Inorg. Chem. **1992,** *31,* 3592-3600

Reactivity of Hydrazines with Organometallic Samarium Complexes and the X-ray Crystal Structures of $(C_5Me_5)_2Sm(\eta^2\text{-}PhNHNPh)(THF)$, $(C_5Me_5)_2Sm(NHPh)(THF)$, and $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$[1]

William J. Evans,* Gabriele Kociok-Köhn, Voon S. Leong, and Joseph W. Ziller

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

Received April 16, 1992

$(C_5Me_5)_2Sm(THF)_2$ reacts with PhNHNHPh in hexane to cleave the NN bond and form $(C_5Me_5)_2Sm(NHPh)(THF)$ (**1**) in 80% yield. The coordinated THF can be removed from **1** by heating to 90 °C at 2×10^{-6} Torr for 2 h, which sublimes $[(C_5Me_5)_2Sm(NHPh)]_x$ (**2**). Addition of THF to **2** regenerates **1** quantitatively. **2** can also be synthesized from the reaction of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ and $PhNH_2$. NN bond cleavage is not observed, however, when $(C_5Me_5)_2Sm$ reacts with PhNHNHPh. This reaction forms a complex, **3**, which can be isolated as the THF adduct $(C_5Me_5)_2Sm(\eta^2\text{-}PhNHNPh)(THF)$ (**4**), in which the NN bond is retained. **3** can also be obtained from the reactions of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with either PhNHNHPh or PhN=NPh as well as from reactions of PhNHNHPh with $[(C_5Me_5)_2Sm]_2(\mu\text{-}PhNNPh)$ and $(C_5Me_5)_2Sm(PhNNPh)(THF)$. The reaction of excess $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with PhNHNHPh forms $[(C_5Me_5)_2Sm]_2(\mu\text{-}PhNNPh)$. $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ reacts with H_2NNH_2 in hexane to form $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$ (**5**) in 60% yield. **5** can also be prepared from $(C_5Me_5)_2Sm$ and H_2NNH_2. **1** crystallizes from THF in space group $P2_1/c$ with $a = 19.052$ (2) Å, $b = 8.484$ (1) Å, $c = 18.572$ (2) Å, $\beta = 113.30$ (1)°, $V = 2757.0$ (6) Å^3, and $D_{calcd} = 1.41$ g cm^{-3} for $Z = 4$. Least-squares refinement of the model based on 6059 reflections ($|F_o| > 0$) converged to a final $R_F = 3.7\%$. **4** crystallizes from hexane at −35 °C in space group $P2_1/c$ with $a = 9.811$ (2) Å, $b = 16.098$ (5) Å, $c = 23.393$ (7) Å, $\beta = 99.20$ (2)°, $V = 3647$ (2) Å^3, and $D_{calcd} = 1.31$ g cm^{-3} for $Z = 4$. Least-squares refinement of the model based on 4380 reflections ($|F_o| > 1.0\sigma(|F_o|)$) converged to a final $R_F = 4.6\%$. **5** crystallizes from hexane at −35 °C in space group $P2_1/c$ with $a = 11.0827$ (13) Å, $b = 14.398$ (2) Å, $c = 25.895$ (3) Å, $\beta = 93.324$ (10)°, $V = 4125.1$ (9) Å^3, and $D_{calcd} = 1.47$ g cm^{-3} for $Z = 4$. Least-squares refinement of the model based on 5824 reflections ($|F_o| > 3.0\sigma(|F_o|)$) converged to a final $R_F = 3.3\%$. The arrangement of the four ligands in both $(C_5Me_5)_2Sm(NHPh)(THF)$ (**1**) and $(C_5Me_5)_2Sm(\eta^2\text{-}PhNNHPh)(THF)$ (**4**) can be roughly described as distorted tetrahedral. Sm—N bond distances are 2.331 (3) Å (Sm—NHPh) in **1** and 2.330 (5) Å (Sm—NPhNHPh) and 2.610 (5) Å (Sm—NHPhNPh) in **4**. The four C_5Me_5 rings in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$ (**5**) form a tetrahedral cavity typical of complexes containing two $(C_5Me_5)_2Sm$ units. However, the $\mu\text{-}\eta^2{:}\eta^2$-HNNH ligand is located in a surprisingly off-center position in the cavity with Sm—N distances of 2.314 (4), 2.316 (4), 2.403 (4), and 2.436 (4) Å.

Introduction

The recent discovery that dinitrogen interacts with an organometallic complex of samarium[2] has shown that there may be previously unexpected opportunities to use lanthanide metal complexes to manipulate and derivatize substrates containing NN linkages. The dinitrogen complex $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[2] is unusual since this trivalent complex formed by reduction of dinitrogen with $(C_5Me_5)_2Sm$ would be expected to contain an $N{=}N^{2-}$ unit. However, the NN distance of 1.088 (12) Å is comparable to the triple-bond distance in free N_2, 1.0975 Å.[3] In contrast, the only other structurally characterized $\mu\text{-}\eta^2{:}\eta^2\text{-}N_2$ complex, $\{[(Pr^iPCH_2SiMe_2)_2N]ZrCl\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, has an NN distance of 1.548 (7) Å, which is the longest NN distance observed in a dinitrogen complex to date.[4] A structural situation similar to that in the samarium dinitrogen complex also exists in $[(C_5Me_5)_2Sm]_2(\mu\text{-}PhNNPh)$,[5] formed by the reduction of azobenzene by $(C_5Me_5)_2Sm(THF)_2$. This product contains trivalent samarium centers, which leads to the expectation that a $PhN{-}NPh^{2-}$ ligand is present. However, the 1.25 (1)-Å NN distance in this complex is more similar to the 1.247-Å N=N distance in PhN=NPh[6] than to the 1.44 (1)-Å distance in trivalent $[(C_5Me_5)(THF)Sm]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}PhNNPh]_2$[5] which has $PhN{-}NPh^{2-}$ units containing the expected N—N single-bond distances.

To obtain more information about the interaction of the $(C_5Me_5)_2Sm$ moiety with substrates containing NN linkages, we have studied reactions of hydrazines with organosamarium complexes. Diphenylhydrazine, PhNHNHPh, was initially studied because it had only two reactive hydrogens and, if complete deprotonation occurred, the resulting complexes could be directly related to the organosamarium azobenzene complexes previously investigated.[5] The opportunity to correlate reaction products with known compounds has proven to be very valuable in elucidating the complicated reaction chemistry in this system. After the diphenylhydrazine results were obtained, the reactivity of hydrazine was examined. We report here on the reactivity of both substrates with the solvated and unsolvated divalent complexes, $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Sm$, as well as the trivalent hydride, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$. The conditions which lead in some cases to NN bond cleavage and in other cases to formation of complexes retaining NN bonds are described as well as a variety of routes for the addition and removal of hydrogen from NN substrates of this type. Also described is the unusual structure of a bridged hydrazido(2−) complex.

---

(1) Reported in part at the 27th Western Regional Meeting of the American Chemical Society, Anaheim, CA, October 1991; Paper 933.

(2) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877–6879.

(3) *Tables of Interatomic Distances and Configurations in Molecules and Ions*; Chemical Society Special Publications; Sutton, L. E., Ed.; The Chemical Society: London, 1958; Vol. 11.

(4) Fryzuk, M. D.; Haddad, T. S.; Rettig, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 8185–8186.

(5) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983–4994.

(6) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146–152.

