Articles

Reaction of $(C_5Me_5)_2Yb(ER)(NH_3)$ with Me_3Al. Formation of $(C_5Me_5)_2Yb(AlMe_4)$ and $[(C_5Me_5)_2Yb(ER)(AlMe_3)_2]_2$

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Addition of 3 molar equiv of $AlMe_3$ to $(Me_5C_5)_2Yb(ER)(NH_3)$ gives two types of products depending on the identity of the ER group. When ER is $OSiMe_3$ or TePh, the isolated metallocene is $[(Me_5C_5)_2Yb(Me_4Al)]_2$, which exists as an equilibrium between monomeric and dimeric forms in toluene solution. When ER is $OCMe_3$, SPh, S-*p*-tolyl, or SePh, the isolated metallocenes have the stoichiometry $(Me_5C_5)_2Yb(ER)(Me_3Al)_2$. The ^1H NMR spectra of these molecules show that several species are present in solution. The crystal structure of the S-*p*-tolyl derivative shows that two $(Me_5C_5)_2Yb$ fragments are bridged by two Me_3Al(S-*p*-tolyl)-$AlMe_3$ units by way of nearly linear $Yb\cdots H_3C{-}Al$ bonds.

Introduction

The synthetic methods used to prepare the base-free ytterbocene methyl derivatives Cp'_2YbMe, where Cp′ represents either C_5H_5 or a substituted cyclopentadienyl group, depends on the nature of the starting materials, the substituents on the cyclopentadienyl ligand, the methyl transfer reagent, and the solvent. This complexity is not apparent from the synthesis of the simplest methyl derivative, $(C_5H_5)_2YbMe$, which was described 28 years ago.[1] In this synthesis $(C_5H_5)_2YbCl$, which is a chloride-bridged dimer in the solid state, is allowed to react with methyllithium in a mixture of tetrahydrofuran−diethyl ether solvent.[2] The orange $(C_5H_5)_2YbMe$ is sparingly soluble in aromatic hydrocarbons but the degree of association in solution was not determined. Evans reproduced this synthetic route and extended it to the C_5H_4Me derivatives.[3,4] These authors noted that careful attention to experimental details is important in order to get pure material. An alternate synthetic route to $(C_5H_5)_2YbMe$ involving the cleavage of the tetramethylaluminate, $(C_5H_5)_2Yb(\mu\text{-}Me)_2AlMe_2$, was developed by Lappert. The base-free tetramethylaluminate is prepared from the reaction of $LiAlMe_4$ with $(C_5H_5)_2YbCl$ in toluene, even though both reagents are very sparingly soluble in that solvent.[5] The tetramethylaluminate is a monomer in the solid state and the structure shows two methyl groups that bridge the Yb and Al centers. Addition of a stoichiometric amount of pyridine in toluene results in the formation of sparingly soluble $(C_5H_5)_2YbMe$ and soluble $Me_3Al(py)$. The low solubility of the ytterbium complex is apparently the key to the success of these synthetic routes.

$(C_5H_5)_2YbMe$ crystallizes from warm toluene and it is a dimer in the solid state with bridging methyl groups.[6] The geometry of the bridging methyl groups is similar to those in $Me_2Al(\mu\text{-}Me)_2AlMe_2$. The *t*-butyl substituted derivative, $(C_5H_4CMe_3)_2YbMe$, was also prepared by addition of MeLi to the chloride in a tetrahydrofuran−diethyl ether mixed solvent system and the base-free methyl complex was crystallized from toluene. This complex is also assumed to be dimeric because a dimeric molecular ion was observed in the mass spectrum.[7] The related cerium methyl complex is a dimer in the solid state and the structure consists of two metallocene fragments bridged by two methyl groups, analogous to the ytterbium methyl complex mentioned above.[8]

When synthetic routes similar to those outlined above are applied to the pentamethylcyclopentadienyl derivatives, the base-free methyl derivatives are not obtained. Thus, addition of 1 or 2 molar equiv of MeLi to $(Me_5C_5)_2YbCl_2Li(OEt_2)_2$ in diethyl ether gives the anionic derivatives $(Me_5C_5)_2Yb(Cl)(Me)Li(OEt_2)_2$ or $(Me_5C_5)_2Yb(Me)_2Li(OEt_2)_2$, respectively. When the reaction solvent is tetrahydrofuran, $(Me_5C_5)_2Yb(Me)(THF)$ is isolated.[9] The inability to isolate the base-free $(Me_5C_5)_2YbMe$ is surprising since the corresponding lutetium methyl com-

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plex is isolable.[10,11] In the solid state, the lutetium methyl complex is dimeric but it is not isostructural with the C_5H_5 or C_5H_4Me derivatives mentioned above since the two $(Me_5C_5)_2Lu$ fragments are bridged by a single methyl group.[12] The unusual and fascinating reactions of the lutetium methyl complex make the ytterbium analogue an important synthetic target.

In this paper we describe experiments aimed at preparing $(Me_5C_5)_2YbMe$. The strategy is to use Me_3Al as the methyl transfer reagent since it is ether-free and soluble in hydrocarbon solvents, in contrast to common methyl transfer reagents such as MeLi, MeMgX, or $MgMe_2$.[13] The ytterbocene starting materials, $(C_5Me_5)_2Yb(ER)(NH_3)$, were chosen because they are readily prepared and soluble in hydrocarbons and the ER leaving group can potentially exchange with one of the methyl groups in $AlMe_3$.[14] Additionally, the coordinated ammonia can be removed as the aliphatic hydrocarbon soluble $Me_3Al(NH_3)$.[15] Although the base-free methyl complex was not successfully obtained by this route, some unusual reaction patterns and an unusual structure was observed for one of the products.

