Acknowledgment. This work was conducted through the Ames Laboratory which is operated by Iowa State University for the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract W-7405-ENG-82. We thank Dr. J. W. Hachgenei for his help in solving the X-ray crystal structures as well as Drs. Vinko Rutar and R. D. Scott for their help in obtaining temperature-dependent and two-dimensional (COSY) NMR data.

Registry No. I, 121268-41-5; II, 121268-43-7; III, 121268-55-1; IV, 121288-51-5; Va, 121268-44-8; Vb, 121268-45-9; VI, 121268-46-0; VII, 121268-48-2; VIIIa, 121268-49-3; VIIIb, 121268-50-6; IX, 121268-51-7; X, 121268-52-8; XI, 121268-53-9; 2,3-DHT, 1120-59-8; $HPt(PEt_3)_2Cl$, 16842-17-4; $HPt(PPh_3)_2Cl$, 16841-99-9; $HPt(PMePh_2)Cl$, 36464-72-9; $CpW(CO)_3^-$, 12126-17-9; $CpMo(CO)_3Na$, 12107-35-6; $CpFe(CO)_2^-$, 12107-09-4; $CpW(CO)_2(PPh_3)Cl$, 12115-03-6; $H_2OS_3(CO)_9(PPh_3)$, 88510-52-5; $H_2OS_3(CO)_{10}$, 41766-80-7; butane, 106-97-8; 2-chlorotetrahydrothiophene, 22342-03-6; thiophene, 110-02-1.

Supplementary Material Available: Listings of bond distances, bond angles, planes, calculated hydrogen positions, and thermal parameters for $[Pt(PEt_3)_2(DHT{\cdot}H)]PF_6$ and $HOs_3(CO)_9(PPh_3)(DHT{\cdot}H)$ (18 pages); listings of calculated and observed structure factors (43 pages). Ordering information is given on any current masthead page.

Electron-Transfer Reactions of Divalent Ytterbium Metallocenes. Synthesis of the Series $[(Me_5C_5)_2Yb]_2[\mu\text{-E}]$ (E = O, S, Se, or Te) and Crystal Structure of $[(Me_5C_5)_2Yb]_2[\mu\text{-Se}]$

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The preparation of the divalent, base-free compounds $(Me_5C_5)_2M$ (M = Eu or Sm) from their respective diethyl ether complexes is described. Reaction of $(Me_5C_5)_2M$ (M = Yb or Sm) with N_2O gives $[(Me_5C_5)_2M]_2[\mu\text{-O}]$ in high yield. Additionally, $(Me_5C_5)_2Yb$ reacts with Ph_3PS or As_2S_3 or COS, Ph_3PSe or elemental Se, or $n\text{-}Bu_3PTe$ or elemental Te, to give the bridging chalcogenides $[(Me_5C_5)_2Yb]_2[\mu\text{-E}]$ where E is S, Se, or Te, respectively. Magnetic susceptibility studies show that there is no magnetic exchange between the paramagnetic f metals across the bridging group 16 dianions. The variable-temperature magnetic studies also show that $(Me_5C_5)_2Sm$ and $[(Me_5C_5)_2Sm]_2[\mu\text{-O}]$ display temperature-independent paramagnetism as predicted by Van Vleck. The crystal structure of $[(Me_5C_5)_2Yb]_2[\mu\text{-Se}]$ is tetragonal, $P\bar{4}2_1c$, with a = 14.984 (5) Å and c = 19.165 (9) Å. For Z = 4 the calculated density is 1.491 g/cm³. The structure was refined by full-matrix least squares to a conventional R factor of 0.031 [3797 data, $F^2 > 2\sigma(F^2)$]. The selenium atom is on a twofold axis and bonds to two Yb atoms in a nearly linear structure (Yb–Se–Yb angle = 171.09 (6)°). The Yb atom is η^5-bonded to two cyclopentadienyl rings and is on a plane defined by the centers of the two rings and the selenium atom. Distances are Yb–Se = 2.621 (1) Å, Yb–C(av) = 2.609 (7) Å, and ⟨Yb–Cp(ring)⟩ = 2.319 (2) Å, and Yb–Se–Yb is 171.09 (6)°.

The divalent lanthanide metallocene $(Me_5C_5)_2Yb(OEt_2)$ has been shown to be an electron-transfer reagent toward a variety of organic and organo-transition-metal compounds.[1] In these reactions $(Me_5C_5)_2Yb(OEt_2)$ acts as a soluble source of an electron (the reduction potential of $(Me_5C_5)_2Yb(OEt_2)$ in acetonitrile is −1.35 V (SCE)[1d]) and the tight ion-pair complexes that result are often readily soluble in and crystallize from hydrocarbon solvents. The tight ion pairs are of considerable interest since deductions about the electronic structure of the anionic fragments can be made from the solid-state structure. In this way insight into the bonding in negative ions, radical anions, and dianions has been obtained. The electron-transfer chemistry of the trivalent uranium metallocene $(RC_5H_4)_3U$ has been explored pairwise with $(Me_5C_5)_2Yb$, and the results have been used in a similar way.[2] One of the most interesting structural features in the uranium studies is the reaction product of $(MeC_5H_4)_3U(thf)$ and Ph_3PS, $[(MeC_5H_4)_3U]_2[\mu\text{-S}]$, in which the U–S–U angle is 164.9 (5)° and the U–S distance of 2.60 (1) Å is the shortest U–S distance so far determined. There is no magnetic interaction in the chalcogenide-bridged complexes $[(MeC_5H_4)_3U]_2[\mu\text{-E}]$, where E is S, Se, or Te, since the magnetic susceptibility as a function of temperature (4–300 K) shows that the $5f^2$ ions behave as isolated paramagnets.[2b] The related ytterbium(III) complexes $[(Me_5C_5)_2Yb]_2[\mu\text{-E}]$ were of interest

Table I. Some Physical Properties of $[(Me_5C_5)_2Yb]_2[\mu\text{-E}]$

E	mp, °C	color	ν(Yb–E–Yb),[a] cm⁻¹	¹H NMR ($\nu_{1/2}$)[b]
O	334–337	orange	673	24.4 (980)
S	278–282	red	379	13.4 (640)
Se	265–270	purple	247	12.1 (500)
Te	235–238	green		12.6 (290)

[a] The asymmetric stretching frequency, assuming a linear molecule, in the infrared spectrum. The assignment is made by comparison of the individual spectra. The band is of strong intensity. [b] The ¹H NMR spectrum in toluene-d_8 at 32 °C; the chemical shift is expressed in δ units and the width at half-height expressed in hz.