0020-1669/92/1331-3592$03.00/0

Table I. Experimental Data for the X-ray Diffraction Studies

compd	**1**	**4**	**5**
formula	$C_{30}H_{44}NOSm$	$C_{36}H_{49}N_2OSm\cdot{}^1/_2C_6H_{14}$	$C_{40}H_{62}N_2Sm_2\cdot{}^1/_2C_6H_{14}$
fw	585.0	719.2	914.7
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ [C_{2h}^5; No. 14]	$P2_1/c$ C_{2h}^5; No. 14]	$P2_1/c$ C_{2h}^5; No. 14]
a, Å	19.052 (2)	9.811 (2)	11.0827 (13)
b, Å	8.484 (1)	16.098 (5)	14.398 (2)
c, Å	18.572 (2)	23.393 (7)	25.895 (3)
β, deg	113.30 (1)	99.20 (2)	93.324 (10)
V, Å^3	2757.0 (6)	3647 (2)	4125.1 (9)
Z	4	4	4
D_{calcd}, Mg m^{-3}	1.41	1.310	1.473
T, K	158	173	173
diffractometer	Nicolet P3	Nicolet P3	Nicolet P3
radiation ($\bar{\lambda}$ = 0.710 730 Å)	Mo Kα	Mo Kα	Mo Kα
monochromator	highly oriented graphite crystal	highly oriented graphite crystal	highly oriented graphite crystal
data collcd	$+h,+k,\pm l$		$+h,+k,\pm l$
scan type	θ–2θ	θ–2θ	ω
scan width, deg	1.2 plus Kα separation	1.2 plus Kα separation	1.2
scan speed (in ω), deg min^{-1}	3.0	3.0	3.0
2θ range, deg	4.0–55.0	4.0–45.0	4.0–48.0
μ(Mo Kα), mm^{-1}	2.16	1.644	2.86
ab corr	semiempirical (ψ-scan method)	semiempirical (ψ-scan method)	semiempirical (ψ-scan method)
no. of reflns collcd	6994	5355	7210
no. of obsd reflns	6059 ($\lvert F_o\rvert > 0$)	4380 ($\lvert F_o\rvert > 1.0\sigma(\lvert F_o\rvert)$)	5824 ($\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)$)
no. of variables	355	373	431
R_F, R_{wF}, %	3.7, 4.1	4.6, 4.7	3.3, 3.8
goodness of fit	1.29	1.61	1.59

Experimental Section

The compounds described below were handled under nitrogen with the rigorous exclusion of air and water using Schlenk, high-vacuum, and glovebox (Vacuum Atmospheres HE-553 Dri-Lab) techniques. Solvents were dried and physical measurements were obtained as previously described.[7,8] Diphenylhydrazine, hydrazine, and aniline were obtained from Aldrich. $(C_5Me_5)_2Sm(THF)_2$,[9] $(C_5Me_5)_2Sm$,[10] $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[11] and $[(C_5Me_5)_2Sm]_2(\mu\text{-PhNNPh})$[5] were prepared as previously described.

Synthesis of $(C_5Me_5)_2Sm(NHPh)(THF)$ (1) from PhNHNHPh. In the glovebox, a solution of diphenylhydrazine (26 mg, 0.14 mmol) in hexane (5 mL) was added dropwise to a slurry of freshly prepared $(C_5Me_5)_2Sm(THF)_2$ (160 mg, 0.28 mmol) in hexane (5 mL). The mixture was stirred overnight, and the precipitated yellow solids were separated from the dark yellow-brown solution by centrifugation and washed with hexane (5 mL). The yellow solids were dried in vacuo to give **1** (115 mg, 0.20 mmol) in 70% yield. Yellow-orange crystals of **1** were grown by slow evaporation of a concentrated THF solution. ^{1}H NMR (C_6D_6, concentration dependent): 11.85–12.08 (1 H, s, br, N*H*Ph), 8.20–8.43, 7.58–7.70, 7.47–7.60 (5 H, m, Ph), 1.32–1.36 (30 H, s, C_5Me_5), –1.7 to –1.9, –2.3 to –2.6 (8 H, s, br, THF). For a 0.05 M sample, the specific shifts are 11.89, 8.38, 7.67, 7.55, 1.36, –1.72, and –2.39. $^{13}C\{^1H\}$ NMR (C_6D_6): 130.4, 114.8, 113.8 (C_5Me$_5$), 111.2, 61.9 (THF), 19.6 (THF), 15.8 (C_5*Me*$_5$). Anal. Calcd for $SmC_{30}H_{44}NO$: Sm, 25.70; C, 61.59; H, 7.58; N, 2.39. Found: Sm, 25.95; C, 61.28; H, 7.37; N, 2.21. Mp: 155 °C.

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(NHPh)(THF)$ (1). A bright yellow crystal of approximate dimensions 0.20 × 0.36 × 0.40 mm was immersed in Paratone-N (Exxon lube oil additive), mounted on a glass fiber, and transferred to the Nicolet P3 automated four-circle diffractometer which is equipped with a modified LT-2 low-temperature apparatus. Subsequent setup operations (determination of accurate unit cell dimensions and orientation matrix) and collection of low-temperature (158 K) intensity data were carried out using standard techniques similar to those of Churchill.[12] Details appear in Table I.

All 6994 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. A careful examination of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/c[C_{2h}^5$; No. 14] is thus uniquely defined.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[13] or the SHELXTL PLUS program set.[14] The analytical scattering factors for neutral atoms were used throughout the analysis;[15a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[15b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Methyl hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.05 Å^2. The remaining hydrogen atoms were located and refined isotropically. Refinement of positional and thermal parameters led to convergence with $R_F = 3.7\%$, $R_{wF} = 4.1\%$, and GOF = 1.29 for 355 variables refined against all 6059 unique data ($|F_o| > 0$) ($R_F = 2.8\%$; $R_{wF} = 3.8\%$ for those 5193 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference-Fourier map was devoid of significant features, $\rho(\max) = 0.95$ e Å^{-3}.

Synthesis of $[(C_5Me_5)_2Sm(NHPh)]_x$ (2) from 1. Complex **1** (100 mg, 0.171 mmol) was heated at 70 °C for 2 h at 2 × 10^{-6} Torr. Sublimation started to occur at this temperature. After an additional 2 h at 90 °C, sublimation was complete and orange-yellow, toluene-soluble **2** was isolated (73 mg, 83%). ^{1}H NMR (C_6D_6, concentration dependent): 13.94–16.28 (1 H, N*H*Ph), 5.0–6.12 (2 H, Ph), 3.34–5.36 (3 H, Ph), 0.62–0.92 (30 H, s, C_5Me_5). For a 0.025 M sample, the C_5Me_5 peak was at 0.69 ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 120.4, 125.6, 128.4, 129.2 (Ph), 118.1 (br, C_5Me$_5$), 20.0, 19.4 (C_5*Me*$_5$). Anal. Calcd for $SmC_{26}H_{36}N$: Sm, 29.32; C, 60.88; H, 7.07; N, 2.73. Found: Sm, 29.30; C, 60.53; H, 6.84; N, 2.59. Isopiestic molecular weight (C_6D_6): calcd for $(SmC_{26}H_{36}N)_2$, 1026, found, 1230 ± 240. The addition of 2 μL of THF by microsyringe to an NMR sample of **2** in C_6D_6 resulted in complete conversion to **1**.

Synthesis of 1 and 2 from $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ and $PhNH_2$. Aniline (16 μL, 0.18 mmol) was added dropwise to a slurry of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (75 mg, 0.09 mmol) in hexane (4 mL). Vigorous gas evolution

---

(7) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671–1679.

(8) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432.

(9) Evans, W. J.; Ulibarri, T. A. *Inorg. Synth.* **1990**, *27*, 155–157.

(10) (a) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272. (b) Evans, W. J.; Hughes, L. A.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1285–1291.

(11) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 1401–1403.

(12) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. *J. Inorg. Chem.* **1977**, *16*, 265–271.

(13) Strouse, C. Personal communication; Modification of the UCLA Crystallographic Computing Package, University of California, Los Angeles, 1981.

(14) Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1988.

(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; (a) pp 99–101, (b) pp 149–150.

was observed on addition. The mixture was stirred for 1 h to give an orange precipitate **2** (60 mg, 0.12 mmol, 66%), which was isolated by centrifugation and identified by ^{1}H NMR spectroscopy. Addition of THF to an NMR sample of the above solid resulted in rapid and complete conversion to $(C_5Me_5)_2Sm(NHPh)(THF)$.

Reaction of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with Diphenylhydrazine. (a) Formation of $(C_5Me_5)_2Sm(PhNHNPh)$ (3). In an ether-free glovebox, a solution of diphenylhydrazine (15 mg, 0.08 mmol) in hexane (5 mL) was added dropwise to a slurry of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (35 mg, 0.04 mmol) in 5 mL of hexane. A sudden color change from orange to dark green was observed. After stirring overnight, a green-yellow solution was obtained. The solution was centrifuged, and the insoluble material was separated. After solvent removal, a green-yellow, tacky residue **3** was obtained (31 mg, 80%). ^{1}H NMR (C_6D_6): 17.20 (1 H, Ph*H*NNPh), 10.95 (1 H, br s), 8.18 (1 H, br s), 8.01 (1 H, d), 7.63 (1 H, t), 7.07 (1 H, m), 6.75 (1 H, t), 6.67 (1 H, d), 6.51 (1 H, t), 6.36 (2 H, br s), 0.50 (C_5Me_5). ^{13}C NMR (C_6D_6): 132.4 (br), 131.0, 129.3, 129.2, 123.2, 122.1, 116.6 (C_5Me_5), 113.3, 112.5, 19.0 ($C_5\mathit{Me}_5$). Anal. Calcd for $SmC_{32}H_{41}N_2$: Sm, 24.9. Found: Sm, 23.8. Addition of THF to an NMR sample of **3** generates **4** (see below) in quantitative yield. Isopiestic molecular weight (toluene): calcd for $SmC_{32}H_{41}N_2$, 604, found, 510.