Results and Discussions

Addition of 3 molar equiv of Me_3Al in pentane to a toluene solution of either $(Me_5C_5)_2Yb(OSiMe_3)(NH_3)$ or $(Me_5C_5)_2Yb(TePh)(NH_3)$ gives dark blue solutions from which the tetramethylaluminate $[(Me_5C_5)_2Yb(AlMe_4)]_2$ **(1)** may be crystallized on cooling (eq 1). Complex **1** can also be prepared by the metathetical reaction of $(Me_5C_5)_2YbCl(THF)$ with $LiAlMe_4$. The yield from either synthetic route is about 70%. The tetramethylaluminate **1** is a high-melting solid (mp 220−222 °C) that is not volatile enough to give a molecular ion in the EI mass spectrum.

$$(Me_5C_5)_2Yb(ER)(NH_3) + 3\,AlMe_3 \longrightarrow \qquad (1)$$

$$1/2\,[(Me_5C_5)_2Yb(AlMe_4)]_2 + (RE)AlMe_2 + Me_3Al(NH_3)$$

$$ER = OSiMe_3,\ TePh$$

$$[(Me_5C_5)_2Yb(AlMe_4)]_2 + 2\,py \longrightarrow \qquad (2)$$

$$2\,(Me_5C_5)_2Yb(Me)(py) + 2\,Me_3Al(py)$$

Compound **1**, and some of the others reported here, consistently analyze 1−3% low in carbon in combustion analysis. This is probably due to the fact that, even though the freshly crystallized materials have well-developed faces, exposure to vacuum results in their collapse into a powder and probable loss of Me_3Al. The reaction in eq 2 with pyridine was monitored by NMR spectroscopy to determine the stoichiometry.

Metallocenes of identical stoichiometry to **1** have been isolated for Y, Sm, and Lu.[16−18] In the solid state, the samarium derivative is a dimer in which the two $(Me_5C_5)_2Sm$ fragments are bridged by Me_4Al groups.[18] The bridging Me_4Al groups are rather unusual since two of the methyl groups on each Me_4Al fragment are terminal and two form nearly linear bridges between the two different metals. In solution these three tetramethylaluminate complexes exist in a dimer−monomer equilibrium that is observed by variable-temperature ^1H NMR spectroscopic studies.

The ytterbocene derivative **1** shows similar solution behavior to the metallocenes discussed above. At room temperature, three resonances at δ 247, 5.2, and −26.5 ppm are observed in a relative area ratio of 6:30:6, respectively. These resonances are assigned to the bridging $AlMe_2$ and $(Me_5C_5)_2Yb$ and terminal $AlMe_2$ resonances in species **A**. In addition to these resonances, a set of two less intense resonances is observed at δ 31.5 and 4.0 ppm in a relative area ratio of 6:30 due to the bridging or terminal $AlMe_2$ and $(Me_5C_5)_2Yb$ resonances, respectively, of species **B**. The other methyl resonance was not located for **B**, presumably because it is too broad to be observed. Assuming that the largest resonances in each set correspond to the Me_5C_5 groups, then the ratio of **A** to **B** at 32 °C is 4:1. Increasing the temperature to 79 °C changes the **A**:**B** ratio to 8:1. The population change as a function of temperature is consistent with a dimer−monomer equilibrium, similar to that studied quantitatively in the diamagnetic compounds mentioned above.[16,17] The increase in the **A**:**B** ratio with increasing temperature is consistent with **A** being the monomeric species. In both **A** and **B**, bridge-terminal methyl exchange is slow on the NMR time scale. Heating the sample to 140 °C results in the disappearance of the resonances assigned to the bridging and terminal aluminum methyl groups and they do not reappear on heating to 175 °C. The resonances assigned to the $(Me_5C_5)_2Yb$ groups sharpen and shift as expected for a paramagnetic metal center. The disappearance of the methyl resonances at high temperature could be due to either intramolecular bridge-terminal methyl site exchange or rapid dissociation and reassociation of $AlMe_3$. Teuben favors the latter explanation in the Y case.[17] However, dissociation of $AlMe_3$ can be ruled out in the Yb case because addition of a small amount of $AlMe_3$ to the NMR sample results in no change in the position or intensity of the NMR resonances observed.

The reaction of $AlMe_3$ with decamethylytterbocene derivatives containing different chalcogenides takes a different course. Addition of 3 molar equiv of $AlMe_3$ to $(Me_5C_5)_2Yb(ER)(NH_3)$, where ER is SPh, S-*p*-tolyl, SePh, or $OCMe_3$, yields 2:1 adducts that crystallize on cooling the reaction mixture (eq 3). These adducts are high-melting blue or purple solids that, like the tetramethylaluminates, give low combustion analyses for carbon, with one exception, viz., the S-*p*-tolyl derivative. As with the tetramethylaluminate, the 2:1 stoichiometry can be confirmed by examining the ^1H NMR spectrum of a C_6D_6 sample of each compound in the presence of a slight excess of pyridine (eq 4).

