# Synthesis and Reactivity of Organosamarium Diarylpnictide Complexes: Cleavage Reactions of Group 15 E−E and E−C Bonds by Samarium(II)

**William J. Evans,* John T. Leman, and Joseph W. Ziller**

Department of Chemistry, University of California, Irvine, California 92717

**Saeed I. Khan**

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

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$(C_5Me_5)_2Sm$ (2 equiv) reacts with $Ph_2EEPh_2$ to give $(C_5Me_5)_2SmEPh_2$ (E: P, **1**; As, **2**), while $(C_5Me_5)_2Sm(THF)_2$ (2 equiv) reacts with $Ph_2EEPh_2$ to give $(C_5Me_5)_2Sm(EPh_2)(THF)$ (E: P, **3**; As, **4**). **3** and **4** are also available from the reactions of **1** and **2** with THF. **3** and **4** undergo further reaction to produce the THF ring-opened products $(C_5Me_5)_2Sm[O(CH_2)_4EPh_2](THF)$ (E: P, **5**; As, **6**). $(C_5Me_5)_2Sm$ (4 equiv) reacts with $Ph_2EEPh_2$ to give the mixed-valent $(C_5Me_5)_2Sm(\mu\text{-}EPh_2)Sm(C_5Me_5)_2$ (E: P, **7**; As, **8**). These compounds are also available from the reaction of **1** and **2** with $(C_5Me_5)_2Sm$. The X-ray crystal structure of **2,** crystallized from hexanes ($P2_1/n$; $a = 26.188(24)$ Å, $b = 9.911(10)$ Å, $c = 23.280(23)$ Å, $\beta = 97.150(12)°$, $V = 5995(2)$ Å$^3$, $D_{calcd} = 1.488$ Mg/m$^3$; $Z = 8$; $T = 156$ K), revealed, in addition to a conventional seven-coordinate bent metallocene geometry with 2.698 Å Sm−C($C_5Me_5$) and 2.970 Å Sm−As average distances, two very different Sm−As−C(Ph) angles, 74.2 and 118.7°. As a result, one phenyl group is closer to the metal (2.901 Å minimum Sm−C distance). **4**, crystallized from toluene ($P2_1/n$; $a = 10.713(9)$ Å, $b = 14.143(11)$ Å, $c = 21.620(16)$ Å, $\beta = 101.08(6)°$, $V = 3215(4)$ Å$^3$, $D_{calcd} = 1.492$ Mg/m$^3$; $Z = 4$; $T = 163$ K), and **6,** crystallized from hexanes ($P2_1/n$; $a = 9.3958(16)$ Å, $b = 22.245(3)$ Å, $c = 17.931(3)$ Å, $\beta = 96.497(11)°$, $V = 3724(1)$ Å$^3$, $D_{calcd} = 1.416$ Mg/m$^3$; $Z = 4$; $T = 163$ K), have conventional eight-coordinate, bent metallocene structures.

## Introduction

Recent studies of the chemistry of the bent metallocene $(C_5Me_5)_2Sm$[1] with inorganic substrates including $N_2$,[2] $BiPh_3$,[3] $Sb^nBu_3$,[4] and elemental S, Se, and Te[5,6] have revealed that this organometallic reagent offers opportunities to isolate and crystallographically characterize new and rare types of main group element compositions and structures. Hence, planar $M_2N_2$ and $M_2Bi_2$ units have been discovered in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)^2$ and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$,[3] the $(Sb_3)^{2-}$ [4] and $(Se_3)^{4-}$ [6] ions have been structurally characterized for the first time, and facile routes to the relatively rare group 16 ions $(S_3)^{2-}$, $(Se_3)^{2-}$, and $(Te_3)^{2-}$ have been found.[5]

In this study, we examine the generality of the reactions which formed the $(Bi_2)^{2-}$ and $(Sb_3)^{3-}$ ions in eqs 1 and 2. The

$$2(C_5Me_5)_2Sm + Ph_3Bi \rightarrow [(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2) \quad (1)$$

$$3(C_5Me_5)_2Sm + 3^nBu_3Sb \rightarrow [(C_5Me_5)_2Sm]_3(\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-}Sb_3)(THF) \quad (2)$$

chemistry of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ with phosphorus and arsenic analogs is described as well as reactions of a series of alternative phenylbismuth precursors which were studied to learn more about reaction 1. These studies have revealed an unusual mixed-valent phosphorus compound and a system in which the stepwise coordination and ring opening of THF by an $AsPh_2$ unit can be documented.

## Experimental Section

All manipulations described below employing $(C_5Me_5)_2Sm$ and workup of subsequent reaction products were carried out under argon in an inert-atmosphere glovebox free of coordinating solvents. All other chemistry was performed under nitrogen with rigorous exclusion of air and water by using Schlenk, vacuum-line, and glovebox techniques. Physical measurements were obtained, solvents were purified, and $(C_5Me_5)_2Sm$[1] and $(C_5Me_5)_2Sm(THF)_2$[7] were prepared as previously described.[8] $Ph_2PPPh_2$,[9] $Ph_2AsAsPh_2$,[10] $Ph_2SbSbPh_2$,[11] and $Ph_2BiBiPh_2$,[12] were prepared by literature procedures. $Ph_2BiCl$ was prepared by ligand redistribution between $Ph_3Bi$ and $BiCl_3$ in a 2:1 molar ratio in refluxing toluene. $Ph_2PH$ and $Ph_2PCl$ (Aldrich) employed in the synthesis of $Ph_2PPPh_2$ were distilled under vacuum before use. $BiCl_3$ was used as received. $Ph_3P$, $Ph_3As$, $Ph_3Sb$, and $Ph_3Bi$ were recrystallized from absolute ethanol and dried under high vacuum.

**$(C_5Me_5)_2Sm(THF)_x$/$Ph_3E$ Reactions ($x = 0, 2$; E = P, As, Sb, Bi).** The following general procedure was used to screen $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ for reactivity toward the triphenylpnictides. A

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small quantity (5−10 mg) of $Ph_3E$ dissolved in 0.5 mL of $C_6D_6$ was treated dropwise with a solution of 2 equiv of the metallocene in an equal volume of the same solvent. The reaction mixtures were homogeneous in all cases. Aliquots were withdrawn and flame-sealed at atmospheric pressure in 5 mm NMR tubes.

**$(C_5Me_5)_2Sm(PPh_2)$, 1.** A solution of $(C_5Me_5)_2Sm$ (100.5 mg, 0.239 mmol) in toluene (3 mL) was added dropwise to a stirred solution of $Ph_2PPPh_2$ (44.1 mg, 0.119 mmol) in toluene (3 mL). The deep-green color of the $(C_5Me_5)_2Sm$ solution was quenched immediately to a pale brown color which increased in intensity as the addition progressed. After 15 min of stirring, the solvent was removed in vacuo to give a dark brown oil, which was triturated with hexanes (1 mL). The resultant brown solid was dried under vacuum to give pure **1** (132 mg, 90%). Anal. Calcd for $C_{32}H_{40}SmP$: C, 63.42; H, 6.65; Sm, 24.81; P, 5.11. Found: C, 63.20; H, 6.77; Sm, 25.10; P, 5.22. Isopiestic molecular weight (0.057 M in $C_6H_6$): calcd for $C_{32}H_{40}SmP$, 606; found, 560. $^1$H NMR ($C_6D_6$, 300 MHz, 25 °C): $\delta$ 5.82 (t, $J$ = 7.3 Hz, 2H, Ph *p*-H), 4.54 (br "t", $\Delta\nu_{1/2}$ = 10 Hz, 4H, Ph *m*-H), 3.43 (br d, $\Delta\nu_{1/2}$ = 20 Hz, 4H, Ph *o*-H), 0.54 (s, 30H, $C_5Me_5$). $^{13}$C NMR ($C_6D_6$, 25 °C): $\delta$ 155.5, 120.5, 118.1 ($C_6H_5$), 118.7 ($C_5Me_5$), 19.6 ($C_5Me_5$)**.** Magnetic susceptibility: $\chi_M^{293K} = 425 \times 10^{-6}$ cgsu; $\mu_{eff} = 1.0\ \mu_B$.

**$(C_5Me_5)_2Sm(AsPh_2)$, 2.** As described above for **1**, $(C_5Me_5)_2Sm$ (96.5 mg, 0.229 mmol) and $Ph_2AsAsPh_2$ (52.5 mg, 0.114 mmol) were combined in toluene (5 mL). Removal of the solvent under vacuum gave a brown powder which was pure by $^1$H NMR spectroscopy. Cooling a warm saturated hexane solution to −36 °C gave dark brown plates of **2** (92 mg, 65%) suitable for X-ray crystallography. Anal. Calcd for $C_{32}H_{40}SmAs$: C, 59.14; H, 6.20; Sm, 23.13; As, 11.53. Found: C, 58.91; H, 6.17; Sm, 23.40; As, 11.35. Isopiestic molecular weight (0.038 M in $C_6H_6$): calcd for $C_{32}H_{40}SmAs$, 650; found, 624. $^1$H NMR ($C_6D_6$, 300 MHz, 25 °C): $\delta$ 5.84 (t, $J$ = 7.3 Hz, 2H, Ph *p*-H), 4.68 (br "t", $\Delta\nu_{1/2}$ = 18 Hz, 4H, Ph *m*-H), 3.75 (br d, $\Delta\nu_{1/2}$ = 18 Hz, 4H, Ph *o*-H), 0.53 (s, 30H, $C_5Me_5$). $^{13}$C NMR ($C_6D_6$, 25 °C): $\delta$ 157.1, 134.8, 122.1, 121.8 ($C_6H_5$), 118.7 ($C_5Me_5$), 19.4 ($C_5Me_5$)**.** Magnetic susceptibility: $\chi_M^{293K} = 437 \times 10^{-6}$ cgsu; $\mu_{eff} = 1.0\ \mu_B$.