(b) Formation of $(C_5Me_5)_2Sm(\eta^2\text{-}PhNHNPh)(THF)$ (4). A solution of diphenylhydrazine (13 mg, 0.070 mmol) was added dropwise to a hexane (5-mL) slurry of $[(C_5Me_5)_2SmH]_2$ (31 mg, 0.036 mmol) to give a dark green solution which, in an atmosphere containing THF vapor, turned yellow-orange in 1 h. Removal of solvent gave tacky yellow-orange solids of $(C_5Me_5)_2Sm(PhNHNPh)(THF)$ (36 mg, 0.054 mmol) in 76% yield. The residue was extracted with hexane and the yellow-orange extracts were recrystallized in the presence of a few drops of THF at −35 °C to give orange-yellow crystals of **4**. ^{1}H NMR (C_6D_6, 0.13 M): 14.78 (1 H, Ph*H*NNPh), 7.45 (1 H), 7.07 (2 H), 6.74 (1 H), 6.62 (2 H), 6.34 (4 H, Ph), 0.91 (30 H, s, C_5Me_5), −0.43 (8 H, THF). The signals for C_5Me_5 have been observed between 0.64 and 1.02 ppm and for Ph*H*NNPh between 14.75 and 16.21 ppm depending on concentration. $^{13}C\{^1H\}$ NMR (C_6D_6): 149.2, 131.4, 129.3, 128.9, 121.1, 115.5, 113.7, 112.5 (Ph), 119.8 (C_5Me_5), 66.9, 24.6 (THF), 17.9 ($C_5\mathit{Me}_5$). Anal. Calcd for $SmC_{36}H_{49}ON_2$: Sm, 22.2. Found: Sm, 21.9. Mp: 55–61 °C.

(c) Formation of $[(C_5Me_5)_2Sm]_2(\mu\text{-}PhNNPh)$. In an ether-free glovebox, a solution of diphenylhydrazine (5 mg, 0.03 mmol) in hexane (7 mL) was added dropwise to solid $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (30 mg, 0.035 mmol). Addition was accompanied by gas evolution and rapid color change to dark blue-green. After the mixture was stirred for 1 h, the excess samarium hydride complex was separated from the dark blue-green solution by centrifugation. Removal of solvent from the supernatant gave a tacky dark material which contained $[(C_5Me_5)_2Sm]_2(\mu\text{-}N_2Ph_2)$[5] in approximately 80% yield by ^{1}H NMR spectroscopy. Addition of excess azobenzene and THF to this product in toluene formed $(C_5Me_5)_2Sm(\eta^2\text{-}N_2Ph_2)(THF)$ according to the literature.[5]

X-ray Data Collection, Structure Determination, and Refinement for $(C_5Me_5)_2Sm(\eta^2\text{-}PhNHNPh)(THF)$ (4). A yellow-gold crystal of approximate dimensions 0.20 × 0.23 × 0.33 mm was handled as described above for **1**. Intensity data were collected at 173 K under conditions described in Table I. All 5355 data were corrected for the effects of absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$. A careful examination of a preliminary data set revealed the systematic extinctions $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is thus uniquely defined.

All crystallographic calculations were carried out as described above for **1**. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0003(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. There is half a molecule of hexane solvent of crystallization present. The hexane is located on a center of inversion (1, 0, 0) such that the C(39)–C(39′) distance is 2.015 Å. Thermal parameters are large and interatomic angles are obtuse: 153.8 and 158.8°. Hydrogen atoms were included using a riding model with $d(C\text{–}H) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å^2 (the hexane hydrogen atoms were not included in the refinement). Refinement of positional and thermal parameters led to convergence with $R_F = 4.6\%$, $R_{wF} = 4.7\%$, and GOF = 1.61 for 373 variables refined against those 4380 data with $|F_o| > 1.0\sigma(|F_o|)$ ($R_F = 3.5\%$, $R_{wF} = 4.6\%$ for those 3691 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference-Fourier map was devoid of significant features, $\rho(\max) = 0.97$ e Å^{-3}.

Formation of 3 from $(C_5Me_5)_2Sm$. Dropwise addition of diphenylhydrazine (8.7 mg, 0.048 mmol) in toluene (3 mL) to a solution of $(C_5Me_5)_2Sm$ (40 mg, 0.095 mmol) in toluene (10 mL) causes a gradual color change from dark green to green-yellow. Removal of solvent leaves a green-yellow powder which has a ^{1}H NMR spectrum consistent with the presence of **3** and $(C_5Me_5)_2Sm$ in a ratio of 5:4. The synthesis of **3** reported above is a better synthetic route to this product.

Synthesis of $[(C_5Me_5)_2Sm]_2(\mu\text{-}HNNH)$ (5). Hydrazine (1.86 μL, 0.06 mmol) was added to a slurry of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (50 mg, 0.06 mmol) in 6 mL of hexane. Gas evolved and the reaction mixture changed color to bright yellow. After stirring overnight, a yellow precipitate formed which was separated from the orange-yellow solution by centrifugation. The solution was concentrated and stored at −40 °C, generating ruby red crystals (30 mg, 58%). ^{1}H NMR (C_6D_6): 0.75 (2 H, N_2H_2), −1.05 (30 H, C_5Me_5). ^{13}C NMR (C_6D_6): 113.4 (C_5Me_5), 21.7 ($C_5\mathit{Me}_5$). Anal. Calcd for $Sm_2C_{40}H_{62}N_2$: Sm, 34.51; C, 55.77; H, 7.77; N, 3.21. Found: Sm, 34.65; C, 54.99; H, 7.14; N, 3.11. IR: 3437 (NH, br), 2962 (s), 2906 (s), 2856 (s), 2715 (s), 1631 (w), 1501 (vw), 1437 (m), 1375 (m), 1256 (w), 1087 (m), 1012 (vw), 706 (vw), 669 (m), 606 (w), 474 (w) cm^{-1}. Mp: crystals lose their transparency above 50 °C, decomposition above 190 °C.

Formation of 5 from $(C_5Me_5)_2Sm$. In the glovebox, hydrazine (1.86 μL, 0.06 mmol) was added by syringe to freshly prepared $(C_5Me_5)_2Sm$ (50 mg, 0.12 mmol) in 10 mL of hexane. The reaction mixture became brown-green. Centrifugation of the reaction mixture after 7 h gave a green residue [$(C_5Me_5)_2Sm$, which formed $(C_5Me_5)_2Sm(THF)_2$ upon addition of THF] and a yellow solution. Removal of solvent by rotary evaporation gave **5** (30 mg, 57%) as an orange, tacky solid which could be recrystallized from hexane or benzene.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Sm]_2(\mu\text{-}HNNH)$ (5). An orange cube of approximate dimensions 0.25 × 0.30 × 0.33 mm was oil-mounted on a glass fiber and handled as described above for **1**. Intensity data were collected at 173 K using an ω scan technique with Mo Kα radiation under the conditions described in Table I. All 7210 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is, therefore, uniquely defined.

All crystallographic calculations were carried out as described above for **1**. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0002(|F_o|)^2$. The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C\text{–}H) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å^2. N–H hydrogens were located from a difference-Fourier map and refined with fixed isotropic temperature factors. There is half a molecule of hexane (located on an inversion center) per dimer. Refinement of positional and thermal parameters led to convergence with $R_F = 3.3\%$, $R_{wF} = 3.8\%$, and GOF = 1.59 for 431 variables refined against those 5824 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(\max) = 2.00$ e Å^{-3} at a distance of 0.86 Å from Sm(1).