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$$(Me_5C_5)_2Yb(ER)(NH_3) + 3\,AlMe_3 \longrightarrow \tag{3}$$
$$1/2\,[(Me_5C_5)_2Yb(ER)(AlMe_3)_2]_2 + Me_3Al(NH_3)$$

$$[(Me_5C_5)_2Yb(ER)(AlMe_3)_2]_2 + 6\,py \longrightarrow \tag{4}$$
$$2\,(Me_5C_5)_2Yb(ER)(py) + 4\,Me_3Al(py)$$

$$ER = SPh,\ S\text{-}p\text{-}C_6H_4Me,\ SePh,\ OCMe_3$$

There are several structural possibilities for these 2:1 adducts and fortunately the S-*p*-tolyl derivative **3** yields crystals suitable for a X-ray diffraction study. An ORTEP drawing showing the structure of **3** is given in Figure 1; the toluene of crystallization has been omitted. The molecule crystallizes in the triclinic space group $P\bar{1}$. Some bond lengths and angles are listed in Tables 1 and 2 and crystal data are given in Table 3. The structure is constructed from two $(Me_5C_5)_2Yb(III)$ fragments that are linked by two anionic Me_3Al-(S-*p*-tolyl)-$AlMe_3$ units to give a molecular unit that contains a 12-membered ring of idealized C_{2h} symmetry. The $(Me_5C_5)_2Yb(III)$ fragment is normal with an averaged Yb−C distance of 2.62(2) Å, a Me_5C_5(centroid)−Yb distance of 2.35 Å, and a Me_5C_5(centroid)−Yb−Me_5C_5(centroid) angle of 148°. These parameters are nearly identical with those found in $(Me_5C_5)_2Yb(S_2CNEt_2)$,[19] $(Me_5C_5)_2Yb(SPh)(NH_3)$,[20] and $(Me_5C_5)_2Yb(TePh)(NH_3)$,[14] with the exception that the (Me_5C_5)(centroid)−Yb−(Me_5C_5)(centroid) angle in these three metallocenes is closed by 10−12° relative to **3**.

The Me_3Al−(S-*p*-tolyl)−$AlMe_3$ fragments are composed of two Me_3Al groups that are connected to the S-*p*-tolyl group so that each Al center is 4-coordinate with an average Al−S distance of 2.375(3) Å. This distance is very similar to the Al−S distance in $Me_4Al_2(\mu\text{-}SMe)_2$ in the gas phase of 2.370(5) Å.[21] The Al−S−Al angle of 119.8(1)° is of course opened relative to the equivalent angle in $Me_4Al_2(\mu\text{-}SMe)_2$ (94.5(5)°). The difference between the average Al−C bridge (2.015(1) Å) and terminal (1.989(5) Å) distances is far less (0.026 Å) in **3** than in Al_2Me_6 (0.17 Å).[22]

The average Yb−C−Al angle is nearly linear (173.2(1)°)—a geometry that has been observed in a few metallocenes of the lanthanides with bridging methyl groups.[12,16,18,23] In the present case, the hydrogen atoms on the bridging carbon atoms, C(28) and C(31), respectively, were located in the difference map and refined isotropically. The averaged C−H distance of 0.99 Å is normal as are the averaged H−C−H angles of 110.5°. The geometry about the bridging carbon atoms requires that the hydrogen atoms point toward the decamethylytterbocene fragment with averaged Yb···C and Yb···H distances of 2.669(1) and 2.53(5) Å, respectively.

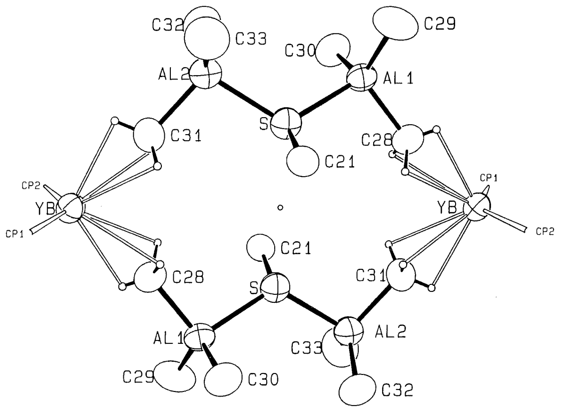

Figure 1. An ORTEP[30] drawing of $[(Me_5C_5)_2Yb(AlMe_3)_2(S\text{-}p\text{-}C_6H_4Me)]_2{\cdot}C_7H_8$ (**3**). The toluene of crystallization is not shown. The Yb−Me_5C_5(ring centroid) distance, represented by CP1 which is C(1−5) and CP2 which is C(11−15), is 2.35 Å and the Me_5C_5(ring centroid)−Yb−Me_5C_5(ring centroid) angle is 148°. The *p*-tolyl ring is represented by its ipso-carbon atom, C(21). The heavy atoms are refined anisotropically and they are shown as 50% probability ellipsoids; the hydrogen atoms on C(28) and C(31) are refined isotropically and they are of arbitrary size.

Table 1. Selected Bond Distances (Å) for $[(Me_5C_5)_2Yb(AlMe_3)_2(S\text{-}p\text{-}C_6H_4Me)]_2{\cdot}PhMe$[a]

Yb−C(1)	2.638(7)	Al(1)−C(28)	2.013(7)
Yb−C(2)	2.639(7)	Al(1)−C(29)	1.984(8)
Yb−C(3)	2.612(7)	Al(1)−C(30)	1.986(8)
Yb−C(4)	2.607(7)	Al(2)−C(31)	2.017(7)
Yb−C(5)	2.608(7)	Al(2)−C(32)	1.999(11)
Yb−C(6)	2.608(7)	Al(2)−C(33)	1.986(12)
Yb−C(7)	2.586(7)	Al(1)−S	2.381(3)
Yb−C(8)	2.633(7)	Al(2)−S	2.369(3)
Yb−C(9)	2.641(8)	C(28)−H(1)	0.996(12)
Yb−C(10)	2.614(7)	C(28)−H(2)	0.998(12)
Yb−C(28)	2.670(7)	C(28)−H(3)	0.992(12)
Yb−C(31)	2.667(6)	C(31)−H(4)	0.991(12)
Yb−H(1)	2.55(7)	C(31)−H(5)	0.995(12)
Yb−H(2)	2.61(7)	C(31)−H(6)	0.996(12)
Yb−H(3)	2.44(7)		
Yb−H(4)	2.50(7)		
Yb−H(5)	2.56(6)		
Yb−H(6)	2.56(6)		

[a] Estimated standard deviations in parentheses.