**$(C_5Me_5)_2Sm(PPh_2)(THF)$, 3.** As described above for **1**, $(C_5Me_5)_2Sm(THF)_2$ (173.6 mg, 0.307 mmol) and $Ph_2PPPh_2$ (56.8 mg, 0.153 mmol) were combined in toluene (5 mL). A dark brown color developed immediately, and after 15 min the solvent was removed under vacuum to give a brown oil. Trituration with hexanes (2 mL), removal of the solvent via pipet, and vacuum-drying gave a green-brown solid, **3** (218 mg, 95%). Anal. Calcd for $C_{36}H_{48}SmOP$: Sm, 22.17. Found: Sm, 21.7. $^1$H NMR ($C_6D_6$ + 1 equiv of THF,[13] 300 MHz, 25 °C): $\delta$ 6.94 (t, $J$ = 7.4 Hz, 2H, Ph *p*-H), 6.59 ("t", $J$ = 7.2 Hz, 4H, Ph *m*-H), 5.82 (d, $J$ = 7.2 Hz, 4H, Ph *o*-H), 1.20 (s, 30H, $C_5Me_5$). $^{13}$C NMR ($C_6D_6$, 25 °C): $\delta$ 148.4, 133.2 (d, $J_{P-C}$ = 22 Hz), 128.2, 121.8 ($C_6H_5$), 117.1 ($C_5Me_5$), 65.7 (br, α-C, THF), 21.4 (br, *β*-C, THF), 18.5 ($C_5Me_5$). Magnetic susceptibility: $\chi_M^{293K} = 419 \times 10^{-6}$ cgsu; $\mu_{eff} = 1.0\ \mu_B$.

**$(C_5Me_5)_2Sm(AsPh_2)(THF)$, 4.** $(C_5Me_5)_2Sm(THF)_2$ (143.5 mg, 0.254 mmol) and $Ph_2AsAsPh_2$ (58.2 mg, 0.127 mmol) were combined in toluene (5 mL) as described for **3**. Trituration with hexanes (2 mL), removal of the solvent, and vacuum-drying gave a green-brown solid, **4** (140 mg, 77%). Anal. Calcd for $C_{36}H_{48}SmAsO$: Sm, 20.82. Found: Sm, 20.20. $^1$H NMR ($C_6D_6$ + 1 equiv THF,[14] 300 MHz, 25 °C): $\delta$ 6.92 (t, $J$ = 7.2 Hz, 2H, Ph *p*-H), 6.57 ("t", $J$ = 7.4 Hz, 4H, Ph *m*-H), 5.64 (d, $J$ = 7.4 Hz, 4H, Ph *o*-H), 1.22 (s, 30H, $C_5Me_5$). $^{13}$C NMR ($C_6D_6$, 25 °C): $\delta$ 149.4, 131.2, 127.8, 122.7 ($C_6H_5$), 117.2 ($C_5Me_5$), 65.4 (br, α-C, THF), 21.3 (br, *β*-C, THF), 18.3 ($C_5Me_5$). Magnetic susceptibility: $\chi_M^{293K} = 354 \times 10^{-6}$ cgsu; $\mu_{eff} = 0.9\ \mu_B$.

**$(C_5Me_5)_2Sm[O(CH_2)_4PPh_2](THF)$, 5.** A solution of **3**, prepared as above from $(C_5Me_5)_2Sm(THF)_2$ (190 mg, 0.34 mmol) and $Ph_2PPPh_2$ (62.1 mg, 0.17 mmol) in THF (5 mL) was placed in a 50 mL, thick-walled glass reaction tube equipped with a Teflon high-vacuum stopcock. The solution was degassed by three freeze−pump−thaw cycles on a high-vacuum line, left under vacuum, and placed in an oil bath at 65 °C. After 60 h, the solution had changed from its initial dark brown color to yellow. The THF was removed under vacuum, and the resultant yellow oil was taken up in hexane (1 mL), centrifuged to remove a small amount of insolubles, and then cooled to −40° C. Yellow crystals of **5** (178 mg, 70%) were isolated by decantation from the mother liquor followed by vacuum-drying. Anal. Calcd for $C_{40}H_{56}SmPO_2$: C, 64.04; H, 7.52; Sm, 20.04. Found: C, 55.77; H, 6.73; Sm, 21.28. $^1$H NMR ($C_6D_6$, 300 MHz, 25 °C): $\delta$ 7.61 ("t", $J$ = 6.9 Hz, 4H, Ph *o*-H), 7.10 (mult, 4H, Ph *m*-H), 7.04 (mult, 2H, Ph *p*-H), 5.50 (br mult, $\Delta\nu_{1/2}$ = 17 Hz, 2H, C$H_2$), 4.05 (br mult, $\Delta\nu_{1/2}$ = 22 Hz, 2H, C$H_2$), 2.77 (br mult, $\Delta\nu_{1/2}$ = 14 Hz, 4H, C$H_2$), 1.40 (s, 30H, $C_5Me_5$), −2.29 (br s, $\Delta\nu_{1/2}$ = 60 Hz, 4H, THF), −3.59 (br s, $\Delta\nu_{1/2}$ = 140 Hz, 4H, THF). $^{13}$C NMR ($C_6D_6$, 25 °C): $\delta$ 140.2 (d, $J_{P-C}$ = 15 Hz, $C_6H_5$), 133.5 ($C_6H_5$), 133.3 (d, $J_{P-C}$ = 18 Hz, $C_6H_5$), 128.6 (mult, $C_6H_5$), 113.5 ($C_5Me_5$), 74.0 [O($CH_2$)$_4$PPh$_2$], 60.8 (br, α-C, THF), 37.8 (d, $J_{P-C}$ = 12 Hz, [O($CH_2$)$_4$PPh$_2$]), 29.6 (d, $J_{P-C}$ = 12 Hz, [O($CH_2$)$_4$PPh$_2$]), 24.8 (d, $J_{P-C}$ = 16 Hz, [O($CH_2$)$_4$PPh$_2$]), 19.4 (br, *β*-C, THF), 17.9 ($C_5Me_5$)**.** Magnetic susceptibility: $\chi_M^{293K} = 537 \times 10^{-6}$ cgsu; $\mu_{eff} = 1.1\ \mu_B$.

**$(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2](THF)$, 6.** A solution of **4**, prepared as above from $(C_5Me_5)_2Sm(THF)_2$ (75.4 mg, 0.133 mmol) and $Ph_2AsAsPh_2$ (30.5 mg, 0.067 mmol) in THF (5 mL) was placed in a 50 mL, thick-walled glass reaction tube equipped with a Teflon high-vacuum stopcock. The solution was degassed by three freeze−pump−thaw cycles on a high-vacuum line, left under vacuum, and placed in an oil bath at 65 °C. After 20 h, the solution had undergone a change from its initial dark brown color to yellow, which was similar to that seen for the conversion of **3** to **5** above. The THF was removed under vacuum, and the resultant yellow oil was taken up in hexane (1 mL), centrifuged to remove a small amount of insolubles, and then cooled to −40 °C. Yellow crystals of **6** (83 mg, 79%) were isolated by decantation from the mother liquor, followed by vacuum-drying. Crystals for the X-ray diffraction study were grown from a dilute solution of **4** in hexane over an extended period of time. Anal. Calcd for $C_{40}H_{56}SmAsO_2$: C, 60.50; H, 7.11; Sm, 18.93. Found: C, 58.63; H, 7.10; Sm, 18.88. $^1$H NMR ($C_6D_6$, 300 MHz, 25 °C): $\delta$ 7.61 (d, $J$ = 7.0 Hz, 4H, Ph *o*-H), 7.11 ("t", $J$ = 7.8 Hz, 4H, Ph *m*-H), 7.04 (t, $J$ = 7.1 Hz, 2H, Ph *p*-H), 5.51 (br mult, $\Delta\nu_{1/2}$ = 15 Hz, 2H, C$H_2$), 4.05 (br mult, $\Delta\nu_{1/2}$ = 15 Hz, 2H, C$H_2$), 2.77 (br mult, $\Delta\nu_{1/2}$ = 15 Hz, 2H, C$H_2$), 2.75 (broad mult, $\Delta\nu_{1/2}$ = 15 Hz, 2H, C$H_2$), 1.40 (s, 30H, $C_5Me_5$), −2.38 (br s, $\Delta\nu_{1/2}$ = 40 Hz, 4H, THF), −3.66 (br s, $\Delta\nu_{1/2}$ = 75 Hz, 4H, THF). $^{13}$C NMR ($C_6D_6$, 25 °C): $\delta$ 141.8, 133.5, 131.6, 128.8 ($C_6H_5$), 113.5 ($C_5Me_5$), 74.0 [O($CH_2$)$_4$AsPh$_2$], 61.3 (br, α-C, THF), 38.3, 29.5, 25.2 [O($CH_2$)$_4$AsPh$_2$], 19.8 (br, *β*-C, THF), 17.9 ($C_5Me_5$)**.** Magnetic susceptibility: $\chi_M^{293K} = 379 \times 10^{-6}$ cgsu; $\mu_{eff}$ = 0.95 $\mu_B$.