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Table II. Magnetic Susceptibility Studies on $[(Me_5C_5)_2Yb]_2[\mu\text{-}E]$

	6–35 K		100–280 K	
E	μ^a	Θ^b	μ	Θ
O	4.07	−2	4.31	−14
S	3.86	−2	4.32	−23
Se	4.14	−1	4.45	−15
Te	4.20	−2	4.42	−10

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

to see if the behavior patterns discovered in the 5f series applied to the 4f series.

In this paper we describe the series $[(Me_5C_5)_2Yb]_2[\mu\text{-}E]$, where E is O, S, Se, or Te, and the crystal structure of the selenium compound.

Results and Discussion

The bridging chalcogenides were prepared by reaction of $(Me_5C_5)_2Yb(OEt_2)$ and R_3PE, where R is Ph or Bu^n and E is S, Se, or Te. The sulfide can be prepared by reaction of $(Me_5C_5)_2Yb(OEt_2)$ with either COS or As_2S_3, but not from elemental sulfur. The selenium and tellurium complexes can be prepared from the non-metals in their massive state with the metallocene in hydrocarbon solvent. The bridging oxide can be made from $(Me_5C_5)_2Yb(OEt_2)$ and nitrous oxide in hexane, though the yield is low. A better synthetic method is to use base-free $(Me_5C_5)_2Yb$ rather than its diethyl ether complex.

Some physical properties are shown in Table I. The melting points monotonically decrease down the series as does the Yb–E–Yb stretching frequency in the infrared spectrum. The solubility in hydrocarbons is inversely related to the melting point, the oxide being only sparingly soluble whereas the telluride is very soluble in hexane. All the compounds give molecular ions in the mass spectrum, and the molecules have substantial thermal stability. The trends in physical properties are similar to those found for the related tetravalent uranium compounds $[(MeC_5H_4)_3U]_2[\mu\text{-}E]$.[2c] It is interesting to note that the chemical shift of the Me_5C_5 group in the ^{1}H NMR spectra moves downfield on going from oxygen to selenium and then moves upfield on going to tellurium, and the width at half-height decreases substantially from oxygen to tellurium.

Magnetic susceptibility data for all of ytterbium compounds were measured as a function of temperature (4–280 K), and these data are tabulated in Table II. A plot of the χ_M^{-1} vs T (K) for the bridging sulfide is shown in Figure 1. All of the ytterbium(III) compounds prepared in this study give similar plots. The plots of χ_M^{-1} are similar in shape, and the value of the effective magnetic moment are similar to other mononuclear compounds of the type $(Me_5C_5)_2Yb(X)(L)$ where X is an anionic ligand and L is a neutral ligand[1,3] and to the free ion and its coordination compounds.[4] This suggests that the extent

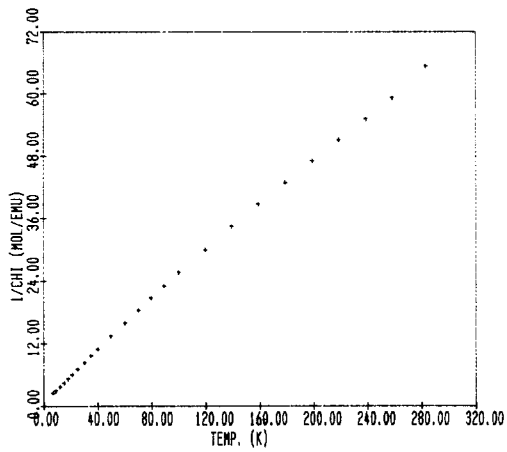

Figure 1. Plot of $\chi_M(\text{corr})^{-1}$ vs T (K) for $[(Me_5C_5)_2Yb]_2[\mu\text{-}S]$.

of magnetic exchange between the $4f^{13}$ ions across the bridging ligand is very small or nonexistent and the Yb(III) centers behave as independent paramagnets. A similar conclusion was reached about the U(IV) centers in $[(MeC_5H_4)_3U]_2[\mu\text{-}E]$.[2c] The plot of χ_M^{-1} vs T from 5 to 35 K for the ytterbium(III) compounds follows the Curie–Weiss law with a small Θ, and μ is slightly lower than that found from 100 to 280 K. The behavior in the high-temperature regime also follows Curie–Weiss behavior with Θ slightly larger than that found at lower temperature and the magnetic moment is ca. 4.4 μ_B for all of the complexes. For the free ion the term symbol is $^2F_{7/2}$ and the magnetic moment is predicted to be 4.50 μ_B at 300 K.[4] The crystal field splitting, the values of which are on the order of kT ($kT = 208$ cm^{-1} at 300 K), will remove the degeneracy of the $^2F_{7/2}$ state, and as a consequence at temperatures less than 100 K the slope of χ_M^{-1} vs T changes as the population of the crystal field levels changes. The crystal field splittings cannot be specified more precisely due to the low symmetry of the complexes, but a rigorous analysis has been done for a Yb(III) complex in D_{3h} symmetry.[4c,5]

With regards to magnetism studies of lanthanide ions with pentamethylcyclopentadienyl ligands, it was of interest to examine the behavior of $(Me_5C_5)_2Sm$[6a] and $[(Me_5C_5)_2Sm]_2[\mu\text{-}O]$[6b] as a function of temperature since Sm(II) and Sm(III), f^6 and f^5 ions, respectively, have interesting magnetic properties as a function of temperature because the splitting of the free ion energy levels is small relative to kT. This behavior has been termed anomalous by Van Vleck.[4a] Trivalent europium compounds are the molecules usually studied as representative f^6 ions, though a trivalent, pentamethylcyclopentadienyl compound cannot be prepared since the $Me_5C_5^-$ is too strongly reducing and the divalent complexes $(Me_5C_5)_2Eu(L)$ are isolated from $EuCl_3$.[7a] The Eu(II) ion is a f^7 ion with term symbol ^8S. The plot of χ_M^{-1} vs T for the base-free $(Me_5C_5)_2Eu$[7b] follows essentially Curie behavior from 5 to 280 K since Θ is near 0 K at 5 and 40 kG with $\mu = 7.70$ and 7.84 μ_B, respectively, close to the spin-only value of 7.94 μ_B.