Table 2. Selected Bond Angles (deg) for $[(Me_5C_5)_2Yb(AlMe_3)_2(S\text{-}p\text{-}C_6H_4Me)]_2{\cdot}PhMe$[a]

C(28)−Yb−C(31)	87.7(3)	Al(1)−S−Al(2)	119.8(1)
Yb−C(28)−Al(1)	171.1(4)	Al(1)−S−C(21)	110.1(3)
Yb−C(31)−Al(2)	175.4(4)	Al(2)−S−C(21)	105.6(3)
C(28)−Al(1)−C(29)	112.8(4)	C(28)−Al(1)−S	110.2(3)
C(28)−Al(1)−C(30)	111.7(4)	C(31)−Al(2)−S	99.8(3)
C(29)−Al(1)−C(30)	117.1(4)	H(1)−C(28)−H(2)	109.8(17)
C(31)−Al(2)−C(32)	110.7(4)	H(1)−C(28)−H(3)	110.5(18)
C(31)−Al(2)−C(33)	112.7(4)	H(2)−C(28)−H(3)	110.4(17)
C(32)−Al(2)−C(33)	118.3(6)	H(4)−C(31)−H(5)	110.9(17)
		H(4)−C(31)−H(6)	110.6(17)
		H(5)−C(31)−H(6)	110.8

[a] Estimated standard deviations in parentheses.

It is useful to compare the geometry of the bridging methyl in **3** with that of two other adducts of $(Me_5C_5)_2$-Yb(II), viz., $(Me_5C_5)_2Yb(\mu\text{-}Me)Be(Me_5C_5)$[23] and $(Me_5C_5)_2$-$Yb(\mu\text{-}Et)AlEt_2(THF)$.[24] The Yb···C distance in these two Yb(II) adducts is 2.746(4) and 2.85(2) Å, respectively, both of which are longer than the equivalent Yb···C distance in the 2:1 adduct. This is consistent with the idea that **3** contains a Yb(III) center because the metal ionic radius is ca. 0.15 Å smaller than that of Yb(II) in

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Table 3. Summary of Crystallographic Data for $[(Me_5C_5)_2Yb(AlMe_3)_2(S\text{-}p\text{-}C_6H_4Me)]_2\cdot PhMe$

formula	$C_{40}H_{64}Al_2SYb$
fw	804.02
cryst syst	triclinic
space group	$P\bar{1}$ (no. 2)
a (Å)	12.894(5)
b (Å)	15.356(6)
c (Å)	11.187(6)
α (deg)	97.13(4)
β (deg)	103.98(4)
γ (deg)	86.45(4)
V (Å^3)	2131.6
Z	2
ρ(calcd) (g cm^{-3})	1.253
μ (cm^{-1})	22.97
radiation, λ (CC)	Mo Kα, 1.542
T (K)	296
$2\theta_{max}$ (deg)	100.2
no. of obsd reflcns	11885
no. of unique reflcns	7557
R^a	0.042
$R_w{}^b$	0.057
R (all data)	0.074

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|^2)/\Sigma w(|F_o|)^2]^{1/2}$.

an equivalent coordination number.[25] Recently, the crystal structure of polymeric $(Et_4Al)_2Yb$ has been reported in which the ethyl groups form bridge bonds between the aluminum and ytterbium metals.[26] The averaged Yb−C distance is 2.67 Å and the methylene group has C−H⋯Yb secondary contacts. In the (Me_5C_5)-BeMe adduct, the averaged Yb⋯H distance of 2.59 Å is comparable to those found in the 2:1 adduct. The similarity of the geometric parameters in these two adducts suggests that the bonding is similar, i.e., that donation of electron density from the C−H bonds to the metal center occurs. Thus, **3** may be viewed as an adduct between a $(Me_5C_5)_2Yb(III)^+$ cation and an $[Me_3Al(S\text{-}p\text{-}tolyl)AlMe_3]^-$ anion.

The ^1H NMR spectra of the four 2:1 adducts (**2**−**5**) are quite complex and inconsistent with the solid-state structure determined for **3**. The ^1H NMR spectra of the SPh (**2**), S-*p*-tolyl (**3**), and SePh (**4**) derivatives are quite similar to each other but differ markedly from that of the $OCMe_3$ adduct **5**. In the case of the sulfur or selenium adducts **2**−**4**, resonances due to $(Me_5C_5)_2Yb(AlMe_4)$ were observed at room temperature. This observation severely complicates the spectra since this species itself exists in solution as an equilibrium between the monomer and dimer (vide supra). In solutions of **2**, **3**, and **4**, the chemical shift and relative integration of the $(Me_5C_5)_2Yb(AlMe_4)$ resonances change with temperature, as observed for the pure compound. Since resonances due to the tetramethylaluminate **1** were observed it seemed reasonable that resonances due to Me_2AlER should also be observed. This was shown to be the case for Me_2AlSPh, since addition of a small amount of this compound to a solution of the 2:1 adduct increased the intensity of the resonances assigned to this compound at room temperature (see Experimental Section for details). In addition, when the ^1H NMR spectrum of a sample of **3** in C_7D_8 was examined as a function of temperature, the $(Me_5C_5)Yb$ resonances did not follow Curie−Weiss behavior since the chemical shift is not linear in T^{-1}, indicating that temperature-dependent processes exist in solution. As a minimum, the net reactions corresponding to the equilibrium shown in eq 5 are occurring in solution; the complexity of this system precludes a quantitative examination.