**$(C_5Me_5)_2Sm(\mu\text{-}PPh_2)Sm(C_5Me_5)_2$, 7.** A solution of $Ph_2PPPh_2$ (23.7 mg, 0.064 mmol) in toluene (3 mL) was treated with a solution of $(C_5Me_5)_2Sm$ (107.9 mg, 0.256 mmol) in toluene (3 mL) and isolated as for **1** above. Anal. Calcd for $C_{52}H_{70}Sm_2P$: C, 60.82; H, 6.87; Sm, 29.29; P, 3.02. Found: C, 60.45; H, 6.72; Sm, 29.65; P, 3.24. $^1$H NMR ($C_6D_6$, 300 MHz, 25 °C, concentration dependent, 5.6 mM): $\delta$ 6.13 (t, $J$ = 7.1 Hz, 1H, Ph *p*-H), 5.20 (br mult, $\Delta\nu_{1/2}$ = 20 Hz, 2H, Ph *m*-H), 3.73 (br mult, $\Delta\nu_{1/2}$ = 20 Hz, 2H, Ph *o*-H), 0.80 (s, 30H, $C_5Me_5$). $^{13}$C NMR ($C_6D_6$, 25 °C): $\delta$ 180.6, 133.3, 128.5, 121.0 ($C_6H_5$), 57.8 ($C_5Me_5$), 17.3 ($C_5Me_5$). Magnetic susceptibility: $\chi_M^{293K} = 2560 \times 10^{-6}$ cgsu; $\mu_{eff} = 2.45\ \mu_B$.

Isolated **1** (39.0 mg, 0.065 mmol) was reacted in a similar fashion with $(C_5Me_5)_2Sm$ (28.7 mg, 0.068 mmol) in toluene (3 mL). The $^1$H NMR spectrum of the resulting brown solid corresponded closely to that for $(C_5Me_5)_2Sm(\mu\text{-}PPh_2)Sm(C_5Me_5)_2$ above. $^1$H NMR ($C_6D_6$, 300 MHz, 25 °C, concentration dependent, 5.6 mM): $\delta$ 6.11 (t, 1H, Ph *p*-H), 5.15 (br "t", 2H, Ph *m*-H), 3.70 (br d, 2H, Ph *o*-H), 0.79 (s, 30H, $C_5Me_5$).

**$(C_5Me_5)_2Sm(\mu\text{-}AsPh_2)Sm(C_5Me_5)_2$, 8.** $Ph_2AsAsPh_2$ (5.0 mg, 0.011 mmol) and $(C_5Me_5)_2Sm$ (18.4 mg, 0.044 mmol) were combined in $C_6D_6$ (1.20 mL), and the NMR spectrum was measured immediately. $^1$H NMR ($C_6D_6$, 300 MHz, 25 °C, concentration dependent, 18 mM): $\delta$ 8.40 (br s, $\Delta\nu_{1/2}$ = 30 Hz, 2H, $C_6H_5$), 7.68 (s, $\Delta\nu_{1/2}$ = 20 Hz, 1H, Ph *p*-H), 5.49 (br s, $\Delta\nu_{1/2}$ = 30 Hz, 2H, $C_6H_5$), 1.00 (s, 30H, $C_5Me_5$).

Isolated **2** (13.5 mg, 0.021 mmol) and $(C_5Me_5)_2Sm$ (8.9 mg, 0.021

(13) In the absence of additional THF, the NMR spectrum of **3** is highly dependent on the extent of drying of the compound and the amount of THF present. Chemical shifts are observed in the following ranges: 6.71−6.94 (Ph *p*-H), 6.16−6.59 (Ph *m*-H), 5.33−5.82 (Ph *o*-H), and 1.08−1.20 ($C_5Me_5$) ppm.

(14) Compound **4** is like **3**.[13] Chemical shifts are observed in the following ranges: 6.81−6.92 (Ph *p*-H), 6.37−6.57 (Ph *m*-H), 5.44−5.64 (Ph *o*-H), and 1.15−1.22 ($C_5Me_5$) ppm.

**Table 1.** Crystal Data and Experimental Details for the X-ray Diffraction Studies of **2**, **4**, and **6**

| | $(C_5Me_5)_2SmAsPh_2 \cdot {}^1/_4C_6H_{14}$ (**2**$\cdot {}^1/_4C_6H_{14}$) | $(C_5Me_5)_2SmAsPh_2(THF)$ (**4**) | $(C_5Me_5)_2SmO(CH_2)_4AsPh_2(THF)$ (**6**) |
|---|---|---|---|
| empirical formula | $C_{32}H_{40}SmAs \cdot {}^1/_4C_6H_{14}$ | $C_{36}H_{48}SmAsO$ | $C_{40}H_{56}SmAsO_2$ |
| fw | 671.45 | 722.0 | 794.1 |
| temp (K) | 156 | 163 | 163 |
| crystal system | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 26.188(24) | 10.713(9) | 9.3958(16) |
| $b$ (Å) | 9.911(10) | 14.143(11) | 22.245(3) |
| $c$ (Å) | 23.280(23) | 21.620(16) | 17.931(3) |
| $\beta$ (deg) | 97.150(12) | 101.08(6) | 96.497(11) |
| $V$ (Å3) | 5995(2) | 3215(4) | 3724(1) |
| $Z$ | 8 | 4 | 4 |
| $D_{calcd}$ (Mg/m$^3$) | 1.488 | 1.429 | 1.416 |
| diffractometer | Picker (Crystal Logic) | Siemens P3 | Siemens P3 |
| radiation ($\lambda$ (Å)) | Mo Kα (0.710 730) | Mo Kα (0.710 730) | Mo Kα (0.710 730) |
| scan type | $\theta-2\theta$ | $\omega$ | $\theta-2\theta$ |
| $2\theta$ range (deg) | 1.0−45.0 | 4.0−40.0 | 4.0−45.0 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 3.080 | 2.874 | 2.490 |
| abs cor | semiempirical ($\psi$-scan method) | none | semiempirical ($\psi$-scan method) |
| $R_F$[a] | 0.068 | 0.080 | 0.045 |
| $R_{wF}$[a] | 0.076 | 0.103 | 0.047 |

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF} = \sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$.

mmol) were combined in $C_6D_6$ (1.13 mL) and analyzed immediately. The $^1$H NMR spectrum of the resulting brown solution was nearly identical to that of $(C_5Me_5)_2Sm(\mu\text{-}AsPh_2)Sm(C_5Me_5)_2$ above. $^1$H NMR ($C_6D_6$, 300 MHz, 25 °C, concentration dependent, 19 mM): $\delta$ 8.47 (br s, $\Delta\nu_{1/2}$ = 30 Hz, 2H, $C_6H_5$), 7.71 (br s, $\Delta\nu_{1/2}$ = 20 Hz, 1H, Ph *p*-H), 5.53 (br s, $\Delta\nu_{1/2}$ = 30 Hz, 2H, $C_6H_5$), 0.99 (s, 30H, $C_5Me_5$).

**Reaction of $(C_5Me_5)_2Sm(\mu\text{-}PPh_2)Sm(C_5Me_5)_2$, 7, with $Ph_2PPPh_2$.** $Ph_2PPPh_2$ (0.8 mg, 0.002 mmol) and $(C_5Me_5)_2Sm(\mu\text{-}PPh_2)Sm(C_5Me_5)_2$ (3.9 mg, 0.004 mmol) were combined in $C_6D_6$ (≈0.5 mL) and allowed to react for 5 min, producing a dark brown solution. The solution was examined by $^1$H NMR spectroscopy, which showed complete reaction to form $(C_5Me_5)_2SmPPh_2$, **1**.

**X-ray Data Collection, Structure Determination, and Refinement for 2.** A deep red, irregularly-shaped crystal of **2** of approximate dimensions 0.30 × 0.26 × 0.20 mm was coated with Paratone oil, mounted on the tip of a glass fiber, and transferred to the 156 K nitrogen cold stream of a modified four-circle Picker diffractometer equipped with a monochromatized Mo X-ray source. Accurate cell dimensions and the crystal orientation matrix were determined by a least-squares fit of the setting angles of 20 reflections in the range $12 < 2\theta < 20°$. Intensity data were collected by the $\theta-2\theta$ method using a scan speed of 3.0°/min up to a maximum $2\theta = 45°$. Three intense reflections were monitored after every 97 reflections collected and showed no significant variation. The intensities of 7856 reflections were measured, of which 4109 had $|F_o| > 6.0\sigma(|F_o|)$ and were considered observed. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on $\psi$-scans was applied. A summary of crystallographic data is included in Table 1.

The structure was solved by Patterson methods and expanded by Fourier techniques in the monoclinic space group $P2_1/n$.[15] Hydrogen atoms were included in calculated positions and were constrained to ride upon the appropriate carbon atoms. For methyl groups, at least one of the hydrogen atoms was located from the difference-Fourier map. A disordered solvent molecule, presumably *n*-hexane, was located close to the inversion center, but could not be refined satisfactorily. The three strongest peaks from the difference map were arbitrarily assigned as carbon atoms and were not refined. A total of 293 parameters with Sm and As anisotropic and all other non-hydrogens atoms isotropic were refined using full-matrix least-squares techniques. Refinement converged at $R_F$ = 6.8%, $R_{wF}$ = 7.6%. An anomalous dispersion correction was applied to all non-hydrogen atoms.[16] The final difference electron density map showed some residual electron density ($\rho$(max) = 2.45 e Å$^{-3}$) close to the disordered solvent molecule; the rest of the map was featureless.

**X-ray Data Collection, Structure Determination, and Refinement for 4 and 6.** A dark orange crystal of **4** of approximate dimensions 0.17 × 0.20 × 0.38 mm was oil-mounted[17] on a glass fiber and transferred to a Siemens P3 diffractometer. The determinations of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described methods similar to those of Churchill.[18] Intensity data were collected at 163 K using an $\omega$-scan technique with Mo Kα radiation under the conditions described in Table 1. All 3393 data were corrected for Lorentz and polarization effects and were placed on an approximately absolute scale. Any reflection with $I$(net) < 0 was assigned the value $|F_o| = 0$. The diffraction symmetry was 2/*m* with systematic absences 0*k*0 for $k = 2n + 1$ and *h*0*l* for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$ [$C_{2h}^5$; No. 14] is therefore uniquely defined.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[15] or the SHELXTL PLUS program set.[19] The analytical scattering factors for neutral atoms were used throughout the analysis[20] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0020(|F_o|)^2$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d$(C−H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. Refinement of positional and thermal parameters led to convergence with $R_F$ = 8.0%, $R_{wF}$ = 10.3%, and GOF = 1.61 for 167 variables refined against those 2232 data with $|F_o| > 4.0\sigma(|F_o|)$. A final difference-Fourier map was devoid of significant features; $\rho$(max) = 2.10 e Å$^{-3}$. The crystal decomposed after data were collected to a $2\theta$(max) of 40.0°. It was therefore not possible to apply an absorption correction since our standard practice is to measure $\psi$ scans at the conclusion of data collection.