The anomalous magnetic behavior of Eu(III) and Sm(III) has been treated by Van Vleck for free ions and applied to simple salts.[4a] The anomaly is due to the fact that

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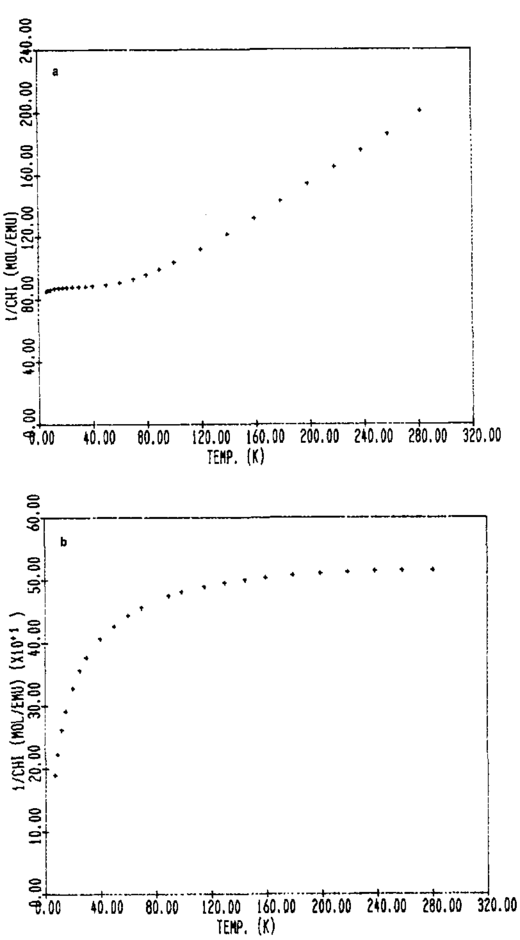

Figure 2. Plot of χ_M(corr)$^{-1}$ vs T (K) for (a) $(Me_5C_5)_2Sm$ and (b) $[(Me_5C_5)_2Sm]_2[\mu\text{-}O]$.

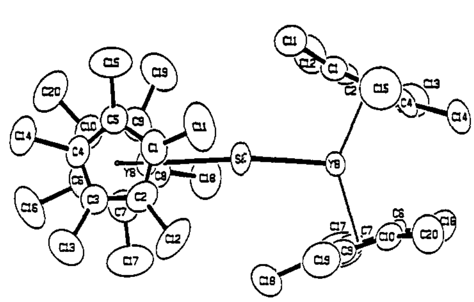

Figure 3. ORTEP drawing of $(Me_5C_5)_2Yb]_2[\mu\text{-}Se]$ viewed down a line connecting the centroids of the rings; thermal ellipsoids are at 50% probability level.

for the Eu(III) and Sm(II) free ions of f^6 electron configuration with term symbol $^7F_0$, the separation of the J = 0 and J = 1 states is ca. 300 cm^{-1} and the separation of the J = 1 and J = 2 states is ca. 200 cm^{-1}, both of which are on the order of kT. Similarly for Sm(III), the free ion ground-state term symbol is $^6H_{5/2}$ and the $J = {}^5/_2$ to $J = {}^7/_2$ transition energy is ca. 900 cm^{-1}, again on the order of $3kT$. In contrast, in the free ion Yb(III) the $J = {}^7/_2$ to $J = {}^5/_2$ transition energy is ca. 10000 cm^{-1}, much larger than kT. When the separation of the ground state from the excited state or states is on the order of kT, complex behavior results. Plots of χ_M^{-1} vs T for simple salts show that f^5 and f^6 ions show temperature-independent paramagnetism (TIP).[4] The plot of χ_M^{-1} vs T for $(Me_5C_5)_2Sm$ shown in Figure 2a is similar to that found for $(Me_5C_5)_2Sm(thf)(OEt_2)$, and these are very similar to those found in simple europium(III) salts.[4] The slope of χ_M^{-1} vs T, when most of the electrons are in the ground state at low T, shows that χ_M is independent of temperature, and as T increases, the J = 1 and J = 2 states become populated so that at 300 K, μ = 3.4–3.5 μ_B according to Van Vleck's model. For $(Me_5C_5)_2Sm(thf)(OEt_2)$ at 40 kG the value of χ_M(corr) at 280.0 K is 4.74 × 10^{-3} emu mol^{-1} which gives μ(280.0 K) of 3.26 μ_B since $\mu = 2.828\,(\chi_M T)^{1/2}$.[8] For $(Me_5C_5)_2Sm$ at 5 kG the value of χ_M(corr) at 281.7 K is 5.016 × 10^{-3} emu mol^{-1} and μ(281.7 K) is 3.36 μ_B. At 40 kG χ_M(corr) is 5.032 × 10^{-3} emu mol^{-1} and μ(282.7 K) is 3.37 μ_B. These solid-state values are in good agreement with the literature values for $(Me_5C_5)_2Sm(thf)_2$ of χ_M(296 K) = 5.490 × 10^{-3} emu mol^{-1} and μ(296 K) = 3.6 μ_B[6c] and for $(Me_5C_5)_2Sm$ of χ_M (297 K) = 5.70 × 10^{-3} emu mol^{-1} and μ(297 K) = 3.7 μ_B[6a] as reported by Evans using the Evans' NMR method.