$$[(Me_5C_5)_2Yb(ER)(AlMe_3)_2]_2 \rightleftharpoons [(Me_5C_5)_2Yb(AlMe_4)]_2 + 2\ Me_2Al(ER) \qquad (5)$$

ER = SPh, S-p-C_6H_4Me, SePh

Although the 2:1 adduct when ER = $OCMe_3$ (**5**) is stoichiometrically identical with those described above, the ^1H NMR spectrum of this compound is much simpler. At 32 °C, only three resonances are observed at δ 42, 4.5, and −26 ppm in a ratio of 9:30:9 in C_6D_6. None of these resonances are due to $(Me_5C_5)_2Yb(AlMe_4)$ at this temperature. Addition of $Me_2AlOCMe_3$ does not alter the appearance of the paramagnetic species and mixing equimolar amounts of this compound with $(C_5Me_5)_2Yb(AlMe_4)$ does not generate the ^1H NMR spectrum of **5**. These results rule out a rapid equilibrium of the type shown in eq 5. However, the observation of three resonances of 9:30:9 ratio is inconsistent with a 2:1 adduct, whether undergoing fast bridge-terminal exchange or not because these structures should give either three resonances in 9:30:18 ratio or four signals in 9:30:6:12 ratio, respectively. One possible explanation for this is that **5** dissociates in a different way from **2**−**4** (eq 6). This would explain the lack of exchange with free $Me_2AlOCMe_3$ or $(Me_5C_5)_2Yb(AlMe_4)$ and it is also consistent with the greater bond strength expected for an Yb−O bond when compared with Yb−S and Yb−Se linkages.

$$[(Me_5C_5)_2Yb(OCMe_3)(AlMe_3)_2]_2 \rightleftharpoons [(Me_5C_5)_2Yb(OCMe_3)(AlMe_3)]_2 + 2\ AlMe_3 \qquad (6)$$

Conclusions

The products isolated from addition of $AlMe_3$ to $(Me_5C_5)_2Yb(ER)(NH_3)$ in hydrocarbon solvents depend on the identity of the ER group. When ER is TePh or $OSiMe_3$, the tetramethylaluminate $[(Me_5C_5)_2Yb(AlMe_4)]_2$ (**1**) is isolated but when ER is SPh, S-*p*-tolyl, or SePh, adducts with the stoichiometry $(Me_5C_5)_2Yb(ER)(AlMe_3)_2$ (**2**−**4**) are obtained. It seems reasonable to assume that the isolated solid compounds represent the thermodynamically favorable forms of several structures that are likely to be present in solution (cf. eqs 5 and 6). A postulate that helps in understanding this situation qualitatively is outlined below. The first step is removal of NH_3 as the $Me_3Al(NH_3)$ adduct and formation of the transient species $(Me_5C_5)_2Yb(ER)(AlMe_3)$. This adduct can react with another equivalent of $AlMe_3$ in two ways: by eliminating $Me_2Al(ER)$ to form $(Me_5C_5)_2Yb(AlMe_4)$ (ER = TePh or $OSiMe_3$) or by adding $AlMe_3$ to form $(Me_5C_5)_2Yb(ER)(AlMe_3)_2$, which rearranges to the solid-state structure observed for **3** and assumed for ER = SPh and SePh. This postulate predicts that the difference in net reaction is related to the A−ER bond

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strength, which is likely to fall in the order O > S > Se $\gg$ Te.[27] Thus, only when the donor strength is high will a 2:1 $AlMe_3$ adduct form; weaker donors such as TePh cannot support this structure and collapse to the tetramethylaluminate (**1**). The case of $OSiMe_3$ relative to $OCMe_3$ is rationalized by these arguments because $SiMe_3$ is electron withdrawing relative to CMe_3 so $OSiMe_3$ is a poorer donor than $OCMe_3$.[28]

Experimental Section

$[(Me_5C_5)_2Yb(AlMe_4)]_2$ (1). (a) From $(Me_5C_5)_2YbCl(THF)$ and $LiAlMe_4$. $(Me_5C_5)_2YbCl(THF)$ (1.80 g, 3.27 mmol) and $LiAlMe_4$ (0.38 g, 4.0 mmol) were weighed into a Schlenk tube and dissolved in 150 mL of toluene with vigorous stirring. The purple solution was stirred at room temperature overnight. After the reaction mixture was allowed to settle, the blue-violet mother liquor was filtered and the filtrate was concentrated to ca. 100 mL. Cooling at −10 °C afforded blue crystals of **1**. Several subsequent crops of crystals were isolated for a total yield of 1.10 g (64%). Mp 220−222 °C. IR (Nujol, CsI): 2720 (w), 1259 (w), 1178 (m), 1119 (vw), 1097 (w), 1061 (w), 1022 (m), 877 (br vs), 801 (br m), 783 (br m), 743 (s), 698 (vw), 677 (s), 623 (s), 592 (vw), 568 (s), 543 (s), 511 (vw), 495 (vw), 385 (m), 314 (vs), 309 (m) cm^{-1}. ^1H NMR (toluene-d_8): resonances due to the C_5Me_5 rings and the terminal CH_3 groups of both monomer and dimer are observed in solution. Resonances due to the bridging CH_3 groups are observed for the monomer but could not be detected for the dimer. The monomer:dimer ratio changes from 4:1 at 32 °C to 8:1 at 79 °C. **32 °C:** monomer, δ 247.0 (μ-CH_3, 6H, $\nu_{1/2} = 600$ Hz), 5.2 (C_5Me_5, 30H, $\nu_{1/2} = 45$ Hz), −26.5 (Al−CH_3, 6H, $\nu_{1/2} = 30$ Hz); dimer, δ 31.5 (Al−CH_3, 6H, $\nu_{1/2} = 40$ Hz), 4.0 (C_5Me_5, 30H, $\nu_{1/2} = 28$ Hz). **79 °C:** monomer, δ 204 (μ-CH_3, 6H, $\nu_{1/2} = 544$ Hz), 4.5 (C_5Me_5, 30H, $\nu_{1/2} = 65$ Hz), −21.2 (Al−CH_3, 6H, $\nu_{1/2} = 56$ Hz); dimer, δ 27.2 (Al−CH_3, 6H, $\nu_{1/2} = 55$ Hz), 4.5 (C_5Me_5, 30H, overlaps monomer resonance). Anal. Calcd for $C_{48}H_{84}Al_2Yb_2$: C, 54.3; H, 7.98. Found: C, 52.8; H, 8.14.