A pale yellow crystal of **6** of approximate dimensions 0.13 × 0.33 × 0.36 mm was handled as described above for **4**. Intensity data were collected at 163 K. Details appear in Table 1. All 5410 data were

(15) UCLA Crystallographic Computing Package, University of California, Los Angeles, 1981; C. Strouse, personal communication.
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(17) The crystal was immersed in a lube-oil additive, which allowed for manipulation on the bench top and prevented decomposition due to air or moisture. The crystal was secured to a glass fiber (the oil acts as the adhesive) which was attached to an elongated brass mounting pin. Further details appear in: Hope, H. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.
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corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. The diffraction symmetry was 2/m with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/n$ [$C_{2h}^5$; No. 14] is therefore uniquely defined. All crystallographic calculations were carried out as described above for **4**. The quantity minimized during least-squares analysis was $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0004(|F_o|)^2$.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d$(C−H) = 0.96 Å and $U$(iso) = 0.08 Å$^2$. Refinement of positional and thermal parameters led to convergence with $R_F = 4.5\%$, $R_{wF} = 4.7\%$, and GOF = 1.42 for 397 variables refined against those 4053 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded $\rho$(max) = 0.81 e Å$^{-3}$.

## Results and Discussion

**Reactions of $(C_5Me_5)_2Sm(THF)_x$ with $Ph_3E$ ($x = 0, 2$; E = P, As, Sb, Bi).** The reactivity of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ with the group 15 triphenyl compounds, $Ph_3E$, was surveyed as shown in Table 2. Each system was periodically monitored by NMR until no further changes in the spectrum occurred. As expected, $(C_5Me_5)_2Sm$ is more reactive than $(C_5Me_5)_2Sm(THF)_2$ and cleavage of the E−C bonds is more facile for the heavier congeners in group 15.

**Table 2.** Summary of Reactivity of $(C_5Me_5)_2Sm(THF)_x$ with Triphenylpnictides

| compd | $Ph_3P$ | $Ph_3As$ | $Ph_3Sb$ | $Ph_3Bi$ |
|---|---|---|---|---|
| $(C_5Me_5)_2Sm$ | adduct formn | no reacn | E−C cleavage | E−C cleavage |
| $(C_5Me_5)_2Sm(THF)_2$ | no reacn | no reacn | no reacn | E−C cleavage |

In the experiments with $(C_5Me_5)_2Sm(THF)_2$ and $Ph_3P$, $Ph_3As$, and $Ph_3Sb$, no significant perturbation of the $Ph_3E$ resonances from their positions in the free ligands was observed and the low-field resonance characteristic for coordinated THF remained.[21] Apparently, none of these group 15 triphenyl complexes are sufficiently Lewis basic to displace the THF. In contrast, addition of base-free $(C_5Me_5)_2Sm$ to $Ph_3P$ causes the multiplets in free $Ph_3P$ at 7.38 and 7.03 ppm (2:3 ratio) to change to a series of triplet-like peaks at 7.80, 7.20, and 7.07 ppm in a ratio of 2:2:1. Selective homonuclear spin-decoupling experiments confirmed these peaks as arising from the *o*-, *m*-, and *p*-protons, respectively. Coordination of the phosphine perturbs the *o*-H resonances the most and removes the near-degeneracy in chemical shift of the *m*-and *p*-protons in the free ligand.

In order to probe the stoichiometry of this system, portions of $(C_5Me_5)_2Sm$ were added to a solution of $Ph_3P$ up to the 2:1 ratio employed above. No further change in the NMR spectrum of the system occurred after the Sm:P ratio exceeded unity, which indicates formation of a 1:1 metal−ligand complex. Similar shifts were not observed between $(C_5Me_5)_2Sm$ and $Ph_3As$. Formation of a phosphine complex of the very electrophilic $(C_5Me_5)_2Sm$[2,22] is not unexpected, given the crystallographically established structures of both divalent and trivalent lanthanide phosphine complexes such as $Yb[N(SiMe_3)_2]_2(Me_2PCH_2CH_2PMe_2)$,[23] $(C_5Me_5)_2YbCl(Me_2PCH_2PMe_2)$,[24] $La[TeSi(SiMe_3)_3]_3(Me_2PCH_2CH_2PMe_2)_2$,[25] $(MeC_5H_4)_3Ce(PMe_3)$,[26] and $Nd[OCH(PMe_2)CH(t\text{-}C_4H_9)_2]_3$.[27]

No evidence for a stable 1:1 acid base adduct, $(C_5Me_5)_2Sm(EPh_3)$, was found in reactions of $(C_5Me_5)_2Sm$ with $Ph_3Sb$ and $Ph_3Bi$, however. Instead, E−C cleavage reactions occur. In the bismuth case, the reaction is immediate and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$ and $(C_5Me_5)_2SmPh$ are formed. For Sb, the reaction is slower. The $C_5Me_5$ resonance of the starting material disappears over a 1−2 day period, and $(C_5Me_5)_2SmPh$ can be identified by $^1$H NMR in the product mixture obtained. No clear evidence for products such as $[(C_5Me_5)_2Sm]_3(\mu\text{-}\eta^2\text{:}\eta^2\text{:}\eta^1\text{-}Sb_3)(THF)$ or $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Sb_2)$ was found. $Ph_3Bi$ also reacts with $(C_5Me_5)_2Sm(THF)_2$ to give $(C_5Me_5)_2SmPh(THF)$, but no other organosamarium products were identifiable.

As previously reported,[3] the reaction of 2 equiv of $(C_5Me_5)_2Sm$ with 1 equiv of $Ph_3Bi$ forms $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$ and $(C_5Me_5)_2SmPh$. Further investigation of this reaction shows that not all of the $Ph_3Bi$ is consumed with this stoichiometry and the complicated mixture of products formed in the 2:1 reaction can be avoided if a 4:1 Sm:Bi ratio is used. As shown in eq 3, a 4:1 ratio leads to complete consumption of both

$$8(C_5Me_5)_2Sm + 2\,Ph_3Bi \rightarrow [(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2) + 6(C_5Me_5)_2SmPh \quad (3)$$

reactants and clean formation of only $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$ and $(C_5Me_5)_2SmPh$.

Cleavage of E−C bonds has previously been observed with group 15 compounds in reactions with alkali metals. For example, Gilman et al.[28] established that alkali metals in liquid ammonia or THF easily cleave the E−C bond in $Ph_3E$ compounds as shown in eq 4. When reactions with excess alkali

$$2M + Ph_3E \xrightarrow{NH_3(l)} MPh + MEPh_2 \quad (4)$$

$$M = Li, Na, K; E = P, As, Sb$$

metal in liquid ammonia were quenched with $NH_4Cl$, the products were $Ph_2EH$ and benzene for P, As, and Sb.[29] The corresponding reduction of $Ph_3Bi$ was different, however, in that only benzene (3 equiv) was observed.

E−C cleavage in reactions of $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$ with $Ph_3E$ is therefore reasonable, since parallels between the reactions of alkali metals and these bent metallocenes have been previously noted in reactions with substrates as diverse as CO[30] and anthracene.[31] The $(C_5Me_5)_2Sm(THF)_x$ reagents differ from alkali metals, however, because they are more soluble and the presence of $(C_5Me_5)_2Sm$ units allows for the assembly and isolation of reduced products either not accessible or unstable with alkali metals. Hence, $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$, rather than metallic bismuth or insoluble, uncharacterized alkali metal bismuthides, is isolated in reaction 1. Since Bi−C bonds are the weakest in the $EPh_3$ series,[32] it is reasonable that $Ph_3Bi$ is the most likely to undergo E−C cleavage and form polyelement anions (Zintl ions).

**Reactions of $(C_5Me_5)_2Sm$ with $Ph_2PPPh_2$ and $Ph_2AsAsPh_2$: Formation of $(C_5Me_5)_2Sm(EPh_2)$ (E = P, As).** Since the $Ph_3E$ compounds of the lighter congeners in group 15 did not undergo E−C cleavage to form homopolyatomic anions, other precursors to these anions were sought. The

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$Ph_2EEPh_2$ compounds were attractive, since they contained one less E−C(phenyl) bond compared to $Ph_3E$. The availability of $Ph_2EEPh_2$ for E = P, As, Sb, and Bi also allows for a comparison of reactivity in a homologous series, as was done for $Ph_3E$.

