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Synthetic, Structural, and Reactivity Studies of the Reduction and CO Derivatization of Azobenzene Mediated by Divalent Lanthanide Complexes[1]

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Abstract: The addition of $(C_5Me_5)_2Sm(THF)_2$ to $C_6H_5N{=}NC_6H_5$ in a 1:1 ratio in toluene forms green $(C_5Me_5)_2Sm(\eta^2\text{-}N_2Ph_2)(THF)$ (**1**). The addition of azobenzene to $(C_5Me_5)_2Sm(THF)_2$ in a 1:2 ratio in toluene forms blue $[(C_5Me_5)_2Sm]_2(N_2Ph_2)$ (**2**). In THF, **2** slowly transforms into $[(C_5Me_5)(THF)Sm]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}N_2Ph_2]_2$ (**3**). Complexes **1**-**3** all have trivalent $(C_5Me_5)_xSm$ moieties coordinated to nitrogen atoms of ligands derived from azobenzene. In **1**, the nitrogen atoms are η^2-coordinated to Sm with an average Sm-N distance of 2.42 (2) Å. In **2**, one $(C_5Me_5)_2Sm$ group is attached to each nitrogen atom in a trans orientation with Sm-N distances of 2.40 (1) and 2.41 (1) Å. In **3**, each $(C_5Me_5)Sm$ unit interacts with both N_2Ph_2 units with Sm-N distances of 2.323 (8) and 2.559 (7) Å to each. The N-N distances are 1.35 (2) Å (average) in **1**, 1.25 (1) Å in **2**, and 1.44 (1) Å in **3**. Addition of azobenzene to $(C_5H_5)_2Yb(THF)$ in a 1:2 ratio in THF forms a green solution which deposits crystals of $[(C_5H_5)(THF)Yb]_2[\mu\text{-}\eta^2{:}\eta^2\text{-}N_2Ph_2]_2$ (**4**) and $Cp_3Yb(THF)$. The structure of **4** is analogous to that of **3**. **4** has Yb-N distances of 2.188 (5), 2.206 (5), 2.487 (5), and 2.572 (5) Å and an N-N length of 1.470 (6) Å. Complex **1** fails to react with CO at 70 psi but **2** reacts to form $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^4\text{-}(PhN)OCCO(NPh)]$ (**5**). In **5**, the two trivalent $(C_5Me_5)_2Sm$ units are bridged by a doubly deprotonated *N,N′*-diphenyloxamide ligand via Sm-N and Sm-O bonds of 2.49 (1) and 2.30 (1) Å, respectively. $(C_5Me_5)_2Sm(THF)_2$ reacts with 3,3′-azotoluene to form **6**, an analogue of **2**. **6** reacts with CO to form **7**, an analogue of **5**. Reaction of CO with an equimolar mixture of **2** and **6** gives **5** and **7** exclusively with no evidence of the crossover product $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^4\text{-}(PhN)OCCO(NC_6H_4Me\text{-}3)]$. Similarly $[(C_5Me_5)_2Sm]_2(PhNNC_6H_4NMe_2\text{-}4)$ reacts with CO to form $[(C_5Me_5)_2Sm]_2[(PhN)OCCO(NC_6H_4NMe_2\text{-}4)]$ exclusively. Complex **1** crystallizes from hexane/THF at -34 °C with one THF molecule of crystallization per two formula units in space group $P\bar{1}$ with a = 10.732 (4) Å, b = 19.548 (9) Å, c = 19.892 (10) Å, α = 110.14 (4)°, β = 104.75 (4)°, γ = 101.21 (3)°, and Z = 4 for D_{calcd} = 1.31 g cm^{-3}. Least-squares refinement on the basis of 6906 observed reflections led to a final R value of 0.066. Complex **2** crystallizes from toluene at -34 °C in space group $P2_1/n$ with a = 10.855 (7) Å, b = 20.435 (5) Å, c = 21.686 (9) Å, β = 106.68 (4)°, and D_{calcd} = 1.48 g cm^{-3} for Z = 4 dimers. Least-squares refinement on the basis of 4130 observed reflections led to a final R value of 0.033. Complex **3** crystallizes from THF at 28-30 °C with two THF molecules of crystallization in space group $C2/m$ with a = 22.409 (8) Å, b = 13.178 (5) Å, c = 9.978 (4) Å, β = 108.84 (5)°, and D_{calcd} = 1.46 g cm^{-3} for Z = 2 (2 dimers per unit cell). Least-squares refinement on the basis of 1278 observed reflections led to a final R value of 0.038. Complex **4** crystallizes from toluene with a toluene molecule of crystallization in space group $P\bar{1}$ with a = 9.645 (2) Å, b = 11.369 (3) Å, c = 10.143 (5) Å, α = 97.33 (3)°, β = 94.36 (3)°, γ = 93.18 (2)°, and D_{calcd} = 1.62 g cm^{-3} for Z = 1. Least-squares refinement on the basis of 3239 observed reflections led to a final R value of 0.030. Complex **5** crystallizes from toluene at -34 °C with a toluene molecule of crystallization in space group $A2/m$ with a = 15.961 (3) Å, b = 14.204 (5) Å, c = 15.612 (8) Å, β = 118.14 (3)°, and D_{calcd} = 1.25 g cm^{-3} for Z = 2. Least-squares refinement on the basis of 2151 observed reflections led to a final R value of 0.053.