The stoichiometry of this complex was also established by examining the ^1H NMR spectrum of a toluene-d_8 solution of **1** to which a few drops of pyridine was added. The resulting red-orange solution clearly showed resonances at δ 3.8 (30H) and −0.27 (9H) ppm for the C_5Me_5 groups of $(C_5Me_5)_2YbMe(py)$ and the Me groups of $Me_3Al(py)$, respectively. No resonance due to the ytterbium-bound methyl group was observable.

(b) From $(C_5Me_5)_2Yb(OSiMe_3)(NH_3)$. Trimethylaluminum (1.8 mL of 1.3 M solution, 2.3 mmol) was added by syringe to a stirred solution of $(Me_5C_5)_2Yb(OSiMe_3)(NH_3)$ (0.43 g, 0.76 mmol) in 150 mL of hexane. An immediate color change from deep orange to blue-violet occurred. After being stirred for 2 h, the solution was filtered and the filtrate was concentrated to 80 mL. Cooling at −10 °C overnight produced violet blocks of **1**. Yield: 0.26 g (64%).

(c) From $(C_5Me_5)_2Yb(TePh)(NH_3)$. Trimethylaluminum (1.6 mmol) as a pentane solution was added to a stirred solution of $(Me_5C_5)_2Yb(TePh)(NH_3)$ (0.36 g, 0.54 mmol) in 100 mL of toluene by syringe. The resulting deep blue solution was stirred for 1 h and filtered and the filtrate was concentrated to 30 mL. Cooling at −10 °C overnight produced large blue crystals of **1** that rapidly lost solvent and became opaque on exposure to vacuum. Yield: 0.26 g (64%).

$[(Me_5C_5)_2Yb(AlMe_3)_2(SPh)]_2$ (2). A solution of trimethylaluminum in pentane (1.4 mmol) was added to a stirred solution of $(Me_5C_5)_2Yb(SPh)(NH_3)$ (0.29 g, 0.46 mmol) in 50 mL of toluene by syringe. The blue solution was stirred 1 h and filtered by cannula and the filtrate was cooled at −78 °C for several days. Blue needles were isolated from the mother liquor by filtration. Yield: 0.25 g (75%). Mp 213−215 °C. IR (Nujol, CsI): 2720 (vw), 1581 (w), 1260 (vw), 1188 (s), 1156 (vw), 1086 (m), 1070 (vw), 1024 (m), 941 (s), 920 (s), 797 (br vs), 745 (s), 729 (m), 696 (vs), 650 (vs), 586 (s), 528 (m), 484 (vw), 464 (vw), 429 (vw), 386 (w), 362 (m), 314 (vs) cm^{-1}. ^1H NMR (toluene-d_8, 32 °C): δ 247 (6H, $\nu_{1/2} > 500$ Hz), 80.1 (4H, $\nu_{1/2} = 350$ Hz), 31.6 (2H, $\nu_{1/2} = 33$ Hz), 29.0 (1H, $\nu_{1/2} = 125$ Hz), 20.5 (16H, $\nu_{1/2} = 175$ Hz), 14.2 (4H, $\nu_{1/2} = 95$ Hz), 6.2 (78H, $\nu_{1/2} = 65$ Hz), 5.3 (30H, $\nu_{1/2} = 60$ Hz), 4.1 (7H, $\nu_{1/2} = 35$ Hz), −0.4 (2H, $\nu_{1/2} = 5$ Hz), −2.6 (2H, $\nu_{1/2} = 35$ Hz), −13.0 (3H, $\nu_{1/2} = 37$ Hz), −27.0 (6H, $\nu_{1/2} = 30$ Hz) ppm. Relative integrated intensities change with temperature. Anal. Calcd for $C_{64}H_{100}Al_4S_2Yb_2$: C, 55.2; H, 7.67; S, 4.60. Found: C, 53.3; H, 7.70; S, 4.28. The stoichiometry of the complex was verified by ^1H NMR after addition of pyridine to a toluene-d_8 solution of **2**: δ 1.7 (30H, $(Me_5C_5)_2Yb(SPh)(py)$), −0.2 (18H, $Me_3Al(py)$) ppm.