$(C_5Me_5)_2Sm$ (2 equiv) reacts quickly and quantitatively with $Ph_2PPPh_2$ and $Ph_2AsAsPh_2$ to give the Sm(III) phosphide and arsenide compounds **1** and **2**, respectively, as shown in eq 5.

$$2(C_5Me_5)_2Sm + Ph_2EEPh_2 \rightarrow 2(C_5Me_5)_2Sm(EPh_2) \quad (5)$$
$$\text{EP P, } \mathbf{1}\text{; As, } \mathbf{2}$$

Both compounds are dark brown crystalline solids which are soluble in hexane and stable in both the solid state and solution at room temperature under an inert atmosphere. These compounds are hydrolytically sensitive and decompose to $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$[33] and $Ph_2EH$ when exposed to moisture. The $^1H$ NMR spectra of **1** and **2** show a single sharp resonance for the $C_5Me_5$ ligand and a single $A_2B_2C$ monosubstituted phenyl ring pattern, arising from the $Ph_2E-$ group. The equivalence of the two phenyl rings dictates either that the $Ph_2E-$ ligand is in a highly symmetrical environment or that there is free rotation about the E-Ph bonds in solution. For the former case, a symmetrical bridging $\mu$-$EPh_2$ mode of coordination, such as that seen in $(C_5H_5)_2Lu(\mu\text{-}EPh_2)_2Li(TMED)$ (E = P,[34] As[35] ), is consistent with the NMR data. However, previous studies have shown that $[(C_5Me_5)_2Sm(\mu\text{-}Z)]_2$ complexes where Z is a large anionic ligand are likely to be too sterically crowded to form simple bridged dimers.[36] Consistent with this supposition, solution molecular weight measurements show **1** and **2** to be monomeric in benzene, which implies a terminal mode of coordination and formally seven-coordinate structures. This is consistent with the spectroscopic and analytical data reported for the related species $(MeC_5H_4)_2Sm(PPh_2)$[37] and $(C_5Me_5)_2Sm(PEt_2)$.[38]

Since all phenyl resonances appear at unusually high field for aromatic protons (3−6 ppm range) and only the lowest field triplets in the $^1H$ NMR spectra, assigned to the *p*-H are well-resolved, additional weak Sm···H-C interactions may exist in solution which serve to increase the effective coordination number. The other resonances for the *o*- and *m*-protons are broadened and may be indicative of further metal−ligand interaction. This is supported by the solid state structure described below for **2** and by the fact that upon addition of THF to these complexes all the resonances become well resolved and move downfield to a more normal range for aromatic protons. A similar situation is observed for the benzyl and phenyl complexes $(C_5Me_5)_2SmCH_2Ph$[39] and $(C_5Me_5)_2SmPh$.[21] For the unsolvated complexes the aryl *o*-H and *m*-H resonances are at high field and are poorly resolved or otherwise unobservable. Addition of THF also sharpens these resonances and causes them to move to the normal aromatic region.

**Reactions of $(C_5Me_5)_2Sm(THF)_2$ with $Ph_2PPPh_2$ and $Ph_2AsAsPh_2$: Formation of $(C_5Me_5)_2Sm(EPh_2)(THF)$ Species (E = P, As).** Both **1** and **2** react immediately with THF to form donor−acceptor adducts which are spectroscopically identical to the products obtained when reaction 5 is repeated using $(C_5Me_5)_2Sm(THF)_2$ as shown in eq 6. This reaction can

$$2(C_5Me_5)_2Sm(THF)_2 + Ph_2EEPh_2 \rightarrow 2(C_5Me_5)_2Sm(EPh_2)(THF) \quad (6)$$
$$\text{E: P, } \mathbf{3}\text{; As, } \mathbf{4}$$

be conducted equally well in either THF or nonpolar solvents such as hexane, benzene, and toluene. However, in light of the further reactivity of **3** and **4** with THF (see below), the nonpolar solvents are preferred. Both **3** and **4** are obtained as dark green-brown powders which have lower solubility in common organic solvents than their THF-free analogs. The THF in **3** and **4** can be partially removed under vacuum, so samples of both compounds exhibit $^1H$ NMR spectra that are dependent on the amount of coordinated solvent removed during workup.[40] Resonances for the aromatic rings and the $C_5Me_5$ ligands move consistently downfield with increasing amounts of THF, reaching limiting values in the presence of an additional 1 equiv of THF. Attempts to completely remove the THF from **3** and **4** to form the unsolvated compounds **1** and **2**, respectively, were only partly successful. Heating **3** at 65 °C for 12 h under high vacuum produced a mixture of the solvent-free compound **1** and a decomposition product **5** (see below). Similar treatment of **4** gave a mixture of partially desolvated **4**, $(C_5Me_5)_2Sm(AsPh_2)(THF)_x$ ($x < 1$), and an analogous decomposition product, **6**.

**Structures of $(C_5Me_5)_2Sm(AsPh_2)$, 2, and $(C_5Me_5)_2Sm(AsPh_2)(THF)$, 4.** Since there are currently no structural data available for Sm−As bonds and only one example of a Ln−As bonded compound in the literature,[35] an X-ray structural determination on **2** was performed. Structural data were also obtained on **4** for comparison with the unusual features in **2**. Selected interatomic distances and angles are given in Tables 3 and 4, and the structures of **2** and **4** are shown in Figures 1 and 2. **2** crystallizes with two independent, but chemically equivalent, molecules in the asymmetric unit, along with one hexane solvent molecule for every four molecules of **2**. The structure consists of discrete monomeric units with no unusual intermolecular contacts, which is consistent with the monomeric solution molecular weight data. **4** also crystallizes as a monomer as expected.

While there is no indication in the solid state of aggregation through bridging arsenido groups for **2**, several aspects of the data suggest an increase in coordination number through *intra*molecular interactions as shown in Figure 1. Both arsenic atoms in the independent molecules of **2** are located asymmetrically between the $C_5Me_5$ rings, as shown by the difference in (ring centroid)−Sm−As angles (117.3 vs 100.5° and 119.1 vs 100.2° for molecule 1 and molecule 2, respectively). The arsenic is also asymmetrically located with respect to the plane determined by the two ring centroids and Sm as illustrated in Figure 3. As(1) is 1.45 Å out of this plane, As(2) is displaced by 1.38 Å, and the angles between the Sm−As vectors and these planes are 29.2° [Sm(1)−As(1)] and 27.6° [Sm(2)−As(2)]. Alternatively, this asymmetry can be described in terms of the deviation of the Sm atoms from the plane formed by arsenic and the ring centroids [Sm(1) 0.35 Å, Sm(2) 0.34 Å]. The arsenic atom in **4** is also located off center (1.76 Å) from the (ring centroid)−Sm−(ring centroid) plane, but this is not unusual

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**Table 3.** Selected Interatomic Distances (Å) and Interatomic Angles (deg) in $2\cdot{}^1/_4C_6H_{14}$, $(C_5Me_5)_2Sm(AsPh_2)\cdot{}^1/_4C_6H_{14}$[a]

| molecule 1 | | molecule 2 | |
|---|---|---|---|
| Sm(1)−As(1) | 2.973(3) | Sm(2)−As(2) | 2.966(3) |
| Sm(1)−Cnt(1) | 2.413 | Sm(2)−Cnt(3) | 2.423 |
| Sm(1)−Cnt(2) | 2.423 | Sm(2)−Cnt(4) | 2.407 |
| As(1)−C(26) | 1.911(19) | As(2)−C(64) | 1.965(18) |
| As(1)−C(32) | 1.919(20) | As(2)−C(58) | 1.990(18) |
| Sm(1)−C(31) | 2.901 | Sm(2)−C(59) | 2.967 |
| Sm(1)−C(32) | 3.031 | Sm(2)−C(64) | 3.117 |
| Sm(1)−C(1) | 2.702(19) | Sm(2)−C(33) | 2.698(19) |
| Sm(1)−C(3) | 2.694(19) | Sm(2)−C(35) | 2.677(21) |
| Sm(1)−C(5) | 2.689(21) | Sm(2)−C(37) | 2.693(19) |
| Sm(1)−C(7) | 2.687(17) | Sm(2)−C(39) | 2.778(19) |
| Sm(1)−C(9) | 2.736(20) | Sm(2)−C(41) | 2.674(19) |
| Sm(1)−C(11) | 2.668(20) | Sm(2)−C(43) | 2.663(21) |
| Sm(1)−C(13) | 2.682(19) | Sm(2)−C(45) | 2.655(22) |
| Sm(1)−C(15) | 2.751(18) | Sm(2)−C(47) | 2.722(22) |
| Sm(1)−C(17) | 2.720(20) | Sm(2)−C(49) | 2.680(20) |
| Sm(1)−C(19) | 2.665(19) | Sm(2)−C(51) | 2.719(21) |
| Cnt(1)−Sm(1)−Cnt(2) | 136.3 | Cnt(3)−Sm(2)−Cnt(4) | 135.1 |
| Cnt(1)−Sm(1)−As(1) | 117.3 | Cnt(3)−Sm(2)−As(2) | 119.1 |
| Cnt(2)−Sm(1)−As(1) | 100.5 | Cnt(4)−Sm(2)−As(2) | 100.2 |
| Sm(1)−As(1)−C(26) | 118.8(5) | Sm(2)−As(2)−C(58) | 118.5(6) |
| Sm(1)−As(1)−C(32) | 73.0(6) | Sm(2)−As(2)−C(64) | 75.4(5) |
| C(26)−As(1)−C(32) | 104.3(8) | C(58)−As(2)−C(64) | 104.9(8) |
| C(31)−C(32)−As(1) | 115.0(15) | C(59)−C(64)−As(2) | 113.1(13) |
| C(27)−C(32)−As(1) | 129.0(16) | C(63)−C(64)−As(2) | 128.8(15) |
| C(21)−C(26)−As(1) | 119.8(14) | C(57)−C(58)−As(2) | 117.3(15) |
| C(25)−C(26)−As(1) | 125.9(14) | C(53)−C(58)−As(2) | 120.5(14) |

[a] Cnt(1) is the centroid of the C(1)−C(3)−C(5)−C(7)−C(9) ring. Cnt(2) is the centroid of the C(11)−C(13)−C(15)−C(17)−C(19) ring. Cnt(3) is the centroid of the C(33)−C(35)−C(37)−C(39)−C(41) ring. Cnt(4) is the centroid of the C(43)−C(45)−C(47)−C(49)−C(51) ring.