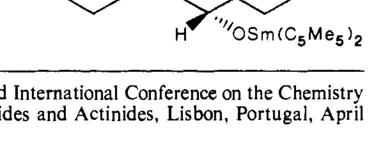
The discovery that $(C_5Me_5)_2Sm(THF)_2$ could completely cleave the multiple bond in CO while it reductively homologated three CO molecules to a ketene carboxylate unit (equation 1) demonstrated that this divalent samarium reagent was capable of unusual

$$4(C_5Me_5)_2Sm(THF)_2 + 6CO \rightarrow \{[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^4\text{-}O_2C{-}C{=}C{=}O](THF)\}_2 + 6THF \quad (1)$$

transformations of unsaturated substrates.[3] Activation of $C_6H_5C{\equiv}CC_6H_5$ by $(C_5Me_5)_2Sm(THF)_2$ followed by treatment with CO also gave an unusual result: the stereospecific synthesis of a complex tetracyclic hydrocarbon (eq 2 and 3).[4] The formation of the indenoindenediolate complex shown in eq 3 could be explained on the basis of CO insertion and CH activation reactions if some assumptions were made about the structure of the intermediate, $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$.[5] Scheme I shows one

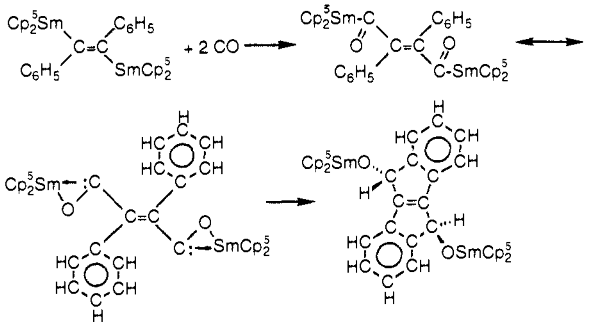
$$2(C_5Me_5)_2Sm(THF)_2 + C_6H_5C{\equiv}CC_6H_5 \rightarrow [(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2 + 4THF \quad (2)$$

$[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2 + 2CO \rightarrow$



(3)

Scheme I



$Cp^5 = C_5Me_5$

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possible structure for the diphenylethyne product and a possible route for formation of the tetracyclic product.[6] This scheme is reasonable as long as $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$ has two reactive Sm–C bonds. Crystallographic confirmation of this structure has not yet been possible due to difficulties in growing crystals of this very soluble complex.[5]

In efforts to further explore the reactivity of $(C_5Me_5)_2Sm(THF)_2$ with unsaturated substrates and to learn more about the possible structural analogues of $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$, we examined the reaction of $(C_5Me_5)_2Sm(THF)_2$ with $C_6H_5N{=}NC_6H_5$. This reaction system is complicated, but it provides us with some detailed information of how $(C_5Me_5)_2Sm(THF)_2$ can interact with unsaturated substrates. We describe here structural studies of three different complexes obtained from the reaction of $(C_5Me_5)_2Sm(THF)_2$ with azobenzene, the structure of an ytterbium analogue, and studies of the reaction of CO with these species. Preliminary results on part of this work were communicated earlier.[7,8]

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, both the syntheses and subsequent manipulations of these compounds were conducted under nitrogen with rigorous exclusion of air and water with Schlenk, vacuum line, and glovebox techniques. The preparation of $(C_5Me_5)_2Sm(THF)_2$ and the methods for drying solvents and taking physical measurements have been described previously.[9] $(C_5H_5)_2Yb(THF)$ was prepared from YbI_2.[10] Azobenzene (Aldrich) was degassed before use and CO (Liquid Carbonic, 99.99%) was used as received. Complexometric metal analyses were obtained as previously described.[11] Mass spectrometric measurements were recorded on a VG Analytical 7070E-HF mass spectrometer.

$(C_5Me_5)_2Sm(N_2Ph_2)(THF)$ (1). In the glovebox, a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (119 mg, 0.21 mmol) in 10 mL of toluene was slowly added to azobenzene (38 mg, 0.21 mmol) in 5 mL of toluene. The solution immediately turned green. After the reaction was stirred for 1 h, the solvent was removed by rotary evaporation and the solids were extracted with hexane. Removal of solvent from the extract gave **1** (113 mg, 80%). Crystals were grown from hexane/THF at −34 °C over several weeks. ^1H NMR (C_6D_6) 3.06 (s, $\Delta\nu_{1/2}$ = 5 Hz, C_5Me_5). ^1H NMR resonances attributable to the aryl protons were not observed. ^{13}C NMR (C_6D_6) 153.4 (s, Ph), 131.8 (d, J = 162 Hz, Ph), 123.9 (d, J_{CH} = 162 Hz, Ph), 123.9 (s, C_5Me_5), 38.9 (q, J = 125 Hz, $C_5(CH_3)_5$). $\chi_M{}^{298} = 1960 \times 10^{-6}$ cgs; $\mu_{eff} = 2.2\ \mu_B$. IR (KBr) 2980–2860 (s), 2220 (w), 1920 (w), 1575 (m), 1470 (m), 1445 (s), 1265 (s), 1220 (m), 1100–1010 (s), 870 (m), 800 (s), 750 (s), 680 (m) cm^{-1}. Anal. Calcd for $SmN_2C_{36}H_{48}O$: Sm, 22.3. Found: Sm, 22.6.

X-ray Crystallography of $(C_5Me_5)_2Sm(N_2Ph_2)(THF)\cdot0.5THF$. General procedures for data collection and reduction have been described previously.[12,13] A crystal measuring 0.20 mm × 0.30 mm × 0.30 mm was placed in a capillary in the glovebox. The capillary was temporarily sealed with grease, removed from the glovebox, sealed with a torch, and mounted on a Nicolet R3m/V diffractometer. Lattice parameters were determined from 25 computer-centered reflections with $20° < 2\theta < 25°$. Partial rotation photographs confirmed the axial lengths and showed no symmetry. The absence of monoclinic or higher symmetry was confirmed by a Delaunay reduction. Data were collected by the θ–2θ scan technique in bisecting geometry. The p factor in the expression[14] for the standard deviations of the observed intensities was given a value of 0.05. Crystal and data collection parameters are given in Table I. During the data collection, the intensities of three standard reflections showed no significant fluctuation. An empirical absorption correction was applied. Patterson and difference Fourier techniques were used to locate all non-hydrogen atoms. The complex crystallizes with two independent molecules per asymmetric unit (i.e., Z = 4). A disordered THF solvent molecule co-crystallized with the two molecules of **1**. All non-hydrogen atoms except the THF solvent atoms were refined anisotropically with full-matrix least-squares methods. The THF solvent atoms were all refined isotropically as carbon atoms. No hydrogen atoms were located. Atomic scattering factors were taken from ref 15. A final difference map contained no recognizable features. Final fractional coordinates are given in Table II.