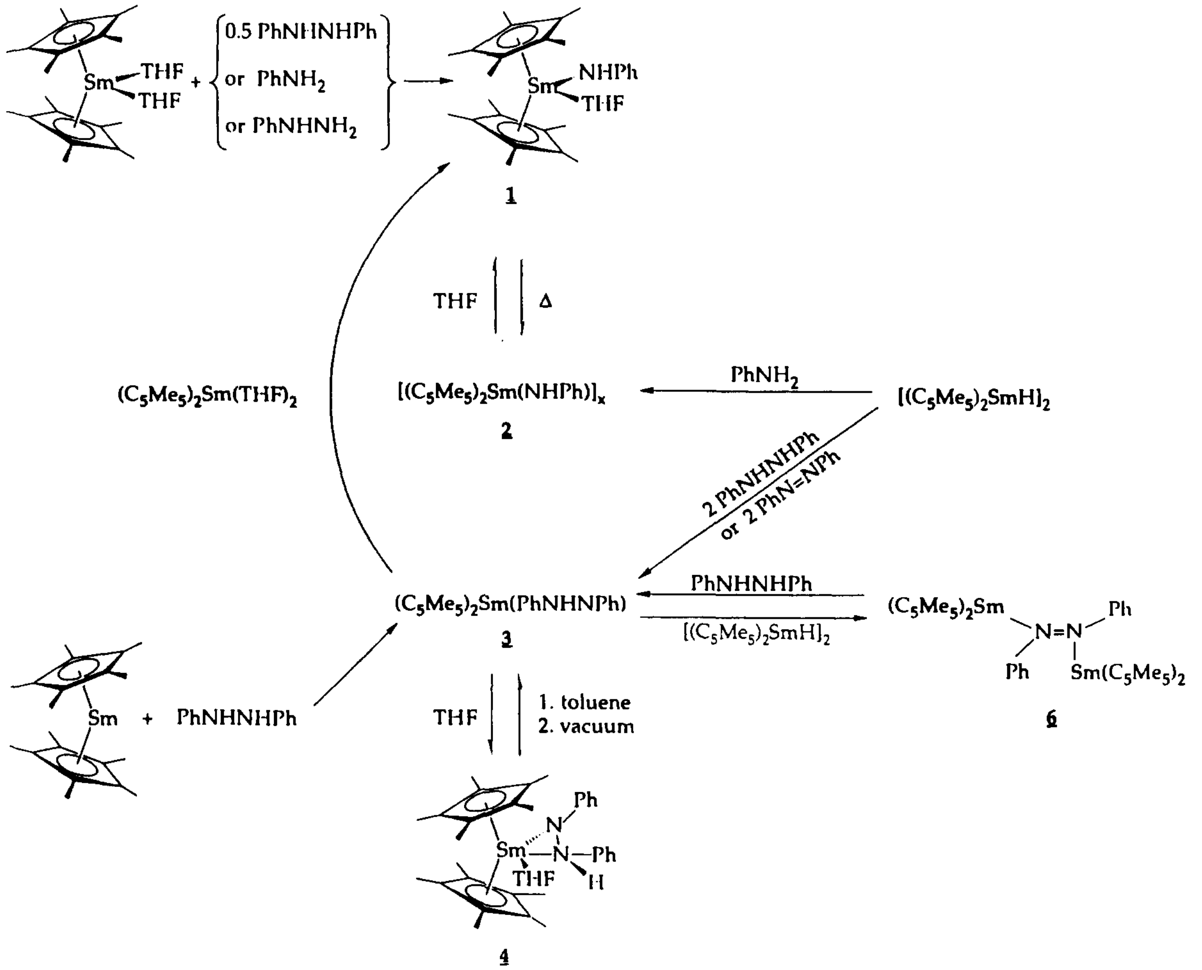
Results

Diphenylhydrazine Reactions. Scheme I presents the reactions described in this section.

Synthesis of $(C_5Me_5)_2Sm(NHPh)(THF)$ (1). $(C_5Me_5)_2Sm(THF)_2$ reacts with diphenylhydrazine in hexane to form a hexane-insoluble yellow compound which can be isolated by filtration. This material can be crystallized from THF and isolated in 55–70% yield. The concentration-dependent ^{1}H NMR spectrum of this complex exhibited a single resonance in the C_5Me_5 region as well as phenyl resonances, but the data were not structurally definitive. Single crystals were examined by X-ray crystallography, and the complex was found to be $(C_5Me_5)_2Sm(NHPh)(THF)$ (**1**) (Figure 1), the product of an NN cleavage reaction, eq 1. The reaction seems to proceed in higher yield if the mono-

$$2(\mathrm{C_5Me_5})_2\mathrm{Sm(THF)_2} + \mathrm{PhHNNHPh} \rightarrow \underset{\mathbf{1}}{2(\mathrm{C_5Me_5})_2\mathrm{Sm(NHPh)(THF)}} + 2\mathrm{THF} \quad (1)$$

Scheme I. Summary of Diphenylhydrazine Reactions



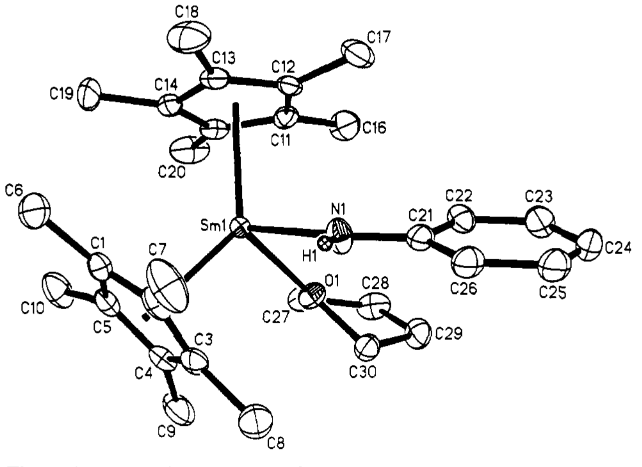


Figure 1. Molecular structure of $(C_5Me_5)_2Sm(NHPh)(THF)$ (**1**) with probability ellipsoids drawn at the 50% level.

Table II. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(NHPh)(THF)$ (1)

Sm(1)–O(1)	2.455 (2)	Sm(1)–N(1)	2.331 (3)
Sm(1)–C(1)	2.753 (4)	Sm(1)–C(2)	2.731 (4)
Sm(1)–C(3)	2.726 (4)	Sm(1)–C(4)	2.731 (4)
Sm(1)–C(5)	2.740 (4)	Sm(1)–C(11)	2.780 (4)
Sm(1)–C(12)	2.737 (4)	Sm(1)–C(13)	2.704 (3)
Sm(1)–C(14)	2.757 (3)	Sm(1)–C(15)	2.781 (3)
Sm(1)–Cn(1)	2.457	Sm(1)–Cn(2)	2.475
O(1)–Sm(1)–N(1)	90.1 (1)	O(1)–Sm(1)–Cn(1)	104.9
O(1)–Sm(1)–Cn(2)	106.2	N(1)–Sm(1)–Cn(1)	102.1
N(1)–Sm(1)–Cn(2)	109.9	Cn(1)–Sm(1)–Cn(2)	134.7
Sm(1)–O(1)–C(27)	130.1	Sm(1)–O(1)–C(30)	125.1 (2)
Sm(1)–N(1)–C(21)	142.8 (3)		

solvate, $(C_5Me_5)_2Sm(THF)$,[16] is used. No product was isolated from a reaction in THF under similar conditions.

Structure of $(C_5Me_5)_2Sm(NHPh)(THF)$ (1). The structure of **1** (Figure 1) is typical of trivalent bis(pentamethylcyclopentadienyl)lanthanide complexes containing two additional ligands. The two C_5Me_5 ring centroids and the N and O donor atoms describe a distorted tetrahedron. The (C_5Me_5 ring centroid)–Sm–(C_5Me_5 ring centroid) angle of 134.7° is in the normal region[17] as is the N–Sm–O angle of 90.1 (1)°.[18] The average Sm–C(ring) and Sm–O(THF) distances, 2.74 (4) and 2.455 (2) Å are also normal for this formally eight-coordinate complex.[17,19,20,22] The Sm–N distance of 2.331 (3) Å is equivalent to the 2.323 (8)-Å Sm–N distance in $[(C_5Me_5)(THF)Sm]_2(N_2Ph_2)_2$[5] and is in the 2.31–2.35-Å range expected for samarium nitrogen single bonds.[5] Selected bond distance and angle data are given in Table II, and complete data are given in the supplementary material.

The hydrogen atom on nitrogen was located in the crystal structure determination. It lies 2.75 Å away from samarium and is oriented away from the samarium center with a Sm–N–H

---

(16) Evans, W. J.; Ulibarri, T. A. *Polyhedron* **1989**, *8*, 1007–1014.

(17) Evans, W. J.; Ulibarri, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 4292–4297.

(18) Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614–3619.

(19) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432.

(20) Evans, W. J.; Foster, S. A. *J. Organomet. Chem.*, in press.

(21) Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309–1312.

(22) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1990**, *9*, 2628–2631.

angle of 113 (3)°. This distance is long compared to the 2.29–2.34-Å Sm(III)–H(phenyl) distances in $[(C_5Me_5)_2Sm]_2(PhNNPh)$.[5] In the latter complex, the ligand was oriented such that two phenyl hydrogens pointed directly at the metal center. The Sm–N–H angle in **1** plus the 142.8 (3)° Sm–N–C(21) angle and the 104 (3)° H–N–C(21) angle indicates that the geometry around nitrogen is nearly planar.