As stated above, Sm(III) shows temperature-independent paramagnetism (TIP) and $[(Me_5C_5)_2Sm]_2[\mu\text{-}O]$ illustrates this very well. The plot of χ_M^{-1} vs T is shown in Figure 2b, and it is similar to that observed for simple Sm(III) salts and explained by Van Vleck.[4] The magnetic moment, evaluated at 300 K, is 1.53 μ_B per Sm(III) which is close to that predicted by Van Vleck of 1.55–1.65 μ_B and found in solution by Evans[6b] (1.8 μ_B at 298 K).

The detailed magnetic susceptibility studies of the pentamethylcyclopentadienyl complexes of the lanthanides reported here and elsewhere[1] are revealing relative to the nature of the metal–ring bonding. In the mononuclear compounds the observed shape of the χ_M^{-1} vs T plots and the value of μ shows that the crystal field splitting caused by the pentamethylcyclopentadienyl ligand is not very different from that caused by negatively charged ligands in simple salts or that of the free ion. The small crystal field splitting due to the $Me_5C_5^-$ ligand in the lanthanide complexes is in contrast to the high crystal field splitting caused by this ligand in d transition-metal chemistry.[10] It is particularly noteworthy that $(Me_5C_5)_2Mn$ is a low-spin complex in solid state and in gas phase,[11a–c] whereas the $(RC_5C_4)_2Mn$ compounds are either high-spin or spin equilibrium molecules.[11d] The $Me_5C_5^-$ ligand molecular orbitals do not interact (mix) with the lanthanide metal atomic orbitals as much as they do with the d transition-metal atomic orbitals, and the crystal field splitting in the lanthanide metallocenes is small relative to that found in d transition metallocenes. The small crystal field splitting is consistent with the widely held view that the 4f transition metal to ligand bonds are rather more ionic than equivalent bonds in the d transition-metal series.[7b,12] The orbital energy mismatch also rationalizes why the bridging complexes $[(Me_5C_5)_2M]_2[\mu\text{-}E]$ do not show magnetic exchange coupling.

The principal structural features of interest in the bridging chalcogenide molecules were the angle at the chalcogenide atom and the metal–chalcogenide distance.

(8) Using the slope of χ_M(corr)$^{-1}$ vs T from T = 100 K to T = 280 K to calculate the magnetic moment, since $\chi_M = C(T - \Theta)^{-1}$ and $\mu = 2.828C^{1/2}$, gives μ = 3.76 μ_B and Θ = −93 K for $(Me_5C_5)_2Sm(thf)(OEt_2)$ and μ = 3.84 μ_B and Θ = −84 K for $(Me_5C_5)_2Sm$, at 40 kG.

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Table III. Positional and Thermal Parameters with Estimated Standard Deviations for $[Me_5C_5]_2Yb[\mu\text{-}Se]$

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Yb	0.04694 (2)	0.33203 (2)	0.15232 (2)	3.266 (6)
Se	0	1/2	0.14169 (6)	4.85 (3)
C(1)	−0.0506 (6)	0.3107 (5)	0.0406 (4)	4.9 (2)
C(2)	−0.1001 (5)	0.2757 (6)	0.0958 (4)	4.9 (2)
C(3)	−0.0561 (5)	0.1980 (5)	0.1196 (4)	4.5 (2)
C(4)	0.0212 (5)	0.1870 (4)	0.0792 (4)	4.6 (2)
C(5)	0.0254 (6)	0.2569 (5)	0.0314 (4)	4.6 (2)
C(6)	0.1364 (5)	0.2381 (5)	0.2434 (5)	4.9 (2)
C(7)	0.1027 (6)	0.3127 (6)	0.2805 (4)	5.1 (2)
C(8)	0.1468 (6)	0.3893 (5)	0.2551 (4)	4.8 (2)
C(9)	0.2049 (6)	0.3652 (6)	0.2033 (5)	5.2 (2)
C(10)	0.1998 (5)	0.2691 (6)	0.1955 (5)	5.3 (2)
C(11)	−0.0800 (11)	0.3876 (8)	−0.0077 (7)	8.5 (4)
C(12)	−0.1896 (7)	0.3104 (8)	0.1199 (8)	8.6 (4)
C(13)	−0.0951 (8)	0.1354 (7)	0.1757 (6)	7.2 (3)
C(14)	0.0816 (7)	0.1036 (6)	0.0776 (6)	6.5 (3)
C(15)	0.0967 (10)	0.2681 (11)	−0.0249 (7)	9.1 (5)
C(16)	0.1213 (8)	0.1390 (7)	0.2630 (7)	7.6 (3)
C(17)	0.0366 (8)	0.3086 (12)	0.3413 (7)	9.1 (4)
C(18)	0.1414 (9)	0.4835 (8)	0.2874 (6)	7.5 (3)
C(19)	0.2677 (8)	0.4245 (8)	0.1595 (8)	8.0 (4)
C(20)	0.2642 (7)	0.2145 (7)	0.1517 (8)	8.5 (4)

[a] $B_{eq} = {}^1/_3\sum B_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table IV. Selected Distances (Å) and Angles (deg) in $[(Me_5C_5)_2Yb]_2[\mu\text{-}Se]$

Bond Distances			
Yb–Cp(1)[a]	2.317	Yb–C(6)	2.613 (7)
Yb–Cp(2)	2.321	Yb–C(7)	2.611 (7)
Yb–Se	2.621 (1)	Yb–C(8)	2.618 (7)
Yb–C(1)	2.612 (7)	Yb–C(9)	2.608 (8)
Yb–C(2)	2.596 (7)	Yb–C(10)	2.612 (7)
Yb–C(3)	2.610 (6)	⟨C(Cp)–C(Cp)⟩	1.406 (21)
Yb–C(4)	2.615 (6)	⟨C(Cp)–C(Me)⟩	1.535 (12)
Yb–C(5)	2.596 (7)		
Bond Angles			
Yb–Se–Yb	171.09 (6)	Cp(2)–Yb–Se	110.63
Cp(1)–Yb–Se	110.39	Cp(1)–Yb–Cp(2)	138.94

[a] Cp(1) and Cp(2) are the centroids of atoms C(1)–C(5) and C(6)–C(10), respectively.