Table I. Crystal Data for $(C_5Me_5)_2Sm(N_2Ph_2)(THF)$ (**1**) and $[(C_5Me_5)_2Sm]_2N_2Ph_2$ (**2**)

compound	**1**·(0.5THF)	**2**
formula	$SmC_{36}H_{48}N_2O\cdot0.5C_4H_8O$	$Sm_2N_2C_{52}H_{70}$
mol wt	711.20	1023.92
space group	$P\bar{1}$	$P2_1/n$
cell constants		
a, Å	10.732 (4)	10.855 (7)
b, Å	19.548 (9)	20.435 (5)
c, Å	19.892 (10)	21.686 (9)
α, deg	110.14 (4)	90
β, deg	104.75 (4)	106.68 (4)
γ, deg	101.21 (3)	90
cell vol, Å^3	3601	4608
molecules/unit cell	4	4 (dimers)
ρ(calcd), g cm^{-3}	1.31	1.48
μ(calcd), cm^{-1}	16.7	25.7
radiation	Mo Kα	Mo Kα
max crystal dimens, mm	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.3
scan width, deg	−1.2 in 2θ from Kα_1 to +1.2 from Kα_2	$0.8 + 0.2 \tan\theta$
std reflctns	040, 3−5−1, 3,5−6	400, 060, 008
decay of stds, %	±3	<4
reflctns measd	9918	6303
2θ range, deg	3–45	1–44
obsd reflctns	6906	4130
no. of parameters varied	741	505
GOF	2.50	1.2
R	0.066	0.033
R_w	0.084	0.036

$[(C_5Me_5)_2Sm]_2(N_2Ph_2)$ (2). In the glovebox, azobenzene (32 mg, 0.177 mmol) in 5 mL of toluene was added dropwise to $(C_5Me_5)_2Sm(THF)_2$ (200 mg, 0.354 mmol) in 10 mL of toluene. The solution immediately turned dark blue. After the reaction was stirred for 6 h, the solvent was removed by rotary evaporation to give **2** as a dark blue solid (0.179 g, 98%). Crystals of **2** were grown from toluene at −34 °C. ^1H NMR (1 mM in toluene-d_8) 1.57 (60 H, C_5Me_5, $\Delta\nu_{1/2}$ = 7 Hz), 2.49 (dd, 2 H, C_6H_5-p), −1.00 (d, J = 6 Hz, 2 H, C_6H_5-m), −6.32 (d, J = 7 Hz, 2 H, C_6H_5-m). Ortho hydrogen atoms were not located presumably due to interaction with the Sm(III) center. The chemical shifts of the aryl protons vary with temperature, but the coupling pattern remains the same down to −60 °C. ^{13}C NMR (C_6D_6) 180.5 (s, $C^1{}_6H_5$), 130.4 (d, J = 155 Hz, C_6H_5), 129.3 (d, J = 147 Hz, C_6H_5), another C_6H_5 peak was obscured by the C_6D_6 peaks, 119.3 (s, C_5Me_5), 97.3 (d, J = 165 Hz, $C^2{}_6H_5$), 22.6 (q, J = 126 Hz, $C_5(CH_3)_5$). $\chi_M{}^{298} = 1560 \times 10^{-6}$ cgs; $\mu_{eff} = 1.9\ \mu_B$. IR (KBr) 2900 (m br), 1580 (s), 1460 (m), 1385 (m), 1330 (m), 1305 (m), 1180 (w), 1020 (w), 840 (w br), 730 (m) cm^{-1}. UV–vis (15.5 mg in 100 mL of toluene) 600 (br, ϵ 1300), 372 (shoulder, ϵ 5300) nm; UV–vis (4.65 mg in 100 mL of toluene) 272 (ϵ 22 000), 210 (ϵ 16 000) nm. Complexometric metal analysis. Calcd for $SmNC_{26}H_{35}$: Sm, 29.37. Found: Sm, 28.6. A Sm, C, H, and N analysis was incomplete (Sm, 27.95; C, 57.28; H, 6.13; N, 2.39) but gave a reasonable elemental ratio Sm:N:C:H = 1:0.92:26:33.

X-ray Crystallography of $[(C_5Me_5)_2Sm]_2(N_2Ph_2)$ (2). A single crystal measuring 0.2 × 0.3 × 0.3 mm was sealed under nitrogen in a thin-walled glass capillary. Lattice parameters were determined from 25 computer-centered reflections. Data were collected on a Enraf-Nonius CAD-4 diffractometer by the θ–2θ technique as previously described.[16] Crystal and data collection parameters are given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects.