It is of interest to compare the structure of **1** with that of $(C_5Me_5)_2HfH(NHMe)$.[21] In the hafnium complex, two idealized structures were considered in terms of optimizing steric factors and Hf–N π bonding. The sterically optimal structure would have a planar NMeH unit in the plane which bisects the (ring centroid)–metal–(ring centroid) angle. In this case, the methyl carbon and nitrogen atom would be in the same plane as hafnium and the terminal hydride ligand, i.e., the C–N–Hf–H torsional angle would be 0°. To optimize Hf–N π bonding, the plane of the NMeH ligand should be perpendicular to the plane bisecting the ring–metal–ring angle; i.e., a C–N–Hf–H torsional angle of 90° should exist. The observed angle of 63 (3)° was evidently a compromise which sacrificed some π-bonding overlap to reduce steric repulsion. The shortness of the Hf–N bond was consistent with "considerable double-bond character". In **1**, the analogous torsional angle, C(21)–N(1)–Sm(1)–O(1), is 34.8° and the Sm–N bond is in the single-bond range.

Synthesis of $[(C_5Me_5)_2Sm(NHPh)]_x$ (2). To determine if an unsolvated analog of **1** was also formed in this system, removal of coordinated THF from **1** was attempted by heating this complex to 90 °C at 2 × 10^{-6} Torr, eq 2. The orange-yellow product

$$\underset{1}{(C_5Me_5)_2Sm(NHPh)(THF)} \xrightarrow{\Delta} THF + \underset{2}{[(C_5Me_5)_2Sm(NHPh)]_x} \quad (2)$$

which sublimes has a concentration-dependent ^{1}H NMR spectrum which, like that of **1**, contains a single C_5Me_5 resonance. However, the ^{1}H NMR resonances in the desolvated product have shifted considerably from those of **1**. The C_5Me_5 peak position has changed from approximately 1.35 ppm for **1** to around 0.69 ppm for **2**. The NH resonance has shifted from approximately 12 ppm for **1** to 14–16 ppm for **2**. No resonances were observed in the phenyl region, but two broad humps, $\Delta\nu_{1/2} > 100$ Hz, appeared at 3–6 ppm. The ^{13}C NMR spectrum contained a broad C_5Me$_5$ resonance and two closely-spaced C_5Me_5 resonances. These data suggested that **3** was not just a simple monomeric seven-coordinate complex and some metal–phenyl ring interaction could be occurring. Consistent with this, the ^{1}H NMR spectrum showed a temperature dependence. At −10 °C, the two broad resonances in the 3–6 ppm region become a single broad resonance, and at −50 °C, they separate again and sharpen. The C_5Me_5 resonance is also split at −50 °C.

Single crystals of **2** suitable for X-ray analysis have not been obtained, but the empirical formula is consistent with the complete elemental analysis and the fact that addition of THF immediately and quantitatively converts **2** to **1**. Isopiestic molecular weight data in benzene are consistent with a dimeric structure in solution (i.e., $x = 2$). A bridged structure involving interaction of the phenyl rings of one NHPh ligand with the other paramagnetic metal center in the molecule would be consistent with the NMR data. A simple nitrogen-bridged $[(C_5Me_5)_2Sm(\mu\text{-NHPh})]_2$ structure seems unlikely for steric reasons,[22] but X-ray data will be needed to definitively know the degree and mode of aggregation of this species.

Alternative Syntheses of 1 and 2. To further establish the identity of **2**, its formation by deprotonation of aniline was attempted using $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$. This reaction proceeds with vigorous evolution of gas, which is presumed to be hydrogen, to give a product identical to **2** which can be quantitatively converted to **1** upon addition of THF, eq 3. Complex **1** can also

$$[(C_5Me_5)_2Sm(\mu\text{-H})]_2 + 2PhNH_2 \xrightarrow{-2H_2} 2\underset{2}{[(C_5Me_5)_2Sm(NHPh)]_x} \xrightarrow{2THF} 2\underset{1}{(C_5Me_5)_2Sm(NHPh)(THF)} \quad (3)$$

be prepared by reacting either $PhNH_2$ or $PhHNNH_2$ with $(C_5Me_5)_2Sm(THF)_2$ in toluene, but both reactions form other products as well and **1** is not readily separated from the product mixture.

Synthesis of $(C_5Me_5)_2Sm(PhNNHPh)$ (3) and $(C_5Me_5)_2Sm(PhNNHPh)(THF)$ (4). Given the NN cleavage by $(C_5Me_5)_2Sm(THF)_2$ in eq 1 and the fact that the reaction proceeds best with the least THF present, one might expect that the unsolvated divalent metallocene $(C_5Me_5)_2Sm$[10] would be most efficient in converting diphenylhydrazine to **2**. *This is not the case, however.* $(C_5Me_5)_2Sm$ reacts with PhNHNHPh to form a green-yellow complex, **3**, rather than orange **2**. When **3** is treated with THF, it does not form **1** but instead forms $(C_5Me_5)_2Sm(PhNNHPh)(THF)$ (**4**) (eq 4), which was identified by an X-ray crystallographic study (Figure 2). The presumed byproduct hydrogen

$$2(C_5Me_5)_2Sm + 2PhNHNHPh \rightarrow H_2 + 2\underset{3}{(C_5Me_5)_2Sm(PhNHNPh)} \xrightarrow{2THF} 2\underset{4}{(C_5Me_5)_2Sm(PhHNNPh)(THF)} \quad (4)$$

was not isolated. Hence, $(C_5Me_5)_2Sm$ reacts with diphenylhydrazine by deprotonation rather than by reductive cleavage. Complex **4** loses THF to form **3** much easier than complex **1** loses THF to form **2**: dissolution of **4** in toluene and removal of solvent by rotary evaporation forms **3**. Attempts to grow crystals of **3** have been unsuccessful. The empirical formula of **3** is based on analytical data, the fact that it is quantitatively converted to fully characterized **4** by THF, its regeneration by desolvation of **4**, and the alternative syntheses described below. The $[PhNHNPh]^-$ complex can be obtained in two ways from $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$: by deprotonation of diphenylhydrazine, eq 5 (with hydrogen as presumed byproduct), and by 1,2-addition to azobenzene, eq 6. Reaction 5 is the better synthetic route to **3**.

$$[(C_5Me_5)_2Sm(\mu\text{-H})]_2 + 2PhNHNHPh \rightarrow 2(C_5Me_5)_2Sm(PhNHNPh) + 2H_2 \quad (5)$$

$$[(C_5Me_5)_2Sm(\mu\text{-H})]_2 + 2PhN{=}NPh \rightarrow 2(C_5Me_5)_2Sm(PhNHNPh) \quad (6)$$

3 can also be prepared by acid–base reactions involving diphenylhydrazine and organosamarium derivatives of azobenzene,[4] eqs 7 and 8.

$$[(C_5Me_5)_2Sm]_2(\mu\text{-PhNNPh}) + PhNHNHPh \rightarrow 2\underset{3}{(C_5Me_5)_2Sm(PhNHNPh)} \quad (7)$$

$$2(C_5Me_5)_2Sm(PhNNPh)(THF) + PhNHNHPh \xrightarrow{-THF} 2\underset{3}{(C_5Me_5)_2Sm(PhNHNPh)} \quad (8)$$

The reaction of **3** with $(C_5Me_5)_2Sm(THF)_2$ was examined to see if the latter complex could cleave the N–N bond of the com-

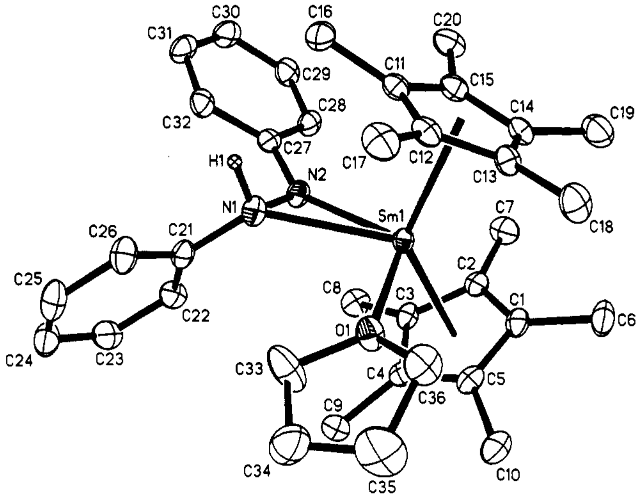


Figure 2. Molecular structure of $(C_5Me_5)_2Sm(\eta^2\text{-}PhNHNPh)(THF)$ (**4**) with probability ellipsoids drawn at the 50% level.