**Table 4.** Selected Interatomic Distances (Å) and Interatomic Angles (deg) in **4**, $(C_5Me_5)_2Sm(AsPh_2)(THF)$[a]

| | | | |
|---|---|---|---|
| Sm(1)−As(1) | 3.049(3) | Cnt(1)−Sm(1)−Cnt(2) | 136.4 |
| Sm(1)−O(1) | 2.471(15) | | |
| Sm(1)−Cnt(1) | 2.464 | Cnt(1)−Sm(1)−As(1) | 100.5 |
| Sm(1)−Cnt(2) | 2.425 | Cnt(1)−Sm(1)−O(1) | 103.3 |
| | | Cnt(2)−Sm(1)−As(1) | 114.7 |
| Sm(1)−C(1) | 2.711(24) | Cnt(2)−Sm(1)−O(1) | 102.4 |
| Sm(1)−C(2) | 2.697(24) | As(1)−Sm(1)−O(1) | 88.8(3) |
| Sm(1)−C(3) | 2.788(22) | | |
| Sm(1)−C(4) | 2.772(22) | Sm(1)−As(1)−C(25) | 120.8(6) |
| Sm(1)−C(5) | 2.737(23) | Sm(1)−As(1)−C(31) | 109.1(6) |
| | | C(25)−As(1)−C(31) | 96.9(9) |
| Sm(1)−C(11) | 2.728(23) | | |
| Sm(1)−C(12) | 2.687(20) | C(32)−C(31)−As(1) | 122.6(16) |
| Sm(1)−C(13) | 2.650(21) | C(36)−C(31)−As(1) | 117.2(16) |
| Sm(1)−C(14) | 2.694(21) | C(30)−C(25)−As(1) | 115.9(16) |
| Sm(1)−C(15) | 2.738(21) | C(32)−C(31)−As(1) | 126.4(18) |

[a] Cnt(1) is the centroid of the C(1)−C(5) ring. Cnt(2) is the centroid of the C(11)−C(15) ring.

considering the presence of the additional THF ligand in the coordination sphere.

Examination of the geometry about the arsenic in **2** shows considerable deviation from either an ideal pyramidal or planar arrangement. The sum of the angles averages 297.4° and the C(ipso)−As−C(ipso) angles are 104.3(8)°-104.9(8). The Sm−As−C(ipso) angles are divided into two distinctly different sets: one group has values close to a planar arrangement [Sm(1)−As(1)−C(26) 118.8(5)° and Sm(2)−As(2)−C(58) 118.5(6)°], and the remaining set is far more acute [Sm(1)−As(1)−C(32) 73.0(6)° and Sm(2)−As(2)−C(64) 75.4(6)°]. Both narrow angles are associated with an *o*-carbon on the side of the ring closer to the samarium, which results in one ring being

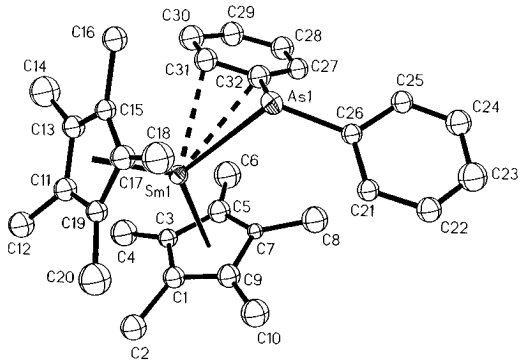


**Figure 1.** Thermal ellipsoid plot of $(C_5Me_5)_2Sm(AsPh_2)$, **2**, with ellipsoids drawn at the 50% probability level.

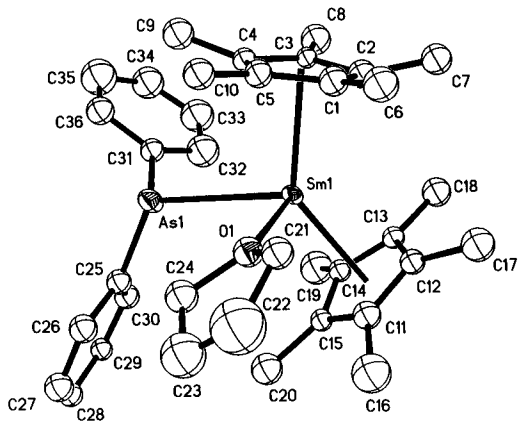


**Figure 2.** Thermal ellipsoid plot of $(C_5Me_5)_2Sm(AsPh_2)(THF)$, **4**. with ellipsoids drawn at the 50% probability level.

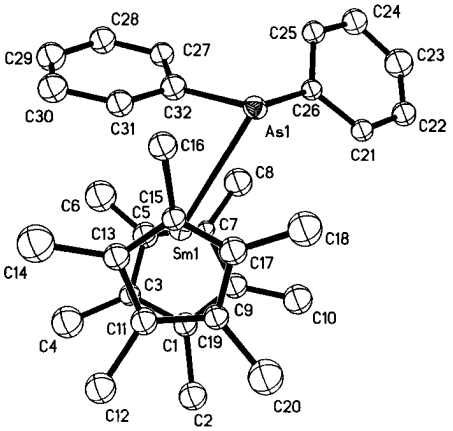


**Figure 3.** Top view of $(C_5Me_5)_2Sm(AsPh_2)$, **2**.

tipped toward the metal in each of the molecules in the unit cell. In each of these tilted phenyl rings, one C(ortho)−C(ipso)−As angle [C(31)−C(32)−As(1) 115.0(15)°, C(59)−C(64)−As(2) 113.1(13)°] is considerably smaller than that on the opposite side of the ring [C(27)−C(32)−As(1) 129.0(16)°, C(63)−C(64)−As(2) 128.8(15)°]. In contrast, the difference between proximal and distal C(ortho)−C(ipso)−As angles observed in the adjacent phenyl rings [C(21)−C(26)−As(1) 119.8(14)°, C(57)−C(58)−As(2) 117.3(15)° vs C(25)−C(26)−As(1) 125.9(14)°, C(53)−C(58)−As(2) 120.5(14)°] is much less dramatic.

In comparison, the geometry around arsenic in $(C_5Me_5)_2Sm(AsPh_2)(THF)$ is distinctly pyramidal (sum of angles = 326.8°) and there is no overt bending of the As−C(ipso) bond toward the samarium. The Sm(1)−As(1)−C(31) angle of 109.1(6)° is perfectly regular, and the more obtuse Sm(1)−As(1)−C(31) angle to the aromatic ring nearer the THF ligand is correspond-

ingly opened to 120.8(6)°. Unlike **2**, there is no trend apparent in the C(ortho)−C(ipso)−As angles [C(32)−C(31)−As(1) 122.6(16)°, C(36)−C(31)−As(1) 117.2(16)°, C(30)−C(25)−As(1) 115.9(16)°, C(32)−C(31)−As(1) 126.4(18)°] based on the proximity of the *o*-carbon to the samarium, nor is the difference between the proximal and distal sides of the phenyl ring as pronounced as in **2**.

The result of the distortions in geometry about arsenic in **2** is that one phenyl ring is oriented toward the samarium center, with the possibility of an $\eta^2$-interaction involving the ipso- and *o*-carbons. The shortest interatomic distances are to the *o*-carbons [Sm(1)−C(31) 2.901 Å, Sm(2)−C(59) 2.967 Å]. The samarium−ipso-carbon distances are longer [Sm(1)−C(32) 3.031 Å, Sm(2)−C(64) 3.117 Å]. In contrast, in **4** the shortest Sm···C(phenyl) distance is 4.13 Å.

In the past, when interactions of this type have been observed in organolanthanide complexes,[41] a measure of their strength has been estimated by comparing the distance of the metal to the carbon in question with the metal−cyclopentadienyl carbon distance. For example, in the styrene complex, $[(C_5Me_5)_2Sm]_2(\mu\text{-PhCHCH}_2)$,[41] a 2.772(17) Å Sm−C(ortho phenyl) distance is observed, which is equivalent to the 2.792(36) Å Sm−C(cyclopentadienyl) average. Since the Sm−C(cyclopentadienyl) distances in **2** are 2.665(19)−2.778(19) Å, the above secondary Sm−C(phenyl) interactions are outside the range consistent with a strong bonding interaction. However, the Sm−C(ortho phenyl) distances are comparable to the long-range interactions clearly extant in molecules like $(C_5Me_5)_2Yb(MeC{\equiv}CMe)$,[42] $(C_5Me_5)_2Yb(\mu\text{-}H_2C{=}CH_2)Pt(PPh_3)_2$,[43] and $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$.[44] All of these structural observations, together with the features from the $^1$H NMR spectrum (see above), support the existence of a weak interaction between the samarium and one phenyl ring in each diphenylarsenido ligand, in accordance with the expected electrophilicity of the formally seven-coordinate samarium center.

The extent of this interaction can also be evaluated by examining the structural parameters of the $(C_5Me_5)_2Sm$ units in **2** and **4**, since a formally seven-coordinate **2** would be expected to have smaller Sm−C($C_5Me_5$) distances than those in formally eight-coordinate **4**.[45] The fact that the 2.665(19)−2.778(19) Å Sm−C($C_5Me_5$) distances in unsolvated **2** are indistinguishable from the analogous 2.650(21)−2.788(22) Å values in solvated **4** is consistent with **2** having an effective coordination number greater than 7. The 135.7° average (ring centroid)−Sm−(ring centroid) angle in **2** is also equivalent to the 136.4° angle in **4**.

However, the 3.049(3) Å Sm−As bond in eight-coordinate $(C_5Me_5)_2Sm(AsPh_2)(THF)$ is about 0.08 Å longer than the 2.966(3) and 2.973(3) Å distances in **2**, which suggests that the extra phenyl coordination in **2** is not fully equivalent to another ligand such as THF. In **4**, THF approaches Sm with a Sm−O(THF) distance of 2.471(15) Å, which is typical.[45]

The Sm−As bonds in both **2** and **4** are significantly longer (0.031−0.077 Å) than the 2.870(2) and 2.895(2) Å Lu−As bonds of $(C_5H_5)_2Lu(\mu\text{-}AsPh_2)_2Li(Me_2NCH_2CH_2NMe_2)$,[35] the only other structurally characterized lanthanide arsenic complex, even when the difference in ionic radius is taken into account. The difference between the extremes of the error limits is only 0.013 Å, but terminal lengths are typically shorter than bridging distances. This elongation may be due to the increased steric demand of the $C_5Me_5$ ligand as compared to $C_5H_5$ in the Lu compound.