The addition of a 5-fold excess of $PhSAlMe_2$ (prepared as described below) to a solution of **2** in toluene-d_8 produced a new ^1H NMR spectrum: δ 80.3 (2H, $\nu_{1/2} = 450$ Hz), 28.9 (1H, $\nu_{1/2} = 325$ Hz), 20.7 (2H, $\nu_{1/2} = 110$ Hz), 19.4 (2H, $\nu_{1/2} = 90$ Hz), 15.3 (4H, $\nu_{1/2} = 95$ Hz), 6.3 (30H, $\nu_{1/2} = 110$ Hz), −2.9 (3H, $\nu_{1/2} = 33$ Hz), −13.7 (4H, $\nu_{1/2} = 85$ Hz). Addition of 1 equiv of $PhSAlMe_2$ to a solution of **1** in toluene-d_8 generated a ^1H NMR spectrum very similar to that of **2** reported above: δ 248 (3H, $\nu_{1/2} > 500$ Hz), 80.0 (3H, $\nu_{1/2} = 380$ Hz), 27.6 (3H, $\nu_{1/2} = 155$ Hz), 20.3 (8H, $\nu_{1/2} = 192$ Hz), 14.2 (6H, $\nu_{1/2} = 175$ Hz), 6.2 (60H, $\nu_{1/2} = 120$ Hz), 5.2 (15H, $\nu_{1/2} = 65$ Hz), −0.1 (6H, $\nu_{1/2} = 10$ Hz), −2.8 (4H, $\nu_{1/2} = 40$ Hz), −12.3 (6H, $\nu_{1/2} = 58$ Hz), −27.3 (3H, $\nu_{1/2} = 34$ Hz).

(a) Preparation of $PhSAlMe_2$. $AlMe_3$ (5.5 mmol) was diluted with 150 mL of pentane and the solution was cooled to −78 °C. Thiophenol (5.4 mmol) was added via syringe with vigorous stirring. After allowing the solution to slowly warm to room temperature, the solvent was removed under reduced pressure and the white residue was redissolved in a minimum of hexane. The solution was filtered and the filtrate cooled at −10 °C overnight. White crystals of $PhSAlMe_2$ were isolated from the mother liquor by cannula filtration. Mp 130−132 °C. ^1H NMR (toluene-d_8, 21 °C): δ 7.47 (2H, m, *o*-Ph*H*), 6.90 (3H, m, *m*- and *p*-Ph*H*), −0.28 (6H, s, Al*Me₂*).

$[(Me_5C_5)_2Yb(AlMe_3)_2(S\text{-}p\text{-}C_6H_4Me)]_2\cdot C_7H_8$ (3). Compound **3** was prepared using the procedure described for **2** starting from 1.00 g (1.56 mmol) of $(Me_5C_5)_2Yb(S\text{-}p\text{-}C_6H_4Me)(OEt_2)$. Several crops of **3** were isolated as blue prisms by cooling the mother liquor at −10 °C. Yield: 0.98 g (78%). Mp 200−202 °C. IR (Nujol, CsI): 2729 (w), 1491 (m), 1208 (w), 1187 (vs), 1087 (m), 1065 (w), 1018 (m), 933 (br s), 897 (br s), 813 (vs), 796 (br s), 695 (br vs), 652 (vs), 585 (vs), 527 (m), 497 (w), 385 (w), 378 (m), 360 (vw), 309 (vs), 290 (w), 281 (vw) cm^{-1}. ^1H NMR (toluene-d_8, 32 °C): δ 247 (6H, $\nu_{1/2} > 500$ Hz), 78.4 (4H, $\nu_{1/2} = 285$ Hz), 27.0 (3H, $\nu_{1/2} = 89$ Hz), 12.0 (5H, $\nu_{1/2} = 37$ Hz), 6.2 (53H, $\nu_{1/2} = 72$ Hz), 5.1 (30H, $\nu_{1/2} = 55$ Hz), −0.2 (1H, $\nu_{1/2} = 12$ Hz), −13.2 (4H, $\nu_{1/2} = 42$ Hz), −26.8 (6H, $\nu_{1/2} = 35$ Hz) ppm. Relative integrated intensities change with temperature. Anal. Calcd for $C_{73}H_{118}Al_4S_2Yb_2$: C, 57.9; H, 7.86; S, 4.24. Found: C, 55.2; H, 7.65; S, 4.78.

The stoichiometry of this complex was also established by examining the ^1H NMR spectrum of a toluene-d_8 solution of **3** to which a few drops of pyridine were added. The resulting orange solution clearly showed resonances at δ 1.6 (30H) and −0.2 (18H) ppm for the C_5Me_5 groups of $(C_5Me_5)_2Yb(S\text{-}p\text{-}C_6H_4Me)(py)$ and the Me groups of $Me_3Al(py)$, respectively.

$[(Me_5C_5)_2Yb(AlMe_3)_2(SePh)]_2$ (4). Compound **4** was prepared using the procedure described for **2** starting from 0.60 g (0.97 mmol) of $(Me_5C_5)_2Yb(SePh)(NH_3)$. Several crops of **4** were isolated as lavender crystals by cooling the mother liquor at −10 °C. The crystals became opaque on exposure to vacuum. Yield: 0.45 g (62%). Mp 230−232 °C. IR (Nujol, CsI): 2720

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(w), 1577 (m), 1189 (s), 1072 (vw), 1022 (m), 1000 (vw), 936 (br vs), 795 (sh w), 760 (sh m), 737 (vs), 694 (vs), 650 (vs), 586 (vs), 527 (br m), 486 (m), 390 (br w), 318 (vs), 303 (vw), 280 (m) cm^{-1}. ^{1}H NMR (toluene-d_8, 32 °C): δ 247 (6H, $\nu_{1/2} > 350$ Hz), 6.0 (21H, $\nu_{1/2} = 80$ Hz), 5.1 (30H, $\nu_{1/2} = 50$ Hz), 3.9 (2H, $\nu_{1/2} = 35$ Hz), -0.5 (4H, $\nu_{1/2} = 30$ Hz), -10.0 (3H, $\nu_{1/2} = 54$ Hz), -27.0 (6H, $\nu_{1/2} = 21$ Hz) ppm. Relative integrated intensities change with temperature. Anal. Calcd for $C_{64}H_{106}Al_4Se_2Yb_2$: C, 51.7; H, 7.18. Found: C, 51.3; H, 7.19.