Table III. Selected Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(PhNNHPh)(THF)$ (**4**)

Sm(1)–O(1)	2.548 (4)	Sm(1)–N(1)	2.610 (5)
Sm(1)–N(2)	2.330 (5)	Sm(1)–C(1)	2.779 (6)
Sm(1)–C(2)	2.763 (6)	Sm(1)–C(3)	2.779 (6)
Sm(1)–C(4)	2.759 (6)	Sm(1)–C(5)	2.774 (6)
Sm(1)–C(11)	2.776 (6)	Sm(1)–C(12)	2.781 (6)
Sm(1)–C(13)	2.758 (6)	Sm(1)–C(14)	2.764 (5)
Sm(1)–C(15)	2.766 (6)	O(1)–C(33)	1.439 (8)
O(1)–C(36)	1.449 (8)	N(1)–N(2)	1.443 (7)
N(1)–C(21)	1.445 (7)	N(2)–C(27)	1.384 (8)
O(1)–Sm(1)–N(1)	82.8 (1)	O(1)–Sm(1)–N(2)	114.6 (2)
N(1)–Sm(1)–N(2)	33.4 (2)	Sm(1)–N(1)–N(2)	62.6 (2)
Sm(1)–N(1)–C(21)	136.4 (4)	N(2)–N(1)–C(21)	117.4 (4)
Sm(1)–N(2)–N(1)	84.0 (3)	Sm(1)–N(2)–C(27)	149.1 (4)
N(1)–N(2)–C(27)	115.6 (5)		

plexed $[PhNHNPh]^-$ ligand. $(C_5Me_5)_2Sm(NHPh)(THF)$ is formed in this reaction in toluene, eq 9.

$$(C_5Me_5)_2Sm(PhNHNPh) + (C_5Me_5)_2Sm(THF)_2 \rightarrow (C_5Me_5)_2Sm(NHPh)(THF) + \text{other products} \quad (9)$$

Structure of $(C_5Me_5)_2Sm(PhNHNPh)(THF)$ (4). The structure of **4** (Figure 2) is similar in many respects to that of **1**, except that an extra nitrogen atom is coordinated to the metal. Selected bond distance and angle data are given in Table III. As a consequence of the higher formal coordination number, the Sm–C(ring) average distance, 2.77 (1) Å, and the 2.548 (4)-Å Sm–O(THF) distance are longer than those in **1**. The 133.4° (ring centroid)–Sm–(ring centroid) angle in **4** is comparable to that in **1**, however.

The structural data on the nitrogen-containing ligand in **4** are consistent with the existence of a $[PhNHNPh]^-$ monoanion. Hence, the 1.443 (7) Å N(1)–N(2) distance is in the single-bond range,[23] a hydrogen atom was located on N(1), the 2.610 (5)-Å Sm–N(1) distance is in the 2.53–2.77-Å range expected for $R_3N{:}\rightarrow Sm$ bonds,[5] and the 2.330 (5)-Å Sm–N(2) distance is indistinguishable from the Sm–N single-bond distance in **1**. As in **1**, the hydrogen atom on nitrogen is neither oriented toward nor close enough to the samarium center to interact.

To our knowledge, this is the first crystallographic data on a diphenylhydrazide(1–) ligand. A survey of structural data on $\eta^2\text{-}RNNR'R''^{\,1-}$ attached to transition metals has been published which indicates that the N–N and M–N distances in **4** are not unusual.[24] In Ti, Mo, and W complexes, N–N distances of 1.39 (1)–1.43 (1) Å were observed and $M\text{–}NRNR_2$ distances differed from $M\text{–}NR_2NR$ distances by 0.1–0.4 Å.

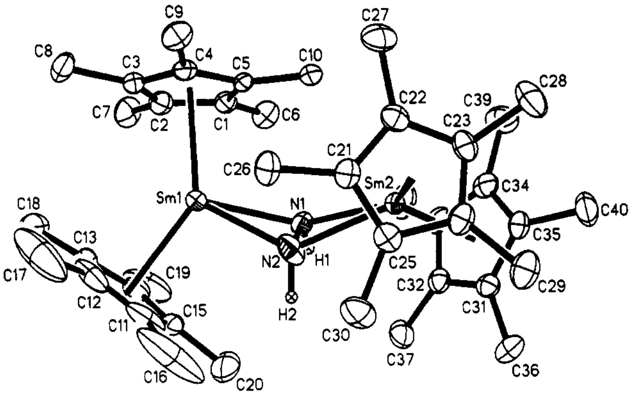


Figure 3. Molecular structure of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$ (**5**) with probability ellipsoids drawn at the 50% level.

The structure of **4** is interesting vis a vis **1** in that it shows that the samarium center in **1** could certainly accommodate coordination by another ligand. Nevertheless, no interaction with the NH hydrogen atom is observed in the crystal structure of **1**. The ability of the trivalent $(C_5Me_5)_2Sm$ unit to accommodate different coordination numbers has been noted previously.[25]

Hydrazine Reactions. Formation of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$ (5). $(C_5Me_5)_2Sm(THF)_2$ reacts with hydrazine to give a complicated mixture of products including pentamethylcyclopentadiene. Fewer byproducts are formed in the reactions of $(C_5Me_5)_2Sm$ and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with hydrazine which generate a primary product, **5**, in 50–60% yield. The ^1H and ^{13}C NMR spectra of the orange product were not structurally specific, but the single ^1H NMR resonance attributable to C_5Me_5 was located at unusually high field, –1.05 ppm. Only a few trivalent $(C_5Me_5)_2Sm$ complexes exhibit C_5Me_5 resonances in this region: $(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)$,[26] –1.11, –1.27 ppm; $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCHCHPh)$,[27] –1.09 ppm; $(C_5Me_5)_2Sm(C_5H_5)$,[17] –1.05 ppm; $(C_5Me_5)_3Sm$,[28] –1.24 ppm; $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[11] –0.80 ppm; $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$,[2] –0.64 ppm.

The identity of **5** as $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$ was determined by an X-ray crystallographic study (Figure 3). Equations 10 and 11 show the two best synthetic routes to **5**.

$$2(C_5Me_5)_2Sm + H_2NNH_2 \rightarrow \underset{5}{[(C_5Me_5)_2Sm]_2(HNNH)} + H_2 \quad (10)$$

$$[(C_5Me_5)_2Sm(\mu\text{-}H)]_2 + H_2NNH_2 \rightarrow \underset{5}{[(C_5Me_5)_2Sm]_2(HNNH)} + 2H_2 \quad (11)$$

Hydrogen is the presumed byproduct in each case. Interestingly, the equimolar reaction of $(C_5Me_5)_2Sm$ with hydrazine forms little **5**. Cleavage products analogous to **2**, e.g., $(C_5Me_5)_2SmNH_2$, have not been identified in these reactions, but C_5Me_5 resonances are observed in the ^1H NMR spectra of the byproducts which are also found among the products of the reaction of $[(C_5Me_5)_2Sm(\mu\text{-}$

---

[23] *Spec. Publ.—Chem. Soc.* **1965**, No. 18.

[24] Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, Chapter 13 (see references therein).

[25] Evans, W. J.; Drummond, D. K.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *Polyhedron* **1988**, *7*, 1693–1703.

[26] Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134–142.

[27] Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219–223.