**THF Ring Opening by $(C_5Me_5)_2Sm(EPh_2)(THF)$ Compounds.** In contrast to **1** and **2**, compounds **3** and **4** are not stable and undergo a further reaction involving the ring opening of the coordinated THF. As shown in eq 7, $EPh_2$-substituted

$$(C_5Me_5)_2Sm(EPh_2)(THF) \rightarrow (C_5Me_5)_2Sm[O(CH_2)_4EPh_2](THF) \quad (7)$$

E: P, **5**; As, **6**

butoxide complexes **5** and **6** result. This ring opening occurs over a period of days at room temperature in benzene, toluene, hexane, or THF. $(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2](THF)$ can be produced on a preparative scale by heating **4** in refluxing THF for 16 h. These reactions go to completion in the presence of just 2 equiv of THF, although the reaction is slower than in neat THF. **5** and **6** also form over a period of several weeks in the solid state when stored at ambient temperature in an inert-atmosphere glovebox containing THF. Ring opening to form a substituted butoxide ligand is further observed when samples of **3** and **4** are heated under vacuum (see above). The presence of both desolvated species as well as **3** and **4** shows that loss of THF from the complexes is accompanied by nucleophilic attack on THF, which must, of necessity, be intramolecular under these conditions. This transformation is remarkable in that the ring opening reaction, which requires THF, is competitive with the loss of THF from the inner coordination sphere, even under vacuum where such loss is irreversible.

**Structure of $(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2](THF)$, 6.** Compounds **5** and **6** were first identified by the distinctive appearance of the butoxide ligand in the $^1$H NMR spectrum and by comparison with spectral data for the related compounds $(C_5Me_5)_2Sm[O(CH_2)_3CH_3](THF)$,[39] $(C_5Me_5)_2Ln[O(CH_2)_4C_5Me_5](THF)$ (Ln = Sm, La, Nd, Tm, Lu),[46,47] and $\{(C_5H_5)_2Lu[\mu\text{-}O(CH_2)_4PPh_2]\}_2$.[48] Where structural information is available for these compounds, the alkoxide ligands function as simple terminal or dinuclear bridging ligands with no further metal−ligand interactions. In the case of compounds **5** and **6**, however, the possibility exists for secondary ligation from the $EPh_2$ terminus to form a seven-membered Sm−$O(CH_2)_4E$ cycle. To explore this possibility, an X-ray structural determination was carried out on **6**, which confirmed the presence of the THF-derived ligand suggested by the spectral data (Figure 4). Selected bond lengths and angles are given in Table 5.

The molecular structure of $(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2](THF)$ shows an eight-coordinate geometry about the samarium with an approximately tetrahedral arrangement of cyclopentadienyl ring centroids and oxygen atoms. The angle between the (ring centroid)−Sm−(ring centroid) and O−Sm−O planes is 89.9°. The butoxide ligand coordinates in a terminal fashion, and there is no interaction between the diphenylarsenido ligand and the samarium. Overall, the $(C_5Me_5)_2SmO_2$ geometry for the complex is quite similar to that of $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$, with the corresponding Sm−O(butoxide), Sm−O(THF), and average Sm−C(ring carbon) distances in both compounds within experimental error of each other. The distinct trend toward linearity in the 165.2(7)° Sm−O-C bond angle in $(C_5Me_5)_2Sm[O(CH_2)_4C_5Me_5](THF)$[46] (and other lanthanide

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(43) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 915.
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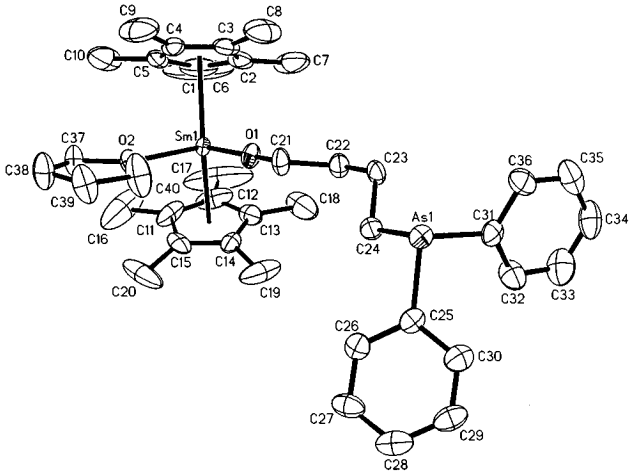


**Figure 4.** Thermal ellipsoid plot of $(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2](THF)$, **6**, with ellipsoids drawn at the 50% probability level.

**Table 5.** Selected Interatomic Distances (Å) and Interatomic Angles (deg) in **6**, $(C_5Me_5)_2Sm[O(CH_2)_4AsPh_2](THF)$[a]

| | | | |
|---|---|---|---|
| Sm(1)−O(1) | 2.085(5) | Cnt(1)−Sm(1)−Cnt(2) | 136.0 |
| Sm(1)−O(2) | 2.475(5) | | |
| Sm(1)−Cnt(1) | 2.478 | Sm(1)−O(1)−C(21) | 175.4(4) |
| Sm(1)−Cnt(2) | 2.479 | O(1)−Sm(1)−O(2) | 85.3(2) |
| | | Cnt(1)−Sm(1)−O(1) | 107.1 |
| Sm(1)−C(1) | 2.754(9) | Cnt(1)−Sm(1)−O(2) | 107.2 |
| Sm(1)−C(2) | 2.699(9) | Cnt(2)−Sm(1)−O(1) | 104.8 |
| Sm(1)−C(3) | 2.729(8) | Cnt(2)−Sm(1)−O(2) | 104.7 |
| Sm(1)−C(4) | 2.760(7) | | |
| Sm(1)−C(5) | 2.790(9) | C(24)−As(1)−C(25) | 98.3(3) |
| | | C(24)−As(1)−C(31) | 97.9(3) |
| Sm(1)−C(11) | 2.749(10) | C(25)−As(1)−C(31) | 101.7(3) |
| Sm(1)−C(12) | 2.752(9) | | |
| Sm(1)−C(13) | 2.731(8) | | |
| Sm(1)−C(14) | 2.742(7) | | |
| Sm(1)−C(15) | 2.767(8) | | |

[a] Cnt(1) is the centroid of the C(1)−C(5) ring. Cnt(2) is the centroid of the C(11)−C(15) ring.

alkoxides)[49] is also followed in **6**, where the Sm(1)−O(1)−C(21) angle reaches an even larger value of 175.4(4)°.

**Reaction of $(C_5Me_5)_2Sm$ with $(C_5Me_5)_2Sm(EPh_2)$ (E = P, As) To Form Mixed-Valent Products.** Formation of Sm−$EPh_2$ complexes from $Ph_2EEPh_2$ precursors is consistent with the relative E−E and E−C bond strengths in these compounds. In efforts to cleave the E−C bonds in these compounds, **1** and **2** were treated with additional $(C_5Me_5)_2Sm$; i.e., reaction 5 was run with a 4:1 stoichiometry as shown in eq 8. Alternatively,

$$4(C_5Me_5)_2Sm + Ph_2EEPh_2 \rightarrow 2(C_5Me_5)_2Sm(\mu_2\text{-}EPh_2)Sm(C_5Me_5)_2 \quad (8)$$
E: P, **7**; As, **8**

isolated $(C_5Me_5)_2Sm(EPh_2)$ can be reacted with $(C_5Me_5)_2Sm$ in a 1:1 ratio as shown in eq 9 to form products that are

$$(C_5Me_5)_2Sm(EPh_2) + (C_5Me_5)_2Sm \rightarrow (C_5Me_5)_2Sm(\mu_2\text{-}EPh_2)Sm(C_5Me_5)_2 \quad (9)$$
E: P, **7**; As, **8**

spectroscopically the same as those formed in eq 8. On the basis of $^1$H NMR data, a new compound is formed in both cases, but only for E = P has a new product, **7**, been isolated and

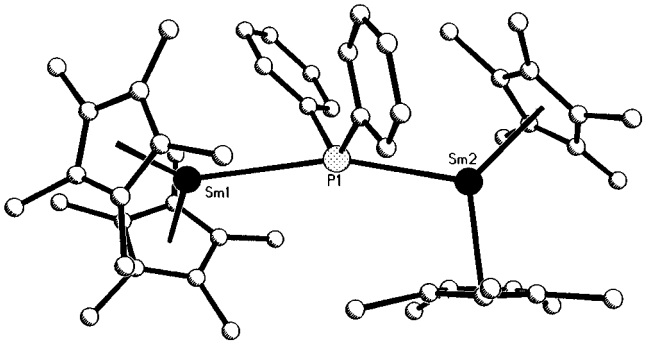


**Figure 5.** Structure of $(C_5Me_5)_2Sm(\mu\text{-}PPh_2)Sm(C_5Me_5)_2$, **7**.

definitively characterized by X-ray crystallography[50] (Figure 5). The corresponding arsenic product, **8** (E = As), is unstable, showing signs of decomposition within 15 min of synthesis, and was characterized only in solution by $^1$H NMR spectroscopy. Neither product results from E−C cleavage; each results instead from coordination of $(C_5Me_5)_2Sm$ to the lone pair of electrons of the respective pnictide. It is noteworthy that these "$(C_5Me_5)_2Sm$" complexation reactions do not occur when $(C_5Me_5)_2Sm(THF)_2$ is substituted for $(C_5Me_5)_2Sm$. In other words, $(C_5Me_5)_2SmEPh_2(THF)$ compounds **3** and **4** do not undergo any further reaction in the presence of additional equivalents of $(C_5Me_5)_2Sm(THF)_2$. The $^1$H NMR spectra of the reaction mixtures are a simple superposition of the two components.