The only complex that we have been able to get as X-ray quality crystals to date is the bridging selenide complex. An ORTEP diagram is shown in Figure 3, positional parameters are in Table III, some bond lengths and angles are in Table IV, and crystal data are in Table V. The molecule lies on a crystallographic twofold axis with a Yb–Se–Yb angle of 171.09 (6)°. If the Yb–Se–Yb angle were linear, then the molecule would have idealized S_4 symmetry like the samarium complex $[(Me_5C_5)_2Sm]_2[\mu\text{-}O]$.[6b] The averaged Yb–C distance is 2.609 ± 0.007 Å, and the Yb–ring centroid distance is 2.32 Å, consistent with Yb(III) in seven-coordination.[1,11]

The Yb–Se distance is 2.621 (1) Å. The only other ytterbium–selenium distances are 2.89 Å in $CdYb_2Se_4$[12a] and 2.83 Å in Yb_2Se_3[12b] in which each trivalent ytterbium is six-coordinate. The Yb–Se distance in $[(Me_5C_5)_2Yb]_2[\mu\text{-}Se]$ is short by this comparison. Using $[(Me_5C_5)_2Sm]_2[\mu\text{-}O]$ as a reference and correcting the bond length for the change in bridging ligand[13] and for the change in the identity of the metal atoms from Sm to Yb in seven-coordinations[14] predict that the Yb–Se distance should be ca. 0.40 Å longer than the Sm–O distance. In fact the Yb–Se distance is 0.63 Å longer. Using the U–S distance in $[(MeC_5H_4)_3U]_2[\mu\text{-}S]$[2c] as a reference and correcting the radius of tetravalent uranium in ten-coordination for trivalent ytterbium in seven-coordination[14] and the radius of sulfur for selenium predict that the Yb–Se distance should be 0.26 Å longer than the U–S distance whereas it is only 0.02 Å longer. Clearly the standard for shortness determines our operational definition of shortness or longness. As pointed out previously,[2c] the near linear Yb–Se–Yb bond angle and the short Yb–Se bond length, as determined by comparison with Yb_2Se_3 or $Cd_2Yb_2S_4$, could imply Yb–Se π-bonding though the lack of magnetic interaction argues against appreciable covalent mixing. On the other hand the near linear Yb–Se–Yb geometry could be as bent as is possible; further bending results in prohibitively large Me_5C_5 nonbonded repulsions. On the basis of the structural information that is currently available to us, it is impossible

Table V. Crystallographic Summary and Data Processing for $[(Me_5C_5)_2Yb]_2[\mu\text{-}Se]$

a,[a] Å	14.984 (5)
c, Å	19.165 (9)
cryst syst	tetragonal
space group	$P\bar{4}2_1c$
V, Å^3	4302.9
d(calcd), g/cm^3	1.491
Z	4
temp, °C	23.0
empirical formula	$C_{40}H_{60}Se_1Yb_2$
f(000), e	1896
fw	965.96
wavelength ($K\alpha_1$, $K\alpha_2$), Å	0.709 30, 0.713 59
cryst size, mm	0.30 × 0.30 × 0.72
abs coeff, cm^{-1}	51.68
abs corr range	3.30–4.28
cryst decay corr range	0.97–1.13
2*θ* limits, deg	14.7–55.1
hkl limits	*h* 0,19; *k* 0,19; *l* −24,19
scan width, deg	1.20 + 0.693 tan *θ*
no. of stds	3
no. of reflctns between stds	250
variatn of standards, %	3.44, 2.60, 2.46
no. of scan data	9998
no. of unique reflctns	4830
R_{int}[b]	0.033
no. of nonzero weighted data	3797 ($F^2 > 2\sigma$)
p[c]	0.060
extinctn *k*[d]	5.91 × 10^{-8}
max % extinctn corr, %	8.1
no. of parameters	195
R (nonzero wtd data)[e]	0.031
R_w[f]	0.039
R (all data)	0.048
goodness of fit[g]	1.00
max shift/esd in least-squares	0.0027
max/min in diff map, e/Å^3	0.96, −0.67

[a] Unit cell parameters from a least-squares fit to the setting angles of the unresolved Mo Kα components of 32 reflections (21° < 2θ < 36°). [b] R_{int} = agreement factor between equivalent or multiply measured reflections = $\sum[I_{hkl} - \langle I_{hkl}\rangle]/\sum\langle I_{hkl}\rangle$. [c] The assigned weights to *F*, $1.0/[\sigma(F)]^2$, derived from $\sigma(F^2) = [S^2 + (pF^2)^2]$, where S^2 is the variance of counting statistics and *p* is an empirical value that results in the weighted residuals of the strong and weak reflection being comparable. [d] Simple extinction correction, $F_o(\text{corr}) = (1 + kI)F_o$, where *I* is the uncorrected intensity and F_o is the observed scattering amplitude. [e] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [f] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$. [g] σ_1 = error in observation of unit weight = $[\sum(w(|F_o| - |F_c|)^2)/(n_o - n_v)]^{1/2}$, where n_o is the number of observations and n_v is the number of variables.

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to choose between these two extreme explanations. More structural information is desireable; we are trying to grow single crystals of the other chalcogenide molecules reported here.[3b]

Experimental Section

All reactions were done under nitrogen. Analyses were done by the microanalytical laboratory of this department. Infrared spectra were recorded as Nujol mulls with the use of a Nicolet 5DX-FTIR instrument. Proton NMR spectra were measured on a JEOL FX-90Q instrument operating at 89.56 MHz on solutions in C_6D_6 or C_7D_8. Chemical shifts are expressed in δ values with positive values to high frequency of tetramethylsilane. Magnetic susceptibility studies were done similar to those previously described.[17] The mass spectra were recorded on a AEI-MS-9 instrument using electron-impact ionization and are expressed as M^+ (observed intensity, calculated intensity); in each case the base peak is $M - C_5Me_5^+$.