[28] Evans, W. J.; Gonzales, S. G.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 7423–7424.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$ (5)

Sm(1)–N(1)	2.313 (4)	Sm(1)–N(2)	2.402 (4)
Sm(1)–C(1)	2.728 (5)	Sm(1)–C(2)	2.809 (5)
Sm(1)–C(3)	2.828 (5)	Sm(1)–C(4)	2.740 (5)
Sm(1)–C(5)	2.683 (5)	Sm(1)–C(11)	2.720 (6)
Sm(1)–C(12)	2.699 (6)	Sm(1)–C(13)	2.720 (5)
Sm(1)–C(14)	2.710 (5)	Sm(1)–C(15)	2.720 (5)
Sm(2)–N(1)	2.436 (4)	Sm(2)–N(2)	2.315 (4)
Sm(2)–C(21)	2.760 (5)	Sm(2)–C(22)	2.809 (5)
Sm(2)–C(23)	2.826 (5)	Sm(2)–C(24)	2.795 (5)
Sm(2)–C(25)	2.719 (5)	Sm(2)–C(31)	2.769 (5)
Sm(2)–C(32)	2.764 (5)	Sm(2)–C(33)	2.752 (5)
Sm(2)–C(34)	2.730 (5)	Sm(2)–C(35)	2.778 (5)
N(1)–N(2)	1.473 (6)		
N(1)–Sm(1)–N(2)	36.4 (2)	Sm(1)–N(1)–Sm(2)	125.7 (2)
N(1)–Sm(2)–N(2)	36.0 (2)	Sm(1)–N(2)–Sm(2)	127.2 (2)
Sm(1)–N(1)–N(2)	75.1 (3)	Sm(1)–N(2)–N(1)	68.5 (2)
Sm(2)–N(1)–N(2)	67.5 (2)	Sm(2)–N(2)–N(1)	76.4 (2)

H)]$_2$ with NH_3. Recently, Nolan et al.[29] have shown that $(C_5Me_5)_2Sm$ reacts with excess hydrazine to form a very complicated tetranuclear complex, $(C_5Me_5)_4Sm_4(N_2H_2)_2(N_2H_3)_4(NH_3)_2$.

Structure of $[(C_5Me_5)_2Sm]_2(HNNH)$ (5). In contrast to the typical nature of the structures of **1** and **4**, the structure of **5** (Figure 3) is significantly different from the structures of related complexes. As discussed below, this difference has interesting implications in organosamarium chemistry. Selected bond distance and angle data are given in Table IV. The overall structure of **5** is one in which the four C_5Me_5 ring centroids define a tetrahedron. The tetrahedral tetrakis(pentamethylcyclopentadienyl) cavity generated by these four rings is like that in the other tetrakis(pentamethylcyclopentadienyl) complexes: $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[11] $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$,[30] $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$,[2] $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^4\text{-}PhCH{=}CH_2)$,[27] and $[(C_5Me_5)_2ThH(\mu\text{-}H)]_2$.[31] However, unlike these other examples, which have the bridging donor atoms symmetrically disposed, the bridging HNNH ligand in **5** is located off to one side of the Sm–Sm vector (Figure 4). This allows the Sm_2N_2 unit to adopt a butterfly arrangement instead of the planar arrangement found in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$. More importantly, this shows that there is more flexibility in bonding within the tetracyclopentadienyl cavity formed by two bridged $(C_5Me_5)_2Sm$ units than has been previously demonstrated.

Not only is the HNNH ligand located asymmetrically with respect to the tetracyclopentadienyl cavity but it is also asymmetrically disposed with respect to the two $(C_5Me_5)_2Sm$ units. It is useful to consider the typical structure of **1** in which the O and N donor atoms lie in the equatorial plane which bisects the (ring centroid)–metal–(ring centroid) angle of the $(C_5Me_5)_2Sm$ unit. In **5**, the nitrogen atoms do not occupy analogous positions with respect to either Sm(1) or Sm(2). However, examination of Figure 4 shows that the nitrogen atoms lie closer to this equatorial plane for Sm(1) than for Sm(2). In fact, the two nitrogen atoms are almost pointing toward the C_5Me_5 ligands of Sm(2) (i.e., the two nitrogen atoms and the two Sm(2) ring centroids are closer to square planar than to tetrahedral). Consistent with this asymmetry, the bonding parameters for the two $(C_5Me_5)_2Sm$ units are slightly different. The biggest difference is seen in the (ring centroid)–Sm–(ring centroid) angles of 135.4 and 129.3° for Sm(1) and Sm(2), respectively. The latter angle is rather small compared to values in the literature[17,20] and suggests more steric crowding around Sm(2). The average Sm–C(ring) distances, 2.74 (4) and 2.77 (3) Å for Sm(1) and Sm(2), respectively, are consistent with a more crowded environment for Sm(2) although the differences are within the error limits. Sm(2) also has one Sm–N distance slightly longer than the analogous distance to Sm(1) (Table IV).

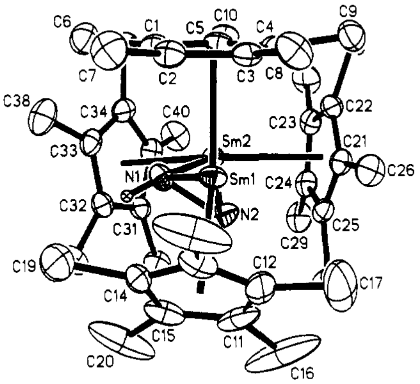


Figure 4. View down the Sm–Sm vector of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$ (5) showing asymmetry in the location of the $[HNNH]^{2-}$ ligand.

Each samarium atom is connected to the HNNH ligand by one bond in the usual single-bond range: Sm(1)–N(1), 2.314 (4) Å, Sm(2)–N(2), 2.316 (4) Å. The second Sm–N bond is longer for each metal: Sm(1)–N(2) 2.403 (4) Å; Sm(2)–N(1), 2.436 (4) Å. These distances are shorter than expected for a $R_3N{:}\rightarrow Sm$ bond, which is expected in the 2.53–2.77-Å range.[5] The NN distance in **5** is 1.473 (6) Å. In comparison, a typical N–N single-bond distance is 1.499 Å[23] and the NN distance in hydrazine is 1.43 Å.[32]

Relatively few HNNH ligands have been structurally characterized in metal complexes. In $[(CO)_5Cr]_2(\mu\text{-}\eta^1{:}\eta^1\text{-}HNNH)$[33] the NN distance is 1.25 Å, a value in the double-bond range.[23] This complex is considered to be a Cr(0) complex of diimine, HN=NH. A diimine complex has also been found in $[HN(CH_2CH_2SC_6H_4\text{—}S\text{-}o)_2Fe]_2(\mu\text{-}HNNH)$, which has an NN distance of 1.300 (7) Å.[34] In $[(C_5Me_4CMe_3)(Me_3CC)IW]_2(\mu\text{-}HNNH)$,[35] the NN distance of 1.410 (9) Å was considered appropriate for a hydrazido dianion, $HNNH^{2-}$. The only $\mu\text{-}\eta^2,\eta^2$-HNNH complex in the literature, $[Me_3(PhN)W](\mu\text{-}\eta^1,\eta^1\text{-}NH_2NH_2)(\mu\text{-}\eta^2,\eta^2\text{-}NHHN)$,[36] has an NN distance of 1.434 (14) Å. In the latter case the hydrazido(2–) ligand is symmetrically bound between the two equivalent metal centers. The recently reported $(C_5Me_5)_2Sm_4(N_2H_2)_2(N_2H_3)_4(NH_3)_2$ complex has N—N distances of 1.474 (16) and 1.518 (16) Å for the $HNNH^{2-}$ ligands.[29]

Discussion

The reaction of $(C_5Me_5)_2Sm(THF)_2$[37,38] with diphenylhydrazine was initially examined to determine if a $[(C_5Me_5)_2Sm]_2$(substrate) complex would form which still retained an NN single bond. Such a complex would allow systematic comparisons in a complete series of $[(C_5Me_5)_2Sm]_2$(substrate) complexes containing triple, double, and single NN bonds for which the first two examples are known: $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$[2] and

---

(29) Wang, K.-G.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1992**, *11*, 1011–1013.

(30) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405–409.

(31) Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science* **1979**, *203*, 172–174.

(32) House, D. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 2, Chapter 13.1 (see also references therein).

(33) Huttner, G.; Gartzke, W.; Allinger, K. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 822–823.

(34) Sellmann, D.; Soglowek, W.; Knoch, F.; Moll, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1271–1272.

(35) Churchill, M. R.; Li, Y.-J.; Blum, L.; Schrock, R. R. *Organometallics* **1984**, *3*, 109–113.

(36) Blum, L.; Williams, I. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 8316–8317.

(37) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

(38) Evans, W. J. *Polyhedron* **1987**, *6*, 803–835.

$[(C_5Me_5)_2Sm]_2(\mu\text{-PhNNPh})$,[5] respectively. Alternatively, a monometallic complex analogous to $(C_5Me_5)_2Sm(\eta^2\text{-PhNNPh})(THF)$,[5] could form or, given the weak strength of N–N single bonds, N–N cleavage[39] could occur. The latter possibility was of considerable interest because in any samarium-mediated conversion of dinitrogen to ammonia, NN cleavage would be needed at some point.

The initial reaction of $(C_5Me_5)_2Sm(THF)_2$ with PhNHNHPh to form $(C_5Me_5)_2Sm(NHPh)(THF)$ (**1**) showed that reductive cleavage of the NN bond was a facile reaction pathway (eq 1). In light of the strong reduction potential of Sm(II)[38] and the fact that hydrazines can be reductively cleaved to amines with reductants as weak as Zn/HCl,[39] this is a reasonable result. It is also reasonable that this reaction should be more facile with the less sterically saturated monosolvated samarium(II) reagent $(C_5Me_5)_2Sm(THF)$. Further deprotonation of **1** by additional $(C_5Me_5)_2Sm(THF)_x$ in the reaction mixture or by KH or $[(C_5Me_5)_2Sm]_2(\mu\text{-H})_2$ has not been demonstrated. This is consistent with the reactivity observed for $(C_5Me_5)_2Zr(H)(NHR)$ (R = H,[40] Me[21]) and the isolation of $[(C_5H_5)_2Y(\mu\text{-OH})]_2$.[41]

The formation of the desolvated analog of **1**, i.e., $[(C_5Me_5)_2Sm(NHPh)]_x$ (**2**), is precedented in a number of organosamarium systems including $(C_5Me_5)_2SmPh(THF)$,[42] $(C_5Me_5)_2Sm(CH_2Ph)(THF)$,[26] and $(C_5Me_5)_2Sm(RCHCHCH_2)(THF)$ (R = H, Me, Ph).[43] Complex **2** is similar to the desolvates of the above complexes in that crystallographic identification has proven elusive. In all of these cases, addition of THF may lock in a preferred orientation of higher coordination number which can crystallize in a more regular fashion.

The existence of the NHPh unit in **1** and **2** suggested that these complexes should form in reactions of aniline with $(C_5Me_5)_2Sm(THF)_2$ and $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$, as shown in eqs 3 and 4. These two reactions as well as others discussed below show that these nitrogen-based ligands are readily accessed by deprotonation using both samarium hydride and samarium(II) reagents.

On the basis of the above results, it was expected that $(C_5Me_5)_2Sm$ would react with PhNHNHPh to form the unsolvated NN cleavage product, $[(C_5Me_5)_2Sm(NHPh)]_x$ (**2**). Surprisingly, the data obtained on this reaction, eq 6, indicate that the NN bond is retained: the initially-isolated product, **3**, can be treated with THF to form $(C_5Me_5)_2Sm(PhNHNPh)(THF)$ (**4**), in which the presence of the NN bond is confirmed by X-ray crystallography. This result showed that the chemistry of Sm(II) with these NN substrates did not just involve simple reductive cleavage. As in the case of **2**, the degree of molecularity of **3** is not structurally defined. Both **2** and **3** tend to form tacky solids which may be a consequence of the fact that the ligand set does give a single optimal arrangement suitable for single crystal growth.

The isolation of **4** suggested a number of reaction pathways which could be traversed to obtain the coordinated $PhNHNPh^-$ monoanion starting from $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$, azobenzene, and organosamarium azobenzene complexes.[5] Scheme I shows how these routes fit together. These reactions further demonstrate the ease with which hydrogen atoms can be moved on NN-bonded substrates attached to samarium. Clearly, acid–base proton-transfer reactions can be accomplished even in the presence of the trivalent $(C_5Me_5)_2Sm$ unit and bimolecular reactions involving two different organosamarium complexes containing $(C_5Me_5)_2Sm$ units are viable. It is interesting to note that $(C_5Me_5)_2Sm(PhHNNPh)$ can be accessed by $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$ both by deprotonation (from PhNHNHPh) and by hydride addition (from PhNNPh).

The success achieved in reactions of organosamarium reagents with diphenylhydrazine suggested that the $(C_5Me_5)_2Sm$ coordination environment would be a viable site to study manipulation of less-substituted nitrogen-containing substrates more closely related to those in nitrogen fixation systems. The $(C_5Me_5)_2Sm$ unit could provide an interesting alternative to the transition-metal sites commonly studied.[34–36,44–46] Accordingly, reactions with the more reactive unsubstituted hydrazine were examined. $(C_5Me_5)_2Sm(THF)_2$, $(C_5Me_5)_2Sm$, and $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$ all react with H_2NNH_2, but the last two reagents give the best results. From these reactions, eqs 10 and 11, the hydrazido^{2-} complex **5** was obtained. The isolation of **5** demonstrates that a samarium $HNNH^{2-}$ complex is an accessible intermediate in any scheme involving the samarium-mediated reduction of N_2. N_2H_2 complexes have been frequently invoked as likely intermediates in nitrogen to ammonia sequences.[34,44–46] The existence of complex **5** and the dinitrogen complex $[(C_5Me_5)_2Sm]_2N_2$ is encouraging in terms of using the $(C_5Me_5)_2Sm$ unit as a new environment in which to study dinitrogen transformation.

The structure of **5** is also significant in the developing area of tetrakis(pentamethylcyclopentadienyl)dilanthanide chemistry. Recently, an increasing number of bimetallic organosamarium complexes have been identified which contain four C_5Me_5 rings.[38] When these complexes of general formula $[(C_5Me_5)_2Sm]_2(\text{ligand})_x$ have small bridging ligands, the four C_5Me_5 rings adopt a tetrahedral geometry.[2,11,27,30,31] Unusual chemistry appears to be possible within the cavity provided by these four rings.[22,43] As the first tetrahedral tetrakis(pentamethylcyclopentadienyl) complex containing asymmetrically located bridging ligands, the structure of **5** shows there is considerable flexibility in the bonding cavity generated by the four C_5Me_5 rings. Substrates within the space defined by the rings obviously need not reside only in symmetrical positions. Furthermore, when a substrate is oriented in one hemisphere of the cavity, as in **5**, there apparently is space for other incoming reagents in the other part of the cavity. This is very encouraging in terms of the potential of these tetracyclopentadienyl complexes.

The specific bonding parameters in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-HNNH})$ (**5**) are of interest with respect to the structure of $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^1{:}\eta^1\text{-PhNNPh})$ (**6**), shown schematically in Scheme I. Although **6** could not adopt the structure observed for **5** for steric reasons, the $\mu\text{-}\eta^1{:}\eta^1$ structure of **6** would be available to **5**. In **6**, the 1.25 (1)-Å NN distance is shorter than expected and in the double-bond range, despite the fact that each nitrogen is also involved with single bonds to Sm and to the phenyl group. In contrast, in **5**, the NN bond is longer than expected. However, in both **5** and **6**, the Sm–N interactions are shorter than expected. This pair of complexes provides the first clues on how the electronic and steric differences of substituents can be used to achieve specific bonding results with $(C_5Me_5)_2Sm$ units.

Conclusion

Clearly, there is much flexibility in the activating and bonding capacity of $(C_5Me_5)_2Sm$ units. From this study, it is apparent that the activated NN-bound systems can be accessed either via divalent organosamarium precursors or via trivalent samarium hydrides. Hydrogen can be moved on and off the NN-bound substrates in a variety of ways, and NN cleavage is an available reaction pathway. $(C_5Me_5)_2Sm$ units exhibit variable reactivity

---

(39) E.g., see: Smith, P. A. S. *Derivatives of Hydrazine and Other Hydronitrogens Having N-N Bonds*; Benjamin/Cummings Publishing Co.: London, 1983; p 22.

(40) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472–5478.

(41) Evans, W. J.; Hozbor, M. A.; Bott, S. G.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 1990–1993.

(42) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1985**, *4*, 112–119.

(43) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314–2324.

(44) Leigh, G. J. *J. Mol. Catal.* **1988**, *47*, 363–379.

(45) Collman, J. P.; Hutchinson, J. E.; Lopez, M. A.; Guilard, R.; Reed, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 2794–2796 and references therein.

(46) Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc.* **1991**, *113*, 725–726.

with NN substrates depending upon the substituents present. Reactions involving both NN cleavage and coordination of nitrogen substrates with the NN bond intact have been observed. These results demonstrate that the $(C_5Me_5)_2Sm$ coordination environment is a viable system in which to examine manipulation of intermediates related to nitrogen fixation. Since the redox chemistry of organosamarium complexes of N_2H_x ligands differs from that of transition-metal analogs, the lanthanide system may provide a comparative basis for separating redox-based reactions from simple proton or hydride transfers. More generally, this study shows that there is sufficient space in the coordination environment generated by two $(C_5Me_5)_2Sm$ units to derivatize substrates bound inside the cavity formed by four C_5Me_5 rings. Studies are continuing to completely map NN activation and derivatization pathways using organosamarium reagents.

Acknowledgment. We thank the National Science Foundation for support for this research. Funds for the purchase of the X-ray equipment were made available from NSF Grant CHE-85-14495. We also thank the Deutsche Forschungsgemeinschaft for a fellowship to G.K.K.

Supplementary Material 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.