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Table II. Atomic Positional Parameters for $(C_5Me_5)_2Sm(N_2Ph_2)(THF)\cdot 0.5THF$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Sm(1)	−0.19363 (8)	0.17344 (4)	0.23737 (4)	C(37)	0.6312 (22)	0.4803 (10)	0.9358 (9)
Sm(2)	0.62055 (8)	0.33119 (4)	0.74252 (4)	C(38)	0.3474 (18)	0.3537 (10)	0.8297 (12)
O(01)	−0.2711 (10)	0.1262 (5)	0.3281 (5)	C(39)	0.2791 (21)	0.3512 (11)	0.6564 (12)
O(02)	0.7598 (11)	0.3754 (5)	0.6697 (5)	C(40)	0.8716 (18)	0.3176 (12)	0.8012 (15)
N(01)	−0.2048 (13)	0.2976 (6)	0.2487 (6)	C(41)	0.7903 (22)	0.2437 (12)	0.7511 (10)
N(02)	−0.2726 (13)	0.2799 (6)	0.2943 (7)	C(42)	0.6932 (18)	0.2179 (9)	0.7825 (10)
N(03)	0.4656 (12)	0.2362 (6)	0.6159 (6)	C(43)	0.7141 (18)	0.2763 (10)	0.8503 (9)
N(04)	0.4227 (12)	0.2210 (6)	0.6675 (6)	C(44)	0.8172 (22)	0.3369 (10)	0.8635 (10)
C(01)	−0.2855 (18)	0.1779 (8)	0.3963 (8)	C(45)	1.0018 (21)	0.3566 (21)	0.8005 (25)
C(02)	−0.2555 (19)	0.1425 (8)	0.4545 (9)	C(46)	0.8088 (40)	0.1914 (19)	0.6810 (16)
C(03)	−0.2889 (20)	0.0557 (8)	0.4061 (8)	C(47)	0.6004 (23)	0.1363 (10)	0.7514 (14)
C(04)	−0.3236 (19)	0.0476 (8)	0.3216 (9)	C(48)	0.6420 (25)	0.2708 (14)	0.9078 (12)
C(05)	0.8570 (19)	0.4480 (8)	0.6946 (10)	C(49)	0.8969 (27)	0.4151 (11)	0.9419 (12)
C(06)	0.9447 (21)	0.4368 (10)	0.6438 (10)	C(50)	−0.2285 (17)	0.3491 (7)	0.2181 (8)
C(07)	0.8753 (17)	0.3540 (9)	0.5815 (9)	C(51)	−0.1355 (16)	0.3636 (8)	0.1782 (8)
C(08)	0.7372 (18)	0.3282 (9)	0.5913 (9)	C(52)	−0.1516 (19)	0.4101 (9)	0.1398 (9)
C(10)	−0.4322 (18)	0.1382 (10)	0.1171 (10)	C(53)	−0.2535 (23)	0.4459 (9)	0.1421 (9)
C(11)	−0.3352 (19)	0.1306 (9)	0.0860 (9)	C(54)	−0.3397 (19)	0.4351 (8)	0.1823 (9)
C(12)	−0.2965 (17)	0.0660 (9)	0.0884 (8)	C(55)	−0.3226 (17)	0.3894 (8)	0.2230 (9)
C(13)	−0.3724 (18)	0.0328 (9)	0.1252 (8)	C(56)	−0.2914 (19)	0.3407 (9)	0.3537 (8)
C(14)	−0.4532 (18)	0.0760 (10)	0.1454 (8)	C(57)	−0.4147 (20)	0.3205 (11)	0.3669 (10)
C(15)	−0.5154 (22)	0.1919 (10)	0.1271 (12)	C(58)	−0.4371 (26)	0.3761 (14)	0.4247 (13)
C(16)	−0.2914 (23)	0.1742 (11)	0.0417 (11)	C(59)	−0.3371 (30)	0.4525 (15)	0.4687 (14)
C(17)	−0.2132 (21)	0.0258 (10)	0.0408 (9)	C(60)	−0.2259 (30)	0.4675 (11)	0.4544 (11)
C(18)	−0.3722 (21)	−0.0445 (9)	0.1291 (10)	C(61)	−0.1972 (19)	0.4132 (8)	0.3936 (8)
C(19)	−0.5623 (17)	0.0599 (11)	0.1785 (10)	C(62)	0.4277 (14)	0.1809 (8)	0.5402 (8)
C(20)	0.0527 (16)	0.2370 (9)	0.3568 (8)	C(63)	0.4122 (14)	0.2077 (9)	0.4828 (8)
C(21)	0.0338 (15)	0.1592 (9)	0.3293 (10)	C(64)	0.3742 (15)	0.1494 (11)	0.4045 (9)
C(22)	0.0416 (15)	0.1346 (8)	0.2522 (9)	C(65)	0.3570 (18)	0.0756 (11)	0.3895 (10)
C(23)	0.0686 (16)	0.2022 (11)	0.2407 (10)	C(66)	0.3767 (17)	0.0520 (9)	0.4467 (10)
C(24)	0.0821 (16)	0.2665 (8)	0.3048 (9)	C(67)	0.4098 (16)	0.1031 (8)	0.5224 (9)
C(25)	0.0727 (19)	0.2900 (12)	0.4384 (9)	C(68)	0.2931 (14)	0.1732 (8)	0.6518 (8)
C(26)	0.0261 (20)	0.1102 (13)	0.3729 (14)	C(69)	0.2714 (16)	0.1556 (8)	0.7123 (8)
C(27)	0.0504 (21)	0.0548 (11)	0.2075 (13)	C(70)	0.1475 (20)	0.1108 (9)	0.7040 (11)
C(28)	0.1126 (23)	0.2077 (14)	0.1720 (11)	C(71)	0.0390 (17)	0.0810 (9)	0.6335 (12)
C(29)	0.1289 (21)	0.3470 (9)	0.3208 (12)	C(72)	0.0558 (17)	0.0993 (9)	0.5743 (10)
C(30)	0.5273 (21)	0.4517 (10)	0.7299 (10)	C(73)	0.1855 (15)	0.1436 (8)	0.5812 (8)
C(31)	0.6228 (17)	0.4818 (8)	0.8051 (9)	C(74)	0.989 (6)	0.851 (3)	0.061 (3)
C(32)	0.5750 (16)	0.4526 (8)	0.8496 (9)	C(75)	0.794 (6)	0.740 (3)	0.053 (3)
C(33)	0.4461 (17)	0.3977 (8)	0.8018 (10)	C(76)	0.906 (6)	0.756 (3)	0.021 (3)
C(34)	0.4177 (19)	0.3979 (9)	0.7297 (10)	C(77)	0.845 (7)	0.812 (4)	0.078 (3)
C(35)	0.5273 (27)	0.4758 (12)	0.6626 (11)	C(78)	1.002 (8)	0.821 (4)	0.111 (4)
C(36)	0.7514 (20)	0.5541 (9)	0.8334 (11)				

Systematic absences established the space group as $P2_1/n$. The two crystallographically independent samarium atoms were located with the aid of MULTAN 80.[17] Fourier techniques provided the location of the remaining non-hydrogen atoms which were refined with anisotropic thermal parameters with full-matrix least-squares methods. A difference map weighted in low-angle reflections showed sufficient H atoms to assign them all. All were put in with fixed positions and thermal parameters. Sm–H distances were calculated by using a fixed C–H distance of 1.05 Å.[18] A final least-squares refinement on the basis of 4130 observed reflections led to a final $R = 0.033$. Final positional parameters are given in Table III.