The stoichiometry of this complex was also established by examining the ^{1}H NMR spectrum of a toluene-d_8 solution of **3** to which a few drops of pyridine were added. The resulting orange solution clearly showed resonances at δ 1.4 (30H) and -0.2 (18H) ppm for the C_5Me_5 groups of $(C_5Me_5)_2Yb(SePh)(py)$ and the Me groups of $Me_3Al(py)$, respectively.

[(Me$_5$C$_5$)$_2$Yb(AlMe$_3$)$_2$(OCMe$_3$)]$_2$ (5) Compound **5** was prepared from 0.20 g (0.37 mmol) of $(Me_5C_5)_2Yb(OCMe_3)(NH_3)$ using a procedure similar to that described for **2** above but using hexane (200 mL) rather than toluene as solvent. Several crops of **5** were isolated as purple plates by cooling the mother liquor at −78 °C. Yield: 0.10 g (46%). Mp 180−182 °C. IR (Nujol, CsI): 2720 (w), 1365 (w), 1309 (vw), 1261 (vw), 1243 (w), 1180 (s), 1090 (vw), 1024 (w), 914 (s), 803 (w), 767 (w), 721 (sh vw), 693 (br vs), 628 (br s), 596 (vw), 499 (m), 472 (vw), 380 (br w), 297 (m) cm^{-1}. ^{1}H NMR (benzene-d_6, 32 °C): δ 41.6 (9H, $\nu_{1/2} = 313$ Hz), 4.5 (30H, $\nu_{1/2} = 150$ Hz), -26.0 (9H, $\nu_{1/2} = 43$ Hz) ppm. Anal. Calcd for $C_{60}H_{114}Al_4O_2Yb_2$: C, 54.5; H, 8.70. Found: C, 53.7; H, 8.49.

Addition of a few drops of pyridine to a solution of **5** in benzene-d_6 confirmed the complex stoichiometry: δ 9.2 (30H, C_5Me_5 rings of $(C_5Me_5)_2Yb(OCMe_3)(py)$), -0.27 (18H, Me of $Me_3Al(py)$) ppm.

Addition of $Me_3COAlMe_2$ (prepared as outlined below) to a solution of **5** in toluene-d_8 did not alter the ^{1}H NMR spectrum of **5**. Similarly, addition of a large excess of $Me_3COAlMe_2$ to **1** in toluene-d_8 did not produce the ^{1}H NMR spectrum of **5**. The spectrum obtained in this case was a simple superposition of **1** and $Me_3COAlMe_2$ alone.

(a) Preparation of Me$_3$COAlMe$_2$. $AlMe_3$ (10.0 mmol) was diluted with 200 mL of pentane and the solution was cooled to −78 °C. A solution of Me_3COH (9.8 mmol) in 100 mL of Et_2O was slowly added by cannula with rapid stirring. The reaction mixture was allowed to warm slowly to room temperature over several hours. Removal of the solvent under reduced pressure afforded a sticky white residue that was redissolved in dry pentane and cooled to −78 °C. White microcrystals of $Me_3COAlMe_2$ were isolated from the mother liquor by cannula filtration. ^{1}H NMR (benzene-d_6, 32 °C): δ 1.18 (9H, s, CMe_3), -0.46 (6H, s, $AlMe_2$) ppm.

X-ray Crystallography of [(Me$_5$C$_5$)$_2$Yb(AlMe$_3$)$_2$(S-*p*-C$_6$H$_4$Me)]$_2$·C$_7$H$_8$ (3). An air-sensitive crystal of **3** was sealed inside a thin-walled quartz capillary under argon and mounted on a modified Picker FACS-1 automated diffractometer equipped with graphite-monochromated Mo radiation. A set of $\theta-2\theta$ scans was collected and corrected for absorption (analytical method),[29] Lorentz, and polarization effects. The Yb, S, and Al atoms were located in the three-dimensional Patterson map and subsequent least-squares refinements and electron density maps revealed the location of all other non-hydrogen atoms. The structure was refined by full-matrix least squares on F. Anisotropic thermal parameters were refined for all non-hydrogen atoms. A toluene of crystallization was located and its atoms were refined isotropically with fixed C−C distances 1.4 Å (C−C) and 1.54 Å (C−Me). The six H atoms on C(28) and C(31) were located in the electron density maps and were refined with one single isotropic thermal parameter for all three hydrogen atoms of each group; the C−H and H−H distances were restrained to 1.0 Å and 1.63 Å, respectively. Additionally, the four aryl H atoms associated with the *p*-tolyl ring were located in the difference maps. These atoms were refined isotropically using a single isotropic thermal parameter for all four atoms. Details of the data collection and least-squares refinements are given in Table 3. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography.[30] With the exception of ORTEP,[31] all computer programs used in this work were developed by Dr. A. Zalkin.

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Supporting Information Available: Tables of atomic coordinates, complete bond distances and angles, and anisotropic thermal parameters for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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