[(Me$_5$C$_5$)$_2$Yb]$_2$[μ-O]. Base-free $(Me_5C_5)_2Yb$[7b,18] (0.41 g, 0.92 mmol) in pentane (40 mL) was treated with nitrous oxide (3 atm) in a heavy-walled pressure bottle for 4 h. The pressure was released, and the orange solution and precipitate were transferred to a Schlenk tube. The volume of the solution was reduced to ca. 5 mL, and the solution was cooled to −25 °C to effect complete precipitation. The solid was collected and then crystallized from a minimum amount of hot toluene as orange crystals in 55% (0.23 g) yield. Anal. Calcd for $C_{40}H_{60}OYb_2$: C, 53.2; H, 6.70. Found: C, 52.7; H, 6.78. IR: 2728 w, 1650 w, 1497 m, 1302 w, 1168 sh, 1154 w, 1133 sh, 1024 m, 957 w, 895 sh, 863 w, 756 w, 735 sh, 724 w, 695 m, 673 s, 641 w, 625 m, 593 w, 566 w, 478 w, 432 sh, 384 m br, 309 sh, 301 vs br, 283 sh cm^{-1}. MS: M^+, 897 (11.9, 3.82); 898 (20.2, 15.1); 899 (44.0, 34.6); 900 (45.2, 58.3); 901 (61.3, 85.5); 902 (100, 100); 903 (78.6, 90.9); 904 (87.5, 92.4); 905 (46.4, 49.5); 906 (25.0, 45.3); 907 (19.0, 16.5); 908 (11.3, 9.70). Reaction of $(Me_5C_5)_2Yb(OEt_2)$ with N_2O in hydrocarbon solution gives a low yield (18%) of the bridging oxide.

[(Me$_5$C$_5$)$_2$Yb]$_2$[μ-S]. An intimate mixture of $(Me_5C_5)_2Yb(OEt_2)$ (0.81 g, 1.6 mmol) and Ph_3PS (0.23 g, 0.78 mmol) was dissolved in toluene (60 mL), and the red solution was refluxed for 5 h. After being cooled to room temperature the red solution was concentrated to ca. 20 mL and cooled to −20 °C. The sulfide was isolated as deep red needles by filtration in 49% yield (0.35 g). Anal. Calcd for $C_{40}H_{60}SYb_2$: C, 52.3; H, 6.58; S, 3.49. Found: C, 53.6; H, 6.71; S, 3.44. IR: 2725 m, 1492 m, 1256 m, 1212 m, 1152 w, 1092 m, 1064 w, 1022 m, 800 w, 728 s, 694 w, 666 m, 638 w, 588 w, 517 w, 482 w, 462 w, 379 vs, 310 vs cm^{-1}. MS: M^+, 914 (9.0, 15.0); 915 (36, 34); 916 (61, 57); 917 (91, 85); 918 (100, 100); 919 (97, 92); 920 (96, 94); 921 (55, 52); 922 (50, 48); 923 (20, 18). The bridging sulfide can also be prepared from $(Me_5C_5)_2Yb(OEt_2)$ and As_2S_3 in hexane in 51% yield or with carbonyl sulfide in diethyl ether in 17% yield. In each case the isolated material was identified by mp and IR.

[(Me$_5$C$_5$)$_2$Yb]$_2$[μ-Se]. An intimate mixture of $(Me_5C_5)_2Yb(OEt_2)$ (0.67 g, 1.3 mmol) and Ph_3PSe[19] (0.22 g, 0.65 mmol) was stirred in hexane (70 mL) for 1 h. The purple solution was filtered, and the filtrate was concentrated to ca. 15 mL. Cooling the filtrate to −25 °C for 2 days afforded purple crystals that were collected and dried under reduced pressure in 64% (0.40 g) yield. Anal. Calcd for $C_{40}H_{60}SeYb_2$: C, 49.7; H, 6.26. Found: C, 49.9; H, 6.49. The infrared spectrum is essentially superimposable on that of the bridging sulfide spectrum with exception of the bands at 379 and 247 cm^{-1}. MS: M^+, 959 (9, 7); 960 (16, 15); 961 (33, 27); 962 (50, 44); 963 (76, 64); 964 (84, 82); 965 (100, 93); 966 (92, 100); 967 (70, 82); 968 (56, 80); 969 (31, 45); 970 (15, 40); 971 (8, 16). The bridging selenide can also be prepared by stirring $(Me_5C_5)_2Yb(OEt_2)$ with selenium metal in hexane for 12 h in 66% isolated yield.

[(Me$_5$C$_5$)$_2$Yb]$_2$[μ-Te]. Tri-*n*-butylphosphine telluride[20] (0.37 g, 1.1 mmol) in hexane (45 mL) at −30 °C was added to $(Me_5C_5)_2Yb(OEt_2)$ (1.2 g, 2.2 mmol) in hexane (80 mL) at room temperature, and the blue-green solution was stirred for 1 h. The solution was filtered, and the filtrate was concentrated to ca. 20 mL and cooled (−20 °C) for several days to give black-green crystals, 0.47 g (41% yield), which were collected and dried under reduced pressure. Anal. Calcd for $C_{40}H_{60}TeYb_2$: C, 47.4; H, 5.96. Found: C, 48.4; H, 6.37. The infrared spectrum was essentially identical with that of the bridging sulfide except for the absorption at 379 cm^{-1} in the latter compound. MS: M^+, 1008 (14, 11); 1009 (22, 21); 1010 (33, 36); 1011 (54, 53); 1012 (76, 71); 1013 (85, 87); 1014 (92, 100); 1015 (100, 96); 1016 (97, 99); 1017 (67, 68); 1018 (63, 65); 1019 (32, 31); 1020 (19, 25). The bridging telluride may be prepared by stirring $(Me_5C_5)_2Yb(OEt_2)$ and an excess of tellurium metal in hexane for 3 days in 54% isolated yield.

(Me$_5$C$_5$)$_2$Sm(OEt$_2$)(thf). A solution of NaC_5Me_5 (1.73 g, 10.9 mmol) in tetrahydrofuran (50 mL) was added to $SmI_2(thf)_2$[21] (3.00 g, 5.47 mmol) in tetrahydrofuran (80 mL), and the brown-red suspension was stirred for 1 h. The solution was filtered, and the filtrate was evaporated to dryness. The residue was extracted with diethyl ether (50 mL), and the brown solution again was evaporated to dryness. The brown residue was redissolved in diethyl ether (25 mL), and the solution was concentrated to incipient crystallization and then cooled to −25 °C. The brown prisms were collected and dried under reduced pressure. The mother liquor gave a second crop of crystals in a combined yield of 78% (2.1 g); mp 134–137 °C. A sample of the complex was dissolved in benzene-d_6 and then hydrolyzed with water. The ^{1}H NMR spectrum of the benzene solution contained equal amounts of diethyl ether and tetrahydrofuran. ^{1}H NMR (C_7D_8, 32 °C): δ 16.03, 4 H ($\nu_{1/2}$ = 16 Hz); 10.99, *t*, J = 6.6 Hz, 6 H; 2.98, 30 H ($\nu_{1/2}$ = 2 Hz); 2.52, 4 H ($\nu_{1/2}$ = 11 Hz); −0.59, q, J = 6.6 Hz, 4 H. IR: 2720 m, 1148 m, 1120 w, 1080 s, 1061 m, 1035 s, 1009 w, 949 w, 932 w, 897 vs, 838 w, 797 w, 725 w, 258 vs cm^{-1}.

(Me$_5$C$_5$)$_2$Sm(thf). The mixed diethyl ether, tetrahydrofuran complex prepared above (0.30 g, 0.53 mmol) was dissolved in toluene (30 mL) and stirred for 1 h, then the brown solution was warmed to 45 °C, and the toluene was removed under reduced pressure to yield a green residue. The residue was dissolved in hexane, the now brown-red solution was filtered, and the filtrate was concentrated to ca. 10 mL and cooled (−25 °C). The large green-brown needles (0.25 g, 96% yield) were collected and dried under reduced pressure; mp 155–157 °C. Anal. Calcd for $C_{24}H_{38}OSm$; C, 58.5; H, 7.77. Found: C, 58.1; H, 7.75. A sample of the compound was dissolved in benzene-d_6 and then hydrolyzed with water. The ^{1}H NMR spectrum of the benzene phase showed resonances due to tetrahydrofuran and no resonances due to diethyl ether. ^{1}H NMR (C_7D_8, 32 °C): δ 11.94, 4 H ($\nu_{1/2}$ = 29 Hz); 3.73, 30 H ($\nu_{1/2}$ = 2 Hz); −0.11, 4 H ($\nu_{1/2}$ = 12 Hz). IR: 2720 m, 1307 w, 1255 m, 1208 w, 1150 m, 1084 s, 1031 w, 977 w, 945 m, 890 s br, 800 s, 726 vs, 610 w, 576 w, 350 m br, 280 vs cm^{-1}.

(Me$_5$C$_5$)$_2$Sm(OEt$_2$). Samarium diiodide bis(tetrahydrofuran) was ground into a fine powder and heated under reduced pressure at 160 °C for 16 h. During this time the color changed from blue-gray to deep green. The green material was shown to be essentially free of tetrahydrofuran by a very thick Nujol mull infrared spectrum. The base-free SmI_2 (4.34 g, 10.7 mmol) and NaC_5Me_5 (3.17 g, 20.0 mmol) in diethyl ether (250 mL) were stirred for 17 h. The brown-green solution was filtered, and the volume of the filtrate was reduced to ca. 125 mL. Cooling (−15 °C) yielded large deep green needles. Two additional crops of crystals were harvested from the mother liquor, giving a combined yield of 3.6 g (73%); mp 190–192 °C. Anal. Calcd for $C_{24}H_{40}OSm$: C, 58.2; H, 8.15. Found: C, 58.0; H, 8.20. A sample of the complex was hydrolyzed in C_6D_6 with D_2O. Examination of the C_6D_6 layer by ^{1}H NMR spectroscopy showed resonances due to diethyl ether and Me_5C_5D in a 1:1 ratio. ^{1}H NMR (C_7D_8, 31 °C): δ 20.73, 6 H, t, J = 6 Hz; 2.77, 30 H ($\nu_{1/2}$ = 4 Hz); −4.50, 4 H, q, J = 6 Hz. $^{13}C\{^1H\}$ NMR (C_7D_8, −30 °C): δ 136 (OCH_2Me), 102.6 (C_5Me_5), 94.94 (OCH$_2$*Me*), −137.9 (C_5Me$_5$). The methylene carbon resonance of the diethyl ether could not be observed at 30 °C as it overlapped with the aryl resonances of C_6D_6. IR: 2723 m, 1468 m, 1164 m, 1145 s, 1080 vs, 1038 s, 1018 m, 929 m, 837 s, 818 w,

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799 w, 774 w, 731 w, 635 w, 611 m, 589 w, 443 w, 364 m br, 307 m, 268 s br cm^{-1}. This complex has been characterized by a single-crystal X-ray crystallographic study.[22]

$(Me_5C_5)_2Sm$. The diethyl ether complex (3.9 g, 7.8 mmol) was dissolved in toluene (200 mL), the deep green solution was heated to 100 °C, and the solvent was slowly removed (ca. 2 h) under reduced pressure. The residue was dissolved in an additional 100 mL of toluene, and the "toluene reflux" was repeated. The green residue was dissolved in toluene (200 mL) and filtered, and the filtrate was concentrated to ca. 120 mL. Cooling to −25 °C gave large brown-green blocks. Two additional crops of crystals were obtained from the mother liquor in a combined yield of 2.7 g (80%); mp 214–217 °C. The compound sublimed at 120–130 °C/(10^{-3} mm). A sample of the compound was hydrolyzed with water in C_6D_6, and examination of the hydrolysate by ^1H NMR spectroscopy showed no diethyl ether resonances. The IR and ^1H NMR spectra were identical with those previously reported,[6a,d] though the region below 800 cm^{-1} was not measured. IR: 2712 w, 1649 w br, 1577 vw, 1497 w, 1436 s, 1162 w, 1146 w, 1058 w, 1018 w, 950 w, 721 w, 656 w, 628 w, 602 w, 557 w, 477 w, 372 sh, 359 m, 299 sh, 268 s cm^{-1}. MS: M^+, 414 (12, 12); 415 (2.5, 2.6); 417 (62, 56); 418 (55, 55); 419 (60, 63); 420 (37, 40); 421 (8.8, 7.4); 422 (100, 100); 423 (26, 23); 424 (79, 87); 425 (16, 19); 426 (1.4, 2.0). Higher mass peaks due to $(Me_5C_5)_2Sm_2$ and $(Me_5C_5)_3Sm_2$ ions are observed in variable abundances though always in small to moderate amounts relative to M^+.

$[(Me_5C_5)_2Sm]_2[\mu\text{-}O]$. Base-free $(Me_5C_5)_2Sm$ (0.31 g, 0.74 mmol) was dissolved in toluene (30 mL), the solution was transferred to a thick-walled pressure bottle, and the bottle was pressurized to 3 atm with N_2O. The color of the solution changed from green to yellow, and the solution was stirred for 6 h. The solution was transferred to a Schlenk flask, and the volume of the solution was reduced to ca. 10 mL. Cooling afforded yellow flakes. A second crop of crystals was obtained from the mother liquor in a combined yield of 60% (0.19 g). The ^1H NMR spectrum was identical with that previously reported.[6h] The mass spectrum does not show a M^+, but a $M - C_5Me_5^+$ envelope is observed. The bridging oxide can also be prepared from $(Me_5C_5)_2Sm(OEt_2)$ and N_2O in toluene in 43% yield.

$(Me_5C_5)_2Eu(OEt_2)$. Europium diiodide (2.7 g, 6.7 mmol), prepared as described in ref 23 or by heating $EuI_2(thf)_2$[21] at 180 °C for 15 h under reduced pressure, and NaC_5Me_5 (2.0 g, 13 mmol) were stirred in diethyl ether (150 mL) for 17 h. The solution was filtered, and the volume of the filtrate was reduced to ca. 180 mL; cooling (−25 °C) gave dark red crystals that were collected and dried under reduced pressure. A second crop of crystals was obtained from the mother liquor in a combined yield of 2.2 g (69%); mp 192–195 °C. Anal. Calcd for $C_{24}H_{40}OEu$: C, 58.1; H, 8.12. Found: C, 57.9; H, 8.07. IR: 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}. A sample of the complex in C_6D_6 was hydrolyzed with D_2O. Examination of the benzene extract by ^1H NMR spectroscopy showed that diethyl ether and C_5Me_5D were present in a 1:2 ratio. The single-crystal X-ray structure of this complex has been determined.[22]

$(Me_5C_5)_2Eu$. The europium diethyl ether complex (2.2 g, 4.4 mmol) was dissolved in toluene (200 mL), and the orange-red solution was heated to 100 °C, and the toluene was removed slowly under reduced pressure (2–3 h) in a greaseless Schlenk flask. The residue was dissolved in toluene (200 mL), and the solvent was removed as before. The orange residue was dissolved in hexane (250 mL), the volume was reduced to ca. 180 mL, cooling to −25 °C afforded a total of two additional crops of crystals in a total yield of 1.6 g (87%); mp 219–222 °C. The complex sublimed at 120–130 °C (10^{-3} mm). Anal. Calcd for $C_{20}H_{30}Eu$: C, 56.9; H, 7.17. Found: C, 55.1; H, 7.18. A sample of the compound in C_6D_6 was hydrolyzed with D_2O. Examination of the benzene extract by ^1H NMR showed resonances due to C_5Me_5D only. IR: 2725 w, 1647 w, 1494 m, 1434 vs, 1160 w, 1149 sh, 1017 s, 948 w, 720 w, 628 w, 602 w, 584 w, 569 sh, 547 w, 478 w br, 398 sh, 364 sh, 351 m, 263 vs br cm^{-1}. MS: M^+, 421 (90.5, 89.6); 422 (10.6, 20.0); 423 (100, 100); 424 (11.8, 22.0). This compound has been studied by single-crystal X-ray crystallography.[6d] In an attempt to get base-free $(Me_5C_5)_2Eu$, the "toluene-reflux" method was applied to $(Me_5C_5)_2Eu(thf)(OEt_2)$.[7a] The mono-tetrahydrofuran complex, $(Me_5C_5)_2Eu(thf)$[7a] was isolated as shown by mp and IR.

X-ray Crystallography of $[(Me_5C_5)_2Yb]_2[\mu\text{-}Se]$. Purple air-sensitive crystals were sealed inside quartz capillaries in an argon-filled drybox. X-ray diffraction intensities (θ–2θ scans) were obtained by using a modified Picker FACS-I automatic diffractometer equipped with a Mo X-ray tube and a graphite monochromator. The data were corrected for absorption (analytical method), crystal decay, and Lorentz and polarization effects. Experimental details of the data collection are tabulated in Table V. The ytterbium position was deduced from three-dimensional Patterson maps, and subsequent least-squares refinements and electron density maps revealed the rest of the non-hydrogen positions. Positional and anisotropic thermal parameters were refined by full-matrix least squares; hydrogen atoms were not included. Atomic scattering factors and anomalous dispersion terms were taken from the ref 24. Statistical results and other details of the least-squares refinements are tabulated in Table V.

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Supplementary Material Available: Tables of thermal parameters, additional distances and angles, and least-squares planes (3 pages); a listing of amplitudes and structure factor (9 pages). Ordering information is given on any curent masthead page.

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