$[(C_5Me_5)(THF)Sm]_2[N_2Ph_2]_2$ (3). $[(C_5Me_5)_2Sm]_2(N_2Ph_2)$ (279 mg, 0.27 mmol) was dissolved in THF and a brown-green solution resulted. This solution slowly deposited orange crystals of **3**. After 1 week, the crystals (36 mg, 24%) were separated from the brown mother liquor by filtration. ^1H NMR (C_4D_8O) 6.65 (dd, 2 H) 6.01 (dd, 2 H), 4.20 (dd, 2 H), 2.15 (s, $\Delta\nu_{1/2} = 4$ Hz, 15 H, C_5Me_5), 0.13 (d, $J = 3$ Hz, 2 H), −1.76 (d, $J = 4$ Hz, 2 H). ^{13}C NMR (C_4D_6O) 22.8 ($C_5\mathit{Me}_5$), the limited solubility of this complex precluded observation of the other signals even with DEPT[19] techniques. IR (KBr) 3000–2880 (s), 1580 (m), 1480–1440 (s), 1370 (w), 1290 (s), 1230 (s), 1170 (s), 1080 (m), 1020 (s), 990 (m), 870 (s), 800 (s), 750 (s), 695 (m). Anal. Calcd for $SmN_2C_{30}H_{41}N_2O_2$: Sm, 24.6. Found: Sm, 25.3. Removal of the solvent from the mother liquor gave a hexane soluble solid which had four peaks in the C_5Me_5 region of the ^1H NMR spectrum in C_6D_6. The main peak at 1.25 ppm was eight times as intense as those at 1.01, 1.71, and 3.06 (complex **1**).

X-ray Crystallography of $[(C_5Me_5)(THF)Sm]_2[N_2Ph_2]_2\cdot 2THF$. A single crystal measuring 0.15 × 0.40 × 0.20 mm was handled as described for **2**. Data collection, reduction, and refinement were also carried out as described for **2**. Crystal and data collection parameters are given in Table IV. Systematic absences (hkl, $h + k$ odd) established the space group as $C2$ or $C2/m$. Solution and refinement showed $C2/m$ to be the correct space group. Least-squares refinement on the basis of 1356 observed reflections led to a final $R = 0.038$. Final positional parameters are given in Table V.

$[(C_5H_5)(THF)Yb]_2[N_2Ph_2]_2$ (4). Addition of azobenzene (60 mg, 0.33 mmol) to a red solution of $(C_5H_5)_2Yb(THF)$ (300 mg, 0.8 mmol) in 20 mL of THF caused a color change to green. After being stirred for 2 days, the THF solution was concentrated and cooled to −34 °C. A mixture of dark green and dark purple crystals formed (200 mg). The two complexes were not easily separated by solvent extraction and instead were individually examined by X-ray crystallography. A unit cell determination on the green crystals showed them to be isostructural with $(C_5H_5)_3Ln(THF)$ (Ln = La,[20] Nd,[21,22] Pr,[21], Gd,[23] Y,[20] Lu[24]), i.e., they are $(C_5H_5)_3Yb(THF)$. The cell parameters are $a = 8.24$ (2) Å, $b = 25.48$ (22) Å, $c = 8.19$ (7) Å, and $\beta = 101.8$ (5)°. The purple crystals

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Table III. Atomic Positional Parameters for $[(C_5Me_5)_2Sm]_2(N_2Ph_2)$