The $^{13}$C NMR and magnetic data for **7** give an indication of the electronic structure of this formally mixed-oxidation-state Sm(II,III) compound. Resonances for the $C_5Me_5$ ring and methyl carbons in the $^{13}$C NMR spectra of compounds **1**−**6** fall in the ranges 113−118 and 18−20 ppm, respectively, as is common for trivalent (pentamethylcyclopentadienyl)samarium complexes. In contrast, the methyl carbons in **7** are observed at 57.3 ppm and the ring carbon resonance appears at 17.8 ppm. These unusual positions do not resemble those found in typical divalent pentamethylcyclopentadienyl compounds but rather lie between the values observed for strictly divalent and trivalent complexes,[1b,51] as is observed for a related mixed-valent complex $(C_5Me_5)_2Sm(\mu\text{-}C_5H_5)Sm(C_5Me_5)_2$.[49]

Similarly, the room-temperature molar magnetic susceptibility of $(C_5Me_5)_2Sm(\mu_2\text{-}PPh_2)Sm(C_5Me_5)_2$ measured in benzene solution[52] is $2560 \times 10^{-6}$ cgsu, giving an effective magnetic moment per samarium of 2.45 $\mu_B$. The former value is close to the average of the susceptibilities per metal center for the individual components $(C_5Me_5)_2Sm$, $5050 \times 10^{-6}$ cgsu,[21] and $(C_5Me_5)_2Sm(PPh_2)$, $425 \times 10^{-6}$ cgsu. The magnetic data alone indicate that **7** is a class I mixed-valence system[53] where the two metals exist in distinct oxidation states. However, the single resonance in the $^1$H NMR spectrum and the unusual shifts for the cyclopentadienyl ligands in the $^{13}$C NMR spectrum are indicative of a single, or perhaps averaged, environment. Together, these data suggest that in solution there is some degree of delocalization mediated through the bridging diphenylphosphido unit, allowing for a change between the Sm(II) and Sm(III) oxidation states that is rapid on the NMR time scale. Irrespective of the actual valence description, the availability of the divalent $(C_5Me_5)_2Sm$ moiety in **7** for further reactivity is

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(50) Several attempts were made to obtain precise metrical data for crystals of **7**, but the data were not of sufficient quality to yield any information other than atom connectivity.

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evidenced by the P−P bond cleavage of $Ph_2PPPh_2$ and its conversion back to $(C_5Me_5)_2Sm(PPh_2)$, eq 10.

$$2(C_5Me_5)_2Sm(\mu_2\text{-}PPh_2)Sm(C_5Me_5)_2 + Ph_2PPPh_2 \rightarrow 4(C_5Me_5)_2Sm(PPh_2) \quad (10)$$

**Reactions of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ with $Ph_2SbSbPh_2$ and $Ph_2BiBiPh_2$.** In contrast to the phosphorus and arsenic systems described above, eqs 5 and 6, the analogous reactions with antimony and bismuth do not simply lead to cleavage of the element−element bond. In each case, E−C bond cleavage occurs with $(C_5Me_5)_2Sm$, as evidenced by the appearance of $(C_5Me_5)_2SmPh$, eqs 11 and 12. The reactions

$$2(C_5Me_5)_2Sm + Ph_2SbSbPh_2 \rightarrow (C_5Me_5)_2SmPh + \text{unreacted } Ph_2SbSbPh_2 \quad (11)$$

$$2(C_5Me_5)_2Sm + Ph_2BiBiPh_2 \rightarrow (C_5Me_5)_2SmPh + Bi(0) + \text{unreacted } Ph_2BiBiPh_2 \quad (12)$$

with $(C_5Me_5)_2Sm(THF)_2$ mirror those of the THF-free reactions, except that $(C_5Me_5)_2SmPh(THF)$ is produced, eqs 13 and 14.

$$2(C_5Me_5)_2Sm(THF)_2 + Ph_2SbSbPh_2 \rightarrow (C_5Me_5)_2SmPh(THF) + \text{unreacted } Ph_2SbSbPh_2 \quad (13)$$

$$2(C_5Me_5)_2Sm(THF)_2 + Ph_2BiBiPh_2 \rightarrow (C_5Me_5)_2SmPh(THF) + Bi(0) \quad (14)$$

With these $Ph_2EEPh_2$ substrates, no $(E_2)^{2-}$ or $(E_3)^{3-}$ products are observed. Only elemental bismuth and antimony are obtained. The bismuth reactions readily deposit elemental bismuth, but the antimony reactions are curious in that elemental antimony does not appear until the reactions have run for 1−3 days. Intermediate products have been neither isolable nor identifiable by $^1H$ NMR spectroscopy. Neither variation in the solvent from hexane to arenes to THF nor low temperature reactions have yielded any other compounds.

**Reactions of $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ with $Ph_2BiX$.** Since the reactivity of $Ph_3Bi$ to form $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$ was found to be unique in the group 15 $Ph_3E$ and $Ph_2EEPh_2$ compounds investigated, the reactions of $Ph_2BiCl$ with $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ were examined to see if they would parallel that of $Ph_3Bi$ or $Ph_2BiBiPh_2$. Halide abstraction was expected to form $(C_5Me_5)_2SmCl$[40] and $(C_5Me_5)_2SmCl(THF)$,[54] respectively. This would leave a $Ph_2Bi$ moiety which could couple to $Ph_2BiBiPh_2$ or react with $(C_5Me_5)_2Sm(THF)_x$ to form $(C_5Me_5)_2Sm(BiPh_2)(THF)_x$. Either pathway would lead to the formation of Sm−Bi or Bi−Bi bonds necessary for the assembly of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$.

Reaction of $(C_5Me_5)_2Sm(THF)_2$ with a 2:1 Sm/Bi ratio as shown in eq 15 gives a variety of products resulting from both

$$2(C_5Me_5)_2Sm(THF)_2 + Ph_2BiCl \rightarrow (C_5Me_5)_2SmCl(THF) + (C_5Me_5)_2SmPh(THF) + Bi(0) + Ph_3Bi \quad (15)$$

Bi−Cl and Bi−Ph cleavage, as well as small amounts of products consistent with limited reductive coupling of $Ph_2BiCl$ (see below). The 1:1 reaction is more selective and leads only to Bi−Cl cleavage, eq 16. Coupling of $Ph_2BiCl$ to form $Ph_2BiBiPh_2$ is implied by the presence of Bi(0) and $Ph_3Bi$ as products of dibismuthine disproportionation, eq 17. Bi(0) is

$$2(C_5Me_5)_2Sm(THF)_2 + 2Ph_2BiCl \rightarrow 2(C_5Me_5)_2SmCl(THF) + Ph_2BiBiPh_2 \quad (16)$$

$$3Ph_2BiBiPh_2 \rightarrow 4Ph_3Bi + 2\ Bi \quad (17)$$

quantitatively recovered according to the net overall reaction shown in eq 18. Reactions conducted with $(C_5Me_5)_2Sm$ in place

$$3(C_5Me_5)_2Sm(THF)_2 + 3Ph_2BiCl \rightarrow 3(C_5Me_5)_2SmCl(THF) + 2\ Ph_3Bi + Bi(0) \quad (18)$$

of $(C_5Me_5)_2Sm(THF)_2$ proceed analogously to eqs 15 and 16, except that the THF-free compounds $(C_5Me_5)_2SmCl$ and $(C_5Me_5)_2SmPh$ are formed. This chemistry is reminiscent of that with alkali metals and $Ph_2BiCl$. A 1:1 ratio of Na:$Ph_2BiCl$ in liquid ammonia leads to reductive coupling and the formation of $Ph_2BiBiPh_2$.[55] Excess alkali metal effects cleavage of the Bi−Bi bond and affords Bi(0) and $Ph_3Bi$.[56]

## Conclusion

$(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ react with aryl-substituted group 15 compounds by three modes: coordination, E−C cleavage, and E−E cleavage. E−C cleavage is most common for the heavier congeners, which have weaker E−C bonds. Hence, $(C_5Me_5)_2SmPh$ products are found in reactions with Sb and Bi but not with P and As. E−E cleavage occurs with all of the systems studied: P, As, Sb, and Bi. For the lighter congeners with stronger E−C bonds, the E−E cleavage products are isolated as the $EPh_2$ complexes $(C_5Me_5)_2Sm(PPh_2)$ and $(C_5Me_5)_2Sm(AsPh_2)$. The THF adducts display further chemistry and provide a system in which THF coordination and ring opening can be separately defined. The base-free complexes interact with additional $(C_5Me_5)_2Sm$ to form mixed-valent compounds. Reaction of $(C_5Me_5)_2Sm$ with $Ph_3Bi$ appears to be a rather special case, since it is the only one in which the $(E_2)^{2-}$ ion is isolated. Hence, the dibismuth complex $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Bi_2)$ is accessible from neither $Ph_2BiBiPh_2$ nor $Ph_2BiCl$ and the only organosamarium products of reactions with other $Ph_3E$ complexes are E−C(phenyl) cleavage products.

The complexes $(C_5Me_5)_2Sm(AsPh_2)$, **2**, and $(C_5Me_5)_2Sm(AsPh_2)(THF)$, **4**, constitute an interesting pair of compounds which show the flexibility of the $(C_5Me_5)_2Sm$ unit to stabilize different ligand systems. The isolation and structural characterization of the lower coordinate **2** are possible, although there is clearly room for the addition of THF to form **4**. The isolation of **4** indicates that this typical eight-coordinate structure is possible even with ligands as large as $AsPh_2$. However, **4** can be desolvated under vacuum and can engage in THF ring-opening reactivity. Studies directed toward exploiting this unusual balance of steric saturation are in progress.

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**Supporting Information Available:** Tables of crystal data, positional parameters, bond distances and angles, and thermal parameters (35 pages). Ordering information is given on any current masthead page.

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