text{C}_5$ -ring methyls.

Crystal Structure of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$

An ORTEP diagram is shown in the Figure. Positional parameters are in Table II, some bond lengths and bond angles are in Table III, and crystal data are in Table IV. The geometry of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$  is similar to that of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SPh})(\text{NH}_3)$ , both compounds are pseudotetrahedral, though the crystals are not isomorphous since the latter crystallizes in the monoclinic crystal system in space group  $\text{P}\bar{1}$ . One of the  $\text{Me}_5\text{C}_5$  rings in the tellurium compound is severely disordered and the carbon atoms C(1-5) and C(11-15) were refined with positional restraints as described in the Experimental Section. The disorder does not appear to affect the other groups in the molecule; in particular the hydrogen atoms in ammonia were located and refined isotropically.

The  $(\text{Me}_5\text{C}_5)_2\text{Yb}$  and  $\text{Yb}(\text{NH}_3)$  fragments in  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SPh})(\text{NH}_3)$  and  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$  are nearly identical. The averaged Yb-C ( $\text{C}_5\text{Me}_5$ ) distances are 2.64(2)Å(S) and 2.63(2)Å(Te), the Yb- $\text{C}_5\text{Me}_5$  centroid distances are 2.35Å in each case, the  $\text{Me}_5\text{C}_5$  centroid-Yb- $\text{Me}_5\text{C}_5$  centroid angle is 136°(S) and 137°(Te) and the Yb-N distance is 2.428(3)Å(S) and 2.45(1)Å(Te). Further, the Yb-S-C(Ph) and Yb-Te-C(Ph) bond parameters change in a predictable manner. The data in Table V show that in simple organic and inorganic compounds the Te-X distance is longer than the equivalent S-X distance by 0.32Å to 0.37Å and the angle at tellurium is smaller by ca. 7°. In the ytterbium compounds, the Yb-Te distance is 0.31Å longer than the Yb-S distance and the Yb-Te-C(Ph) angle is closed by 4.5°. Thus, the  $(\text{Me}_5\text{C}_5)_2\text{Yb}$  (III) fragment behaves in a consistent and predictable manner.

Experimental Section

All operations were done under nitrogen. Microanalyses were performed by the microanalytical laboratory of this department. The  $^1\text{H}$  NMR spectra were measured at 89.56 MHz and the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were measured at 36.25 MHz on a JEOL-FX90Q instrument. The  $^1\text{H}$  chemical shifts are reported in Table I. Infrared spectra were recorded as Nujol mulls between CsI plates on a Nicolet 5DX-FTIR instrument. Mass spectra were obtained on an AEI-MS-12 machine equipped with a direct inlet using electron ionization.

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SPh})(\text{NH}_3)$ . An intimate mixture of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  (0.84g, 1.6 mmol) and  $\text{Ph}_2\text{S}_2$  (0.18g, 0.81 mmol) was placed in a Schlenk flask and diethyl ether (60 mL) was added. The purple solution was stirred for 1h, filtered and the filtrate was concentrated to ca. 20 mL. Cooling ( $-10^\circ\text{C}$ ) afforded purple needles in 40% (0.37g) yield, mp 62-65 $^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{30}\text{H}_{45}\text{OSYb}$ : C, 57.5; H, 7.24, S, 5.12. Found C, 56.3; H, 6.74; S, 5.28.  $\underline{\text{M}}^+$ ; 553 (M-OEt<sub>2</sub>). Hydrolysis of a small amount of the complex with  $\text{D}_2\text{O}$  in  $\text{C}_6\text{D}_6$  and examination of the  $\text{C}_6\text{D}_6$  soluble portion showed the presence of OEt<sub>2</sub> and  $\text{Me}_5\text{C}_5\text{D}$  in a ratio of 1:2. IR: 2720w, 1576w, 1142w, 1082s, 1020s, 732vs, 690s, 472w, 420w, 375br,w, 300br,s, 225br,m  $\text{cm}^{-1}$ .

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S-p-tolyl})\text{OEt}_2$ . This complex was prepared and isolated in a manner similar to that of the phenylthiolate above, as purple crystals in 70% yield, mp 127-129 $^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{31}\text{H}_{47}\text{OSYb}$ : C, 58.1; H, 7.40. Found: C, 57.7; H, 7.21.  $\underline{\text{M}}^+$ ; 567 (M-OEt<sub>2</sub>)<sup>+</sup>. IR: 2730w, 1595w, 1480m, 1220w, 1085m, 1072m, 1012m, 800s, 788w,sh, 720w, 625w, 490m, 390w, 380w, 310s  $\text{cm}^{-1}$ .

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S-m-tolyl})(\text{OEt}_2)$ . This complex was prepared in a manner similar to that of the phenylthiolate, above, and isolated as purple prisms in 86% yield, mp 130-132°C.  $\underline{M}^+$ ; 567 (M-OEt<sub>2</sub>)<sup>+</sup>. IR: 3080w, 2720m, 1585s, 1569s, 1260w, 1212w, 1160m, 1098m, 1076s, 1019m, 862w, 849s, 800w, 760vs, 684s, 679s,sh, 591m, 518w, 490w, 441w, 420w, 375vs,br cm<sup>-1</sup>.

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S-mesityl})$ . This compound was prepared from  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  (0.63g, 1.2 mmol) and dimesityldisulfide<sup>15</sup> (0.18g, 0.61 mmol) in a manner similar to that of the phenylthiolate, above, and crystallized as purple blocks from diethyl ether in 89% (0.65g) yield, mp 159-163°C. Anal. Calcd for C<sub>29</sub>H<sub>41</sub>SYb: C, 58.6; H, 6.95; S, 5.39. Found: C, 58.3; H, 6.95; S, 5.25.  $\underline{M}^+$ : 595(M<sup>+</sup>), IR: 3060w, 3020w, 2725w, 1717w, 1600w, 1560wbr, 1345w, 1295w, 1171m, 1150m, 1090s, 1051s, 1018s, 962w, 948w, 923w, 843vs, 799m, 710m, 703w, 669w, 619s, 560w, 549m, 395s, 323vs, 312w,sh, 300w,sh cm<sup>-1</sup>.

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SCH}_2\text{Ph})(\text{OEt}_2)$ . This complex was prepared in a manner similar to that of the phenylthiolate, above, and crystallized as purple crystals from diethyl ether in 61% yield, mp 152-156°C.  $\underline{M}^+$ : 595 (M-OEt<sub>2</sub>)<sup>+</sup>. IR: 3063w, 2720w, 1600w, 1492m, 1322w, 1289w, 1262w, 1221w, 1187w, 1143w, 1121w, 1090wbr, 1067w, 1039m, 1033m, 998w, 915w, 890w, 850w, 803sbr, 768sbr, 709vs, 697vs, 680w, 623w, 595w, 563m, 523w, 468w, 377mbr, 350w, 310vs, 301vs, 290ssh cm<sup>-1</sup>.

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SePh})(\text{OEt}_2)$ . An intimate mixture of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  (0.68g, 1.3 mmol) and Ph<sub>2</sub>Se<sub>2</sub> (0.20g, 0.64 mmol) was placed in a Schlenk

flask and hexane (100 mL) was added. The purple solution was stirred for 1hr, filtered, and the filtrate was concentrated to ca. 25 mL. Cooling (-25°C) produced purple crystals in 76% (0.67g) yield, mp 156-160°C.  $\underline{m}^+$ : 601 (M-OEt<sub>2</sub>)<sup>+</sup>. IR: 3066w, 2723w, 1576s, 1469vs, 1460wsh, 1151w, 1093w, 1072s, 1021s, 802mbr, 728vs, 690s, 668m, 580wbr, 462mbr, 384mbr, 304vs, 281s cm<sup>-1</sup>.

$\underline{(Me_5C_5)_2Yb(TePh)(OEt_2)}$ . An intimate mixture of  $(Me_5C_5)_2Yb(OEt_2)$  (0.62g, 1.2 mmol) and diphenylditelluride<sup>16</sup> (0.24g, 0.59 mmol) was placed in a Schlenk flask and hexane (100 mL) was added. The blue-green solution was stirred for 3h, filtered, and the filtrate was concentrated to ca. 20 mL, then cooled (-78°C) to produce olive green crystals in 29% (0.25g) yield, mp 142-145°C. IR: 3064w, 2725w, 1570s, 1434s, 1325w, 1298w, 1261w, 1155w, 1093wbr, 1059w, 1016s, 1000w, 904w, 802mbr, 727vs, 696s, 653m, 460w, 386m, 306vs cm<sup>-1</sup>.

$\underline{(Me_5C_5)_2Yb(SPh)(NH_3)_4}$ . A mixture of  $(Me_5C_5)_2Yb(NH_3)_4$  (0.57g, 1.2 mmol) and Ph<sub>2</sub>S<sub>2</sub> (0.13g, 0.60 mmol) was placed in a Schlenk flask and toluene (60 mL) was added. The mixture was stirred for 2h, the red solution was filtered and the filtrate was concentrated to ca. 25 mL. Cooling (-20°C) afforded red crystals which were isolated and dried under reduced pressure. The color of the crystals turned to magenta upon exposure to vacuum. Yield was 0.53g (78%), mp 206-208°C. Anal. Calcd for C<sub>26</sub>H<sub>38</sub>NSYb: C, 54.8; H, 6.72; N, 2.46. Found: C, 54.7; H, 6.84; N, 2.34. IR: 3350w, 3266w, 3058w, 2723w, 1596wsh, 1577s, 1560w,

1220vs, 1188w, 1130w, 1085s, 1062w, 1023m, 893w, 800w, 740vs, 735wsh, 700s, 693s, 596w, 507mbr, 484m, 429w, 382w, 302vs, 280wsh  $\text{cm}^{-1}$ .

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S-p-tolyl})(\text{NH}_3)$ . This complex was prepared and isolated in a manner similar to that of the phenylthiolate, above, in 88% yield, mp 208-211°C. Anal. Calcd for  $\text{C}_{27}\text{H}_{40}\text{NSYb}$ : C, 55.6; H, 6.91; N, 2.40. Found: C, 55.4; H, 6.72; N, 2.24. IR: 3360m, 3275m, 3090w, 3060w, 2730m, 1890w, 1790w, 1642w, 1595sbr, 1481s, 1212vs, 1100w, 1087s, 1012sbr, 808vs, 792wsh, 720w, 630m, 595w, 510wsh, 495s, 395mbr, 370mbr, 295s, 275wsh  $\text{cm}^{-1}$ .

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S-m-tolyl})(\text{NH}_3)$ . This complex was prepared and isolated in a manner similar to that of the phenylthiolate, above, in 78% yield, mp 206-207°C. Anal. Calcd for  $\text{C}_{27}\text{H}_{40}\text{NSYb}$ : C, 55.6, H, 6.91; N, 2.40. Found: C, 55.3; H, 6.90; N, 2.28. IR: 3356w, 3267w, 2724w, 1599wsh, 1585s, 1566m, 1217vs, 1161w, 1097w, 1075w, 1021wbr, 893w, 854mbr, 809wbr, 774vs, 729wbr, 696s, 679m, 510sbr, 438m, 381w, 300s, 279w, 255w  $\text{cm}^{-1}$ .

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{SCH}_2\text{Ph})(\text{NH}_3)$ . This complex was prepared in a manner analogous to that of the phenylthiolate, above, and crystallized from a mixture of toluene: hexane at -10°C in 66% yield, mp 221-223°C. Anal. Calcd for  $\text{C}_{27}\text{H}_{40}\text{NSYb}$ : C, 55.6; H, 6.91; N, 2.40; S, 5.49. Found: C, 55.7; H, 7.09; N, 2.36; S, 5.46. IR: 3362w, 3318w, 3201w, 3119m, 2725m, 1597m, 1492m, 1260vs, 1221w, 1156w, 1065m, 1023m, 1000w, 920w, 803m, 775m, 725w, 704vs, 691w, 562w, 516mbr, 375wbr, 313m, 303vs, 282wsh  $\text{cm}^{-1}$ .

(Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Yb(SMe)(NH<sub>3</sub>). This complex was prepared and isolated in a manner analogous to that of the phenylthiolate described above, in 49% yield, mp 174-176°C. Anal. Calcd for C<sub>21</sub>H<sub>36</sub>NSYb: C, 49.7; H, 7.13; N, 2.75; S, 6.32. Found: C, 49.8; H, 7.28; N, 2.95; S, 602. M<sup>+</sup>: 491 (M-NH<sub>3</sub>)<sup>+</sup>. IR: 3374m, 3320m, 3203w, 3115m, 2722m, 1773wbr, 1595s, 1309m, 1259wsh, 1227vs, 1166w, 1152w, 1090w, 1060w, 1022m, 944wbr, 803mbr, 726m, 702m, 656w, 542sbr, 386mbr, 375m, 305vs, 282wsh cm<sup>-1</sup>.

(Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Yb(SePh)(NH<sub>3</sub>). This complex was prepared and isolated in a manner similar to that used to prepare the phenylthiolate, above, in 87% yield, mp 195-198°C. Anal. Calcd for C<sub>26</sub>H<sub>38</sub>NSeYb: C, 50.6; H, 6.21; N, 2.27. Found: C, 50.2; H, 6.21; N, 2.07. IR: 3355w, 3314w, 3264w, 3056m, 2726w, 1594wbr, 1574s, 1221vs, 1067s, 1021s, 734vs, 694s, 675m, 525mbr, 470m, 384mbr, 301vs cm<sup>-1</sup>.

(Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Yb(TePh)(NH<sub>3</sub>). This complex was prepared in a manner similar to that used to prepare and isolate the thiolate, above, in 54% yield, mp 190-191°C. Anal. Calcd for C<sub>26</sub>H<sub>38</sub>NTeYb: C, 46.9; H, 5.76; N, 2.10. Found: C, 46.9; H, 5.75; N, 2.08. M<sup>+</sup>: 649 (M-NH<sub>3</sub>)<sup>+</sup>. IR: 3353w, 3254w, 3063w, 3047w, 2724w, 1955w, 1941w, 1882w, 1867w, 1811w, 1753w, 1570m, 1487m, 1430m, 1298w, 1226vs, 1155w, 1059w, 1018m, 999w, 803wbr, 730vs, 696s, 650w, 597w, 517mbr, 491mbr, 458m, 388m, 308vs cm<sup>-1</sup>.

(Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Yb(OCMe<sub>3</sub>)(NH<sub>3</sub>). Di-tert-butylperoxide (0.30 mL, 1.6 mmol) was added to (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Yb(NH<sub>3</sub>)<sub>2</sub> (0.49g, 1.0 mmol) suspended in toluene (50 mL). The color changed to orange after stirring for 30 min. The solution was stirred for a further 2h then the toluene was removed under



reduced pressure. The residue was extracted with hexane (60 mL), the extract was filtered and the filtrate was concentrated to ca. 40 mL and cooled (-10°C). The orange-red crystals were collected and several additional crops were collected from the mother liquors on concentration and cooling. The combined yield was 0.35g (64%), mp 184-186°C. Anal. Calcd for  $C_{24}H_{42}NOYb$ : C, 54.0; H, 7.93; N, 2.62. Found: C, 53.0; H, 7.91; N, 2.49.  $M^+$ : 517 ( $M-NH_3$ )<sup>+</sup>. IR: 3368m, 3264w, 2720w, 1592w, 1349m, 1310w, 1196vs, 1096w, 1060w, 1000vs, 893w, 803w, 789w, 727m, 501m, 483m, 378w, 350w, 285sbr  $cm^{-1}$ .

$(Me_5C_5)_2Yb(OSiMe_3)(NH_3)$ . The siloxide was prepared from  $(Me_5C_5)_2Yb(NH_3)_2$  and  $(Me_3Si)_2O_2$ <sup>17</sup> in a manner similar to the t-butoxide and crystallized as orange plates from hexane in 48% yield, mp 221-222°C. Anal. Calcd for  $C_{23}H_{42}NOSiYb$ : C, 50.3; H, 7.70; N, 2.55. Found: C, 47.1; H, 7.85; N, 2.03.  $M^+$ : 533 ( $M-NH_3$ )<sup>+</sup>. IR: 3374w, 3289w, 2724w, 1597w, 1253s, 1240vs, 1200vs, 980vsbr, 865wsh, 827vsbr, 803wsh, 746s, 669s, 495sbr, 385wbr, 309s, 295s, 279vs  $cm^{-1}$ .

$(Me_5C_5)_2Yb(S_2CNEt_2)_2$ . A mixture of  $(Me_5C_5)_2Yb(OEt_2)$  (0.62g, 1.2 mmol) and tetraethylthiuramdisulfide (0.18g, 0.61 mmol) were stirred in pentane (50 mL) for 2h. The purple solution was filtered and the filtrate was concentrated to ca. 20 mL and cooled (-10°C). The large purple crystals were collected and identified by mp 227-228°C (lit. 226-227°C)<sup>11</sup> and IR.

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S}_2\text{PMe}_2)$ . A mixture of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  (0.54g, 1.0 mmol) and  $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$  (0.20g, 1.1 mmol) was stirred in toluene (60 mL) for 2h. The blue-violet solution was concentrated to ca. 30 mL and cooled ( $-10^\circ\text{C}$ ) affording dark violet crystals in 81% yield (0.48g), mp  $78-82^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{36}\text{PSYb}$ : C, 46.5; H, 6.38; S, 11.3. Found: C, 46.3; H, 6.37; S, 10.9.  $M^+$ : 569. IR: 2920s, 2720w, 1290w, 1280m, 1260w, 1015w, 945s, 910m, 845w, 795w, 730wsh, 720s, 622w, 590s, 495s, 375wbr, 298s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $21^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.5 (30H,  $\nu$  1/2 = 70Hz), -23.1 (6H,  $\nu$  1/2 = 30Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $21^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ) -28.2. In a separate reaction,  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  (40mg) and  $\text{Me}_2\text{P}(\text{S})\text{P}(\text{S})\text{Me}_2$  (15 mg) were mixed in  $\text{C}_6\text{D}_6$  (2 mL) for 15 min and the mixture was then placed in a 5 mm NMR tube, the contents of which were examined by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. In addition to a resonance due to  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S}_2\text{PMe}_2)$  there were resonances due to  $\text{Me}_2\text{PPMe}_2$  at -58.4 (lit. -58.7)<sup>18a</sup> and a doublet of doublets at 36.2 and -59.1 with  $J_{\text{PP}} = 220\text{Hz}$  due to  $\text{Me}_2\text{P}(\text{S})\text{PMe}_2$  (lit. 35.6 and -58.7 with  $J_{\text{PP}} = 224\text{Hz}$ ).<sup>18b</sup> The total integrated intensity of the resonances due to trivalent phosphorus was approximately equal to that of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S}_2\text{PMe}_2)$ .

$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S}_2\text{PEt}_2)$ . This complex was prepared and isolated in a manner similar to that of its dimethyldithiophosphate homologue in 96% yield, mp  $75-77^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{40}\text{PS}_2\text{Yb}$ : C, 48.3; H, 6.76; S, 10.7. Found: C, 48.5; H, 6.92; S, 10.6.  $M^+$ : 597. IR: 2724w, 1407w, 1260w, 1227w, 1157w, 1097w, 1039s, 1028s, 977w, 802m, 767s, 744m, 738m, 712m, 671s, 623w, 616vs, 507s, 386mbr, 307vsbr  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $32^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 7.4 (30H,  $\nu$  1/2 = 71Hz), -7.5 (6H,  $\nu$  1/2 = 31Hz), -27.9 (4H,  $\nu$  1/2 = 32Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $32^\circ\text{C}$ ,  $\text{C}_6\text{D}_6$ ): 5.1. In a separate experiment

50 mg of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$  and  $\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2$  (30 mg) were mixed in  $\text{C}_6\text{D}_6$  (1.5 mL) and the mixture was transferred into a 5 mm NMR tube and the contents were monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. In addition to the resonance due to the Yb complex, resonances were found at -32.0 due to  $\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2$  (lit. -32.7),  $^{18a}$  at 50.7 due to  $\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2$  (lit. 51.3)  $^{18a}$  and a doublet of doublets at 55.3 and -37.1 with  $J_{\text{PP}}$  of 244 Hz due to  $\text{Et}_2\text{P}(\text{S})\text{P}(\text{S})\text{Et}_2$  (lit. 55.3 and -37.1 with  $J_{\text{PP}} = 243\text{Hz}$ ).  $^{18c}$  The total integrated intensity of the trivalent phosphorus resonances was approximately equal to that of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{S}_2\text{PEt}_2)$ .

#### X-Ray Crystallography of $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$

The air-sensitive crystals were sealed inside thin-walled quartz capillaries under argon and then mounted on a modified Picker FACS-1 automatic diffractometer equipped with a Mo X-ray tube and a graphite monochromator. A set of  $\theta$ -2 $\theta$  scan data was collected and corrected for absorption (analytical method)  $^{19}$  and Lorentz and polarization effects. The Yb and Te atoms were located with the use of three-dimensional Patterson maps, and subsequent least-squares refinements and electron-density maps revealed the locations of the other atoms. The structure was refined by full-matrix least squares. Anisotropic thermal parameters were assigned to all of the non-hydrogen atoms with the exception of the methyl carbon atoms on the C1-C5 cyclopentadienyl ring. The pentamethylcyclopentadienyl carbon atoms C1-C5 and C11-C15 exhibited severe anisotropic thermal motion, and it was expedient to refine these positional parameters with distance restraints  $^{20}$  [C-C(ring)  $1.38 \pm 0.01$  Å; C-C(methyl)  $1.54 \pm 0.01$  Å]. The three ammonia hydrogen atoms were indicated in the electron difference maps and were included in the

least-squares refinements with imposed N-H and H-H distance restraints<sup>21</sup> of  $0.92 \pm 0.02$  Å and  $1.59 \pm 0.03$  Å respectively, and a single isotropic thermal parameter was used for all three atoms. The calculated positional parameters of the five phenyl hydrogen atoms were included (C-H 0.95 Å) but not refined; a single isotropic thermal parameter for the five atoms was refined. Details of the data collection and the least-squares refinements are given in Table IV. A Rogers<sup>22</sup> parameter of 1.07(3), ideally 1.0, confirms the absolute configuration of the crystal as described by the coordinates in Table II. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-Ray Crystallography.<sup>21</sup> With the exception of the ORTEP program all of the computer programs used are our own.

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Supplementary Material Available. Thermal parameters, least-squares planes, additional bond lengths and distances and structure factor tables ( pages).

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Table I

<sup>1</sup>H NMR Spectra of (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Yb(ER)(L)<sup>a</sup>

E	R	L	Me <sub>5</sub> C <sub>5</sub>	o-R	m-R	p-R
S	Ph	OEt <sub>2</sub>	9.7(540)	5.5(50)	73.2(300)	42.6(100)
S	p-tolyl	OEt <sub>2</sub>	8.5(500)	5.5(35)	76.4(300)	30.3(50), Me
S	m-tolyl	OEt <sub>2</sub>	9.2(500)	9.2(b)	78.4(250)	44.7(60)
				5.9(100)	56.0(100), Me	
S	mesityl	OEt <sub>2</sub>	9.2(460)	3.7(25)	c	18.6(80)
Se	Ph	OEt <sub>2</sub>	9.7(300)	9.7(d)	62.7(170)	37.9(65)
Te	Ph	OEt <sub>2</sub>	8.5(145)	11.9(80)	46.2(300)	16.4(280)
S	CH <sub>2</sub> Ph	OEt <sub>2</sub>	4.2(100) <sup>e</sup>	-14.0(100)	-16.0(120)	-25.9(70)
S	Ph	NH <sub>3</sub>	3.8(55)	40.0(95)	12.8(25)	8.7(20)
S	p-tolyl	NH <sub>3</sub>	3.8(65)	38.8(110)	12.7(22)	3.8(b), Me
S	m-tolyl	NH <sub>3</sub>	3.8(57)	51.6(120)	14.0(20)	9.8(b)
				41.7(100)	9.8(b), Me	
Se	Ph	NH <sub>3</sub>	4.3(45)	25.1(60)	9.6(30)	7.4(35)
Te	Ph	NH <sub>3</sub>	4.2(45)	16.5(280)	6.7(34)	6.0(44)
S	CH <sub>2</sub> Ph	NH <sub>3</sub>	4.0(70) <sup>e</sup>	-2.4(49)	9.1(30)	11.2(46)
S	Me	NH <sub>3</sub>	4.1(65)	-5.9(67), Me		
O	CMe <sub>3</sub>	NH <sub>3</sub>	6.1(260)	-57.5(124), Me		
O	SiMe <sub>3</sub>	NH <sub>3</sub>	4.8(210)	-37.5(67), Me		



Table I. (continued)

- (a) 32°C in either  $C_6D_6$  or  $C_7D_8$ . The chemical shifts are expressed in  $\delta$ -units, positive values to high frequency, and the width at half-height is expressed in Hz which appear in parenthesis after  $\delta$ .
- (b) The methyl resonance is under the  $Me_5C_5$  resonance at 32°C, but it moves out at high and low temperature.
- (c) not observed.
- (d) Assigned on the basis of the integrated intensity.
- (e) The chemical shift of the methylene group is assigned at -6.8(100) in  $OEt_2$  and -16.0(78) in  $NH_3$  complexes.

Table II. Positional Parameters with Estimated Standard  
Deviations for  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$

Atom	x	y	z
Yb	0.05903(3)	0.12049(1)	0.12454(5)
Te	0.12370(6)	0.03861(3)	-0.11399(11)
N	0.1678(9)	0.0734(5)	0.3224(13)
C1	-0.1607(8)	0.1149(6)	0.0854(11)
C2	-0.1418(9)	0.1561(4)	0.1838(16)
C3	-0.1034(9)	0.1358(5)	0.3251(12)
C4	-0.0967(10)	0.0832(5)	0.3113(14)
C5	-0.1309(9)	0.0706(4)	0.1621(16)
C6	0.1259(11)	0.2169(4)	0.1316(17)
C7	0.1091(11)	0.2064(4)	-0.0234(13)
C8	0.1872(8)	0.1722(4)	-0.0785(10)
C9	0.2615(8)	0.1594(4)	0.0461(12)
C10	0.2225(11)	0.1881(5)	0.1795(12)
C11	-0.202(4)	0.1159(13)	-0.0876(25)
C12	-0.196(5)	0.2098(10)	0.165(5)
C13	-0.079(5)	0.1653(12)	0.4773(29)
C14	-0.075(4)	0.0414(10)	0.4370(29)
C15	-0.160(3)	0.0144(7)	0.114(4)
C16	0.0852(19)	0.2600(6)	0.2373(24)
C17	0.0238(12)	0.2345(6)	-0.1398(29)
C18	0.2065(13)	0.1574(5)	-0.2498(12)
C19	0.3653(11)	0.1247(8)	0.0340(22)

Table II. (continued)

C20	0.2916(24)	0.1902(10)	0.3366(17)
C21	0.0414(8)	-0.0331(4)	-0.0749(13)
C22	0.0683(12)	-0.0637(5)	0.0457(18)
C23	0.0114(16)	-0.1096(6)	0.0712(20)
C24	-0.0712(13)	-0.1263(5)	-0.0288(19)
C25	-0.0954(10)	-0.0954(5)	-0.1583(16)
C26	-0.0381(9)	-0.0505(4)	-0.1777(12)

Table III.

Selected Interatomic Distances (Å) and Angles in  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$ 


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Distances (Å)			
N - Yb	2.50(1)	C8 - Yb	2.66(1)
Te - Yb	3.039(1)	C9 - Yb	2.68(1)
C1 - Yb	2.62(1)	C10 - Yb	2.65(1)
C2 - Yb	2.60(1)	H1 - Yb	2.74(7)
C3 - Yb	2.60(1)	H2 - Yb	2.72(6)
C4 - Yb	2.62(1)	H3 - Yb	2.76(6)
C5 - Yb	2.61(1)	Cp1 - Yb <sup>a</sup>	2.33
C6 - Yb	2.62(1)	Cp2 - Yb <sup>a</sup>	2.37
C7 - Yb	2.63(1)	C21 - Te	2.12(1)

Angles (°)			
N - Yb - Te	89.0(3)	Cp1 - Yb - Te	113.0
Cp1 - Yb - Cp2	136.9	Cp2 - Yb - Te	100.9
Cp1 - Yb - N	102.9	C21 - Te - Yb	113.0(3)
Cp2 - Yb - N	103.5		

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<sup>a</sup>) Cp1 is the centroid of carbon atoms C1-C5 and Cp2 is the centroid of carbon atoms C6-C10.

Table IV. Crystallographic Summary and Data Processing for

	$(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$
a, Å	11.823(3)
b, Å	25.917(6)
c, Å	8.539(2)
cryst syst	orthorhombic
space group	$P2_12_12_1$
volume, Å <sup>3</sup>	2616.5
d(calcd), g/cm <sup>-3</sup>	1.689
Z	4
temp, °C	23
empirical formula	$\text{C}_{26}\text{H}_{38}\text{NTeYb}$
f(000)	1292
fw	665.24
color	red
reflection rules	$h00:h = 2n$
x-ray	MoK $\alpha$ (graphite monochromated)
wave-length (K $\alpha_1$ , K $\alpha_2$ ), Å	0.70930, 0.71359
crystal size (mm)	0.16x0.17x0.69
$\mu$ , cm <sup>-1</sup>	46.72
abs corr range	1.39-2.05
cryst decay corr range	0.83-1.23
diffractometer	modified Picker FACS-1
2 $\theta$ limits, °	14.7-55.1
$\sin\theta/\lambda$ , min,max	0.180, 0.651
hkl limits	$h 0,15; k 0,33; l -11,11$

Table IV. (continued)

scan type	$\theta$ -2 $\theta$
scan width, °	$1.00 + 0.693 \tan \theta$
no. of standards	3
no. reflections between stds	250
variation of standards (%)	15.1, 15.6, 15.4
no. scan data	6435
no. unique reflections	5996 (includes Friedel pairs)
$R_{int}^b$	0.031
no. non-zero weighted data	4991 ( $F^2 > 1\sigma$ )
$p^c$	0.070
extinction $k^d$	$0.473 \times 10^{-7}$
max % extinction corr	11.9 %
no. parameters	249
R (non-zero wtd dat) <sup>e</sup>	0.046
$R_w^f$	0.059
R (all data)	0.067
Goodness of fit <sup>g</sup>	1.26
max shift/esd in lst-sqrs	0.0304
max/min in diff map ( $e/A^3$ )	0.94, -1.49

<sup>a</sup> Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved MoK $\alpha$  components of 25 reflections ( $20 < 2\theta < 33$ ).

<sup>b</sup>  $R_{int}$  = agreement factor between equivalent or multiply measured reflections =  $\Sigma [ I(hkl) - I(hkl)_{ave} ] / \Sigma [ I(hkl)_{ave} ]$

Table IV. (continued)

<sup>c</sup> In the least-squares, the assigned weights to the data are  $[\sigma(F)]^{-2}$  were derived from  $\sigma(F^2) = S^2 + (pF^2)^2$ , where  $S^2$  is the variance due to counting statistics and  $p$  is assigned a value that adjusts the weighted residuals of the strong reflections to be comparable to the weak ones.

<sup>d</sup> Simple extinction correction has the form  $(F_{obs})_{corr} = (1 + kI)F_{obs}$ , where  $I$  is the uncorrected intensity and  $F_{obs}$  is the observed scattering amplitude.

$$\frac{e}{f} R = \frac{\Sigma[|F_{obs}| - |F_{cal}|]}{\Sigma[|F_{obs}|]}$$

$$\frac{f}{g} R_w = \sqrt{\{\Sigma[w \times (|F_{obs}| - |F_{cal}|)^2] / \Sigma(w \times F_{obs}^2)\}}$$

$$\frac{g}{h} \sigma_1 = \text{error in observation of unit weight} = \sqrt{\{\Sigma(w \times [ |F_{obs}| - |F_{cal}| ]^2) / (no - nv)\}},$$

where  $no$  is the number of observations and  $nv$  is the number of variables.

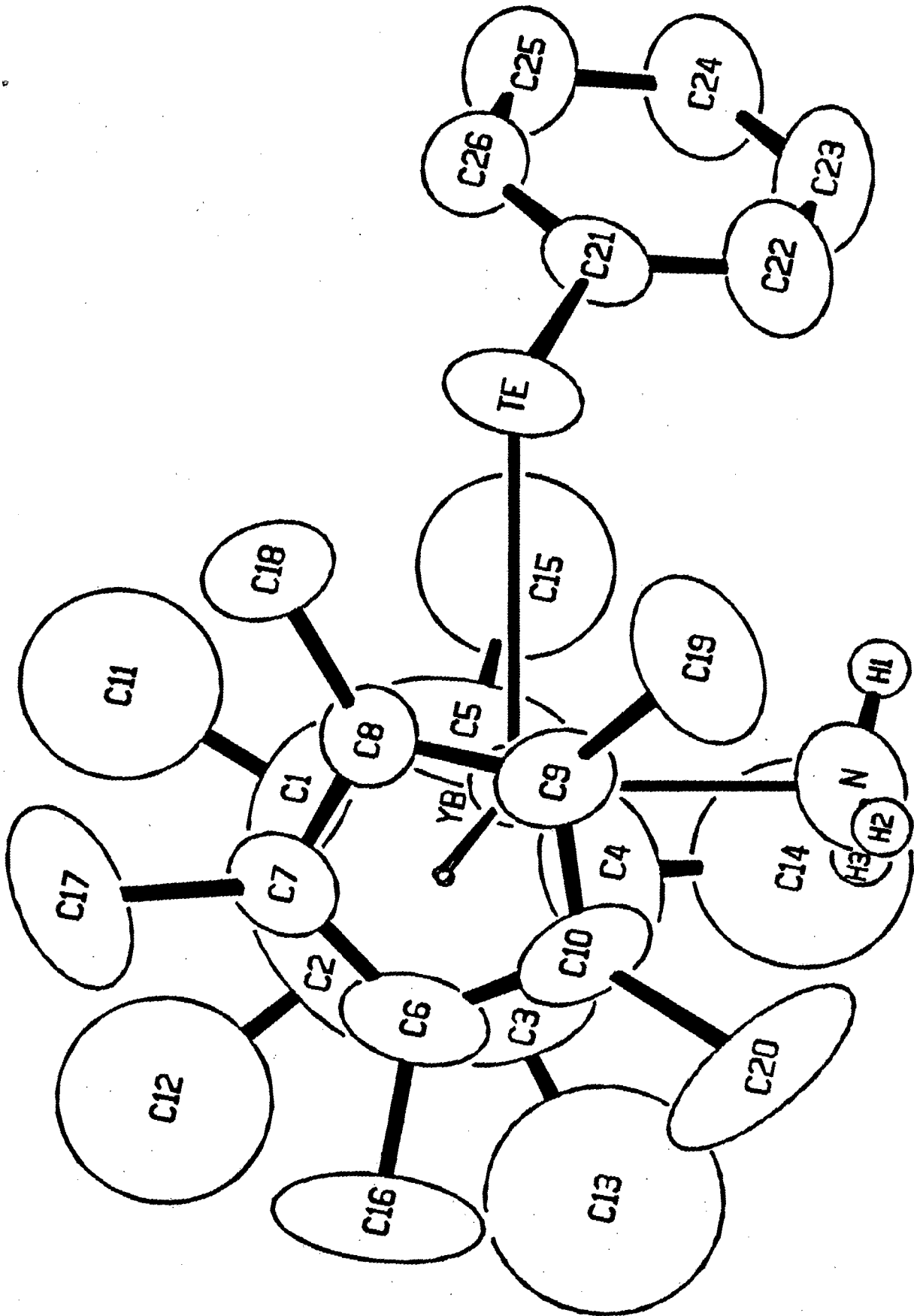
Table V.

Comparison of Bond Length and Bond Angle  
Data for Some Sulfur and Tellurium Compounds

Compound	E-X(A)	EEX or XEX(deg)	E-M(A)	Reference
Me <sub>2</sub> S	1.807(1)	99.5(2)		14a
Me <sub>2</sub> Te	2.142(5)	94(2)		14a
Cl <sub>2</sub> S	2.005(4)	103.0(4)		14b
Cl <sub>2</sub> Te	2.329(3)	97.0(6)		14c
PhSSPh	1.80(1)	106.2(2)		14d
PhTeTePh	2.12(2)	98.9(7)		14e
Re <sub>2</sub> (CO) <sub>6</sub> (μ-Br) <sub>2</sub> <sup>-</sup> (μ-PhSSPh)	1.81(2)	109.1(1)	2.487(6)	14f
Re <sub>2</sub> (CO) <sub>6</sub> (μ-Br) <sub>2</sub> <sup>-</sup> (μ-PhTeTePh)	2.18(2)	101.4(1)	2.794(5)	14g
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Yb(SPh)(NH <sub>3</sub> )	1.771(8)	118.5(2.3)	2.675(5)	5
(Me <sub>5</sub> C <sub>5</sub> ) <sub>2</sub> Yb(TePh)(NH <sub>3</sub> )	2.12(1)	113.0(3)	3.039(1)	This work



Figure Caption: ORTEP drawing of  $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{TePh})(\text{NH}_3)$ . All atoms are shown as 50% probability surfaces except those of the hydrogen atoms which are arbitrary. The carbon atoms C1-C5 and C11-C15 are refined isotropically.



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