atom	*x*	*y*	*z*
Sm(1)	−0.58266 (4)	−0.28136 (2)	0.43314 (2)
Sm(2)	−0.34514 (4)	−0.08576 (2)	0.30878 (2)
N(1)	−0.4920 (9)	−0.2239 (5)	0.3598 (6)
N(2)	−0.4626 (7)	−0.1669 (4)	0.3495 (5)
C(1)	−0.415 (1)	−0.3842 (5)	0.4505 (5)
C(2)	−0.531 (1)	−0.4085 (6)	0.4582 (6)
C(3)	−0.545 (1)	−0.3843 (6)	0.5160 (6)
C(4)	−0.441 (1)	−0.3428 (6)	0.5439 (5)
C(5)	−0.359 (1)	−0.3434 (5)	0.5031 (5)
C(6)	−0.351 (1)	−0.4026 (6)	0.4002 (6)
C(7)	−0.614 (1)	−0.4602 (6)	0.4170 (7)
C(8)	−0.637 (1)	−0.4089 (7)	0.5517 (7)
C(9)	−0.416 (1)	−0.3084 (7)	0.6081 (5)
C(10)	−0.224 (1)	−0.3154 (7)	0.5192 (6)
C(11)	−0.8374 (8)	−0.3019 (5)	0.4254 (5)
C(12)	−0.7980 (8)	−0.2484 (5)	0.4668 (5)
C(13)	−0.7717 (8)	−0.1958 (4)	0.4297 (5)
C(14)	−0.7954 (7)	−0.2182 (4)	0.3659 (4)
C(15)	−0.8346 (8)	−0.2841 (5)	0.3632 (5)
C(16)	−0.903 (1)	−0.3636 (5)	0.4394 (6)
C(17)	−0.796 (1)	−0.2438 (7)	0.5365 (5)
C(18)	−0.737 (1)	−0.1270 (5)	0.4523 (6)
C(19)	0.7914 (9)	−0.1770 (5)	0.3089 (5)
C(20)	−0.882 (1)	−0.3254 (6)	0.3043 (6)
C(21)	−0.1465 (7)	−0.1710 (4)	0.3445 (4)
C(22)	−0.1432 (7)	−0.1470 (4)	0.2842 (4)
C(23)	−0.1038 (8)	−0.0808 (5)	0.2919 (4)
C(24)	−0.0886 (8)	−0.0627 (4)	0.3561 (4)
C(25)	−0.1132 (7)	−0.1192 (5)	0.3884 (4)
C(26)	−0.1692 (9)	−0.2404 (5)	0.3614 (5)
C(27)	−0.161 (1)	−0.1879 (5)	0.2232 (5)
C(28)	−0.0617 (9)	−0.0427 (5)	0.2414 (5)
C(29)	−0.040 (1)	0.0017 (6)	0.3871 (6)
C(30)	−0.0911 (9)	−0.1238 (6)	0.4606 (4)
C(31)	−0.3797 (8)	0.0315 (4)	0.2424 (4)
C(32)	−0.4501 (8)	0.0384 (4)	0.2882 (4)
C(33)	−0.5564 (7)	−0.0040 (4)	0.2698 (4)
C(34)	−0.5513 (8)	−0.0379 (4)	0.2147 (4)
C(35)	−0.4416 (8)	−0.0166 (4)	0.1976 (4)
C(36)	−0.2759 (9)	0.0785 (5)	0.2385 (6)
C(37)	−0.423 (1)	0.0881 (5)	0.3412 (4)
C(38)	−0.6690 (8)	−0.0044 (5)	0.2974 (5)
C(39)	−0.654 (1)	−0.0832 (5)	0.1760 (5)
C(40)	−0.410 (1)	−0.0351 (6)	0.1368 (5)
Ph(1)	−0.508 (1)	−0.2504 (7)	0.2907 (5)
Ph(2)	−0.562 (1)	−0.3133 (8)	0.2812 (6)
Ph(3)	−0.583 (1)	−0.3445 (6)	0.2249 (8)
Ph(4)	−0.551 (1)	−0.3204 (6)	0.1754 (6)
Ph(5)	−0.500 (1)	−0.2596 (6)	0.1818 (6)
Ph(6)	−0.479 (1)	−0.2250 (5)	0.2383 (7)
Ph(7)	−0.4293 (8)	−0.1415 (5)	0.4225 (4)
Ph(8)	−0.3942 (9)	−0.1732 (5)	0.4808 (7)
Ph(9)	−0.355 (1)	−0.1415 (8)	0.5368 (5)
Ph(10)	−0.341 (1)	−0.0747 (8)	0.5395 (6)
Ph(11)	−0.377 (1)	−0.0415 (5)	0.4818 (7)
Ph(12)	−0.4221 (9)	−0.0743 (5)	0.4245 (5)

are described in the next paragraph.

X-ray Crystallography of $[(C_5H_5)(THF)Yb]_2[N_2Ph_2]_2\cdot C_7H_8$. A crystal measuring 0.09 × 0.17 × 0.20 mm was handled as described above for **1** and mounted on a Syntex $P2_1$ diffractometer. Data collection, reduction, and refinement were also done as described for **1**. Crystal and data collection parameters are given in Table IV. During the data collection, three standard reflections showed a linear decay of 8%. The data were corrected for this decay. Patterson and difference Fourier techniques were used to locate all atoms. All non-hydrogen atoms were refined anisotropically with full-matrix least-squares methods. All hydrogen atoms were included with fixed thermal and positional (C–H = 0.95 Å) parameters.[18] A final difference map contained no recognizable features; its largest peak was of height 2.11 eA^{-3}. Fractional coordinates are given in Table VI.

$[(C_5Me_5)_2Sm]_2[(PhN)OCCO(NPh)]$ (5). In the glovebox, $[(C_5Me_5)_2Sm]_2(N_2Ph_2)$ (210 mg, 0.12 mmol) was dissolved in 10 mL of THF and placed in a 3-oz Fischer-Porter aerosol reaction vessel capped with a valve and pressure gauge assembly. The apparatus was attached to a high-pressure manifold and pressurized with CO to 80 psi. The reaction turned green overnight. THF was removed by rotary evaporation, and the solids were washed with hexane to give green **5** (100 mg, 80%). Crystals of **5** were obtained by cooling a saturated toluene solution to −34 °C overnight. ^{1}H NMR (C_4D_8O): 1.91 (s, C_5Me_5). ^{13}C NMR (C_4D_8O) 121.4 (s, C_5Me_5), 20.12 (q, J = 125 Hz, $C_5(\mathit{C}H_3)_5$). IR (KBr) 2940 (s), 2900 (s), 2860 (s), 1590 (s), 1540 (s), 1495 (s), 1450 (s), 1380 (s), 1340 (s), 1260 (m), 1200 (m), 1170 (m), 1100 (m), 1020 (m), 800 (m), 760 (m), 680 (m) cm^{-1}. The visible spectrum in toluene contained no distinct maxima; extinction coefficients of the tail of the UV absorption were 50 at 600 nm, 130 at 500 nm, and 700 at 400 nm. Anal. Calcd for $SmNC_{27}H_{35}O$: Sm, 27.9. Found: Sm, 27.6.

X-ray Crystallography of $[(C_5Me_5)_2Sm]_2[(PhN)OCCO(NPh)]\cdot 2C_7H_8$. A single crystal measuring 0.25 × 0.25 × 0.25 mm was handled as described above for **4**. Lattice parameters were determined from 15 computer-centered reflections. Crystal and data collection parameters are given in Table IV. During the data collection, the intensities of three standard reflections measured every 100 reflections exhibited only random fluctuations within ±3%. An absorption correction was applied. Only one systematic absence (*hkl*, *k* + 1 odd) established the space group as *A*2 or *A*2/*m*. Solution and refinement of the structure showed *A*2/*m* to be the correct choice. MULTAN and difference Fourier techniques were used to locate all non-hydrogen atoms. All non-hydrogen atoms except the toluene carbon atoms were refined with anisotropic temperature factors with full-matrix least-squares methods. The toluene carbon atoms were refined isotropically and no hydrogen atoms were located. Atomic scattering factors were taken from ref 15. A final difference map contained no recognizable features; its largest peak was of height 1.20 eA^{-3}. Fractional coordinates are given in Table VII.

$[(C_5Me_5)_2Sm]_2[N_2(C_6H_4Me\text{-}3)_2]$ (6). 3,3′-Azotoluene (31 mg, 0.15 mmol) was added to $(C_5Me_5)_2Sm(THF)_2$ (167 mg, 0.30 mmol) in toluene in a manner identical with the synthesis of **2**. **6** (146 mg, 94%) was isolated as a dark-blue powder with use of the same procedure used to isolate **2**. ^{1}H NMR (C_6D_6) 6.78 (d, $C_6\mathit{H}^5{}_4Me$), 2.22 (d, $C_6\mathit{H}^4{}_4Me$) 1.43 (s, C_5Me_5), --4.09 (s, $C_6H_4C\mathit{H}_3$). The H-2 and H-6 resonances were not located presumably due to their proximity to the paramagnetic metal center. ^{13}C NMR (C_6D_6) 181.17 (s, $\mathit{C}^1{}_6H_4Me$), 139.96 (s, $\mathit{C}^3{}_6H_4Me$), 126–129 ($\mathit{C}^{4-6}{}_6H_4Me$, partially obscured by C_6D_6 peaks), 119.65 (s, C_5Me_5), 98.52 (d, $\mathit{C}^2{}_6H_4Me$), 23.11 (s, $C_5\mathit{Me}_5$), 14.03 (s, $C_6H_4\mathit{C}H_3$).

$[(C_5Me_5)_2Sm]_2[(3\text{-}MeC_6H_4N)OCCO(NC_6H_4Me\text{-}3)]$ (7). In a manner identical with the preparation of **5**, $[(C_5Me_5)_2Sm]_2[N_2(C_6H_4Me\text{-}3)_2]$ (340 mg, 0.32 mmol) was treated with 60 psi of CO for 12 h. **7** (351 mg, 98%) was isolated as a dark-green solid. ^{1}H NMR (C_6D_6) 6.2–8.0 (m, $C_6\mathit{H}_4Me$), 1.96 (s, C_5Me_5), −1.81 (s, $C_6H_4C\mathit{H}_3$).

Reaction of 2 and 6 with CO. Equimolar quantities of **2** and **6** (0.037 mmol) were dissolved in THF and placed in a Fischer-Porter aerosol vessel as described in the synthesis of **5**. The vessel was pressurized with CO to 60 psi. After 18 h, the solvent was removed to give the expected dark green solid. ^{1}H NMR (C_6D_6) 1.92 (s, C_5Me_5 of **5**), 1.96 (s, C_5Me_5 of **7**). No other resonances were found in the C_5Me_5 region. Mass spectroscopy (EI): 1107 (parent ion for **7**), 1080 (parent ion for **5**), 972 (parent − C_5Me_5 for **7**), 943 (parent − C_5Me_5 for **5**). No evidence for the presence of $[(C_5Me_5)_2Sm]_2[(C_6H_5N)OCCO(NC_6H_4Me\text{-}3)]$ was found.

$[(C_5Me_5)_2Sm]_2(C_6H_5NNC_6H_4NMe_2\text{-}4)$ (8). In a manner identical with the preparation of **2** and **6**, a toluene solution of methyl yellow, $C_6H_5N{=}NC_6H_4NMe_2\text{-}4$ (41.8 mg, 0.186 mmol), was added dropwise to $(C_5Me_5)_2Sm(THF)_2$ (210 mg, 0.372 mmol) in toluene. The purple solution immediately turned dark green. After 5 min, the solution was evaporated to dryness leaving the product as a dark-green solid (188 mg, 95%). ^{1}H NMR (C_6D_6) 2.38 (t, $C_6H^4{}_5$), 1.421, 1.402 (C_5Me_5), −1.034 ($C_6H_4N\mathit{Me}_2$), −6.85 (d, $C_6H^{3,5}{}_5$), −7.19 (d, $C_6\mathit{H}^{3,5}{}_4NMe_2$). ^{13}C NMR ($C_6D_6$) 180.92 ($\mathit{C}^1{}_6H_5$), 178.57 ($\mathit{C}^1{}_6H_4NMe_2$), 125.9–130.9 (other ring carbons obscured by C_6D_6 peaks), 119.13 (C_5Me_5), 118.79 (C_5Me_5), 36.6 ($C_6H_4N\mathit{Me}_2$), 23.01 ($C_5\mathit{Me}_5$), 22.94 ($C_5\mathit{Me}_5$).

$[(C_5Me_5)_2Sm]_2[(C_6H_5N)OCCO(NC_6H_4NMe_2\text{-}4)]$ (9). Following the procedure used to prepare **5** and **7**, **8** (188 mg, 0.176 mmol) was treated with 60 psi of CO in toluene. A quantitative yield (198 mg) of dark brown **9** was obtained. ^{1}H NMR (C_6D_6) 2.335 (NMe_2), 2.015 (s, C_5Me_5), 1.997 (s, C_5Me_5). No evidence for the presence of **5** was found.

Reaction of 2 and 8 with CO. Equimolar quantities of **2** and **8** (0.039 mmol) were treated with 60 psi of CO as in the preparation of **5**, **7**, and **9**. The product mixture was brown after solvent removal. The ^{1}H NMR spectrum contained resonances for **5** and **9** only. The mass spectrum of this product contained peaks consistent only with **5** and **9**. No evidence for $[(C_5Me_5)_2Sm]_2[(4\text{-}Me_2NC_6H_4N)OCCO(NC_6H_4NMe_2\text{-}4)]$ was found.

Results

Synthesis and Properties of $[(C_5Me_5)_2Sm]_n(N_2Ph_2)$ Complexes (n = 1, 2). The addition of a solution of azobenzene to a purple toluene solution of $(C_5Me_5)_2Sm(THF)_2$ results in the immediate

Table IV. Crystal Data for $[(C_5Me_5)(THF)Sm]_2(N_2Ph_2)_2$ (**3**), $[(C_5H_5)(THF)Yb]_2(N_2Ph_2)_2$ (**4**), and $[(C_5Me_5)_2Sm]_2[(PhN)OCCO(NPh)]$ (**5**)

compound	**3**·(2THF)	**4**·(C_7H_8)	**5**·($2C_7H_8$)
formula	$Sm_2C_{60}H_{82}N_4O_4$	$Yb_2C_{49}H_{54}N_4O_2$	$Sm_2C_{68}H_{86}N_2O_2$
mol wt	1224.05	1077.08	1264.14
space group	$C2/m$	$P\bar{1}$	$A2/m$
cell constants			
a, Å	22.409 (8)	9.645 (2)	15.961 (3)
b, Å	13.178 (5)	11.369 (3)	14.204 (5)
c, Å	9.978 (4)	10.143 (5)	15.612 (8)
α, deg		97.33 (3)	
β, deg	108.84 (5)	94.36 (3)	118.14 (3)
γ, deg		93.18 (2)	
cell vol, $Å^3$	2789	1097	3121
molecules/unit cell	2	1	2
ρ(calcd), g cm^{-3}	1.46	1.62	1.25
μ(calcd), cm^{-1}	21.8	42.7	20.3
radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
max crystal dimens, mm	0.15 × 0.40 × 0.20	0.09 × 0.17 × 0.20	0.15 × 0.22 × 0.14
scan width, deg	0.80 + 0.20 tan θ	-1.2 in 2θ from $K\alpha_1$ to +1.2 from $K\alpha_2$	-1.2 in 2θ from $K\alpha_1$ to +1.2 from $K\alpha_2$
std reflctns	400, 020, 004	-210, 1-31, 042	20-2, 1-40, -5-13
decay of stds, %	±2	8	±3
reflctns measd	1674	3877	3907
2θ range, deg	2-42	4-50	4-50
obsd reflctns	1278	3239	2151
no. of parameters varied	184	253	165
GOF	0.93	1.20	1.74
R	0.038	0.030	0.053
R_w	0.044	0.040	0.065

Table V. Atomic Positional Parameters for $[(C_5Me_5)(THF)Sm]_2[N_2Ph_2]_2{\cdot}2THF$

atom	x/a	y/b	z/c
Sm	-0.08043 (3)	0.0000	0.40457 (8)
N	0.0006 (3)	0.1178 (6)	0.5724 (7)
O(1)	-0.1464 (4)	0.0000	0.570 (1)
O(2)	0.3703 (8)	0.0000	0.261 (2)
C(1)	-0.0318 (4)	0.1965 (7)	0.6116 (9)
C(2)	-0.0297 (5)	0.2059 (9)	0.752 (1)
C(3)	-0.0616 (5)	0.278 (1)	0.796 (1)
C(4)	-0.0984 (6)	0.349 (1)	0.702 (1)
C(5)	-0.1024 (5)	0.0341 (1)	0.563 (1)
C(6)	-0.0695 (4)	0.2664 (8)	0.516 (1)
C(7)	-0.1221 (6)	0.0000	0.112 (1)
C(8)	-0.1503 (5)	-0.0873 (9)	0.149 (1)
C(9)	-0.1944 (4)	-0.0543 (9)	0.213 (1)
C(10)	-0.0759 (8)	0.0000	0.033 (1)
C(11)	-0.1408 (5)	-0.1951 (9)	0.116 (1)
C(12)	-0.2379 (5)	-0.126 (1)	0.255 (1)
C(13)	-0.1681 (9)	0.085 (1)	0.625 (2)
C(14)	-0.223 (1)	0.055 (2)	0.669 (4)
C(15)	0.3363 (9)	0.0000	0.123 (2)
C(16)	0.379 (1)	0.0000	0.041 (2)
C(17)	0.441 (1)	0.0000	0.145 (4)
C(18)	0.436 (1)	0.0000	0.283 (3)

formation of a blue solution. If only 1 mol of azobenzene is added per 2 mol of $(C_5Me_5)_2Sm(THF)_2$, this blue color persists and a dark-blue product, **2**, can be isolated in 80% yield according to eq 4 ($Cp^5 = C_5Me_5$; $Ph = C_6H_5$). If more azobenzene is added,

$$2Cp^5_2Sm(THF)_2 + PhN{=}NPh \rightarrow \underset{\mathbf{2}}{(Cp^5_2Sm)_2N_2Ph_2} + 4THF \qquad (4)$$

the solution turns green and a new product, **1**, is formed according to eq 5. This green product, **1**, which can be obtained in approximately 90% yield via eq 5, can also be synthesized by adding $(C_5Me_5)_2Sm(THF)_2$ directly to an azobenzene solution in a 1:1 ratio. By using this reverse order of addition, a 90% yield of the green product can be obtained according to eq 6. The addition of excess $(C_5Me_5)_2Sm(THF)_2$ to **1** will generate **2**, but only in about 50% yield (eq 7). Due to the interconversions shown in eq 5 and 7, traces of **1** will be present in preparations of **2** and vice versa if the reagent stoichiometries are not exact. Since **1** has greater solubility in hexane than **2**, it can be readily separated by hexane extraction. Both **1** and **2** have been characterized by analytical and spectroscopic methods and by X-ray crystallography as described in the following paragraphs.

$$(Cp^5_2Sm)_2N_2Ph_2 + PhN{=}NPh \rightarrow \underset{\mathbf{1}}{2Cp^5_2SmN_2Ph_2} \qquad (5)$$

$$Cp^5_2Sm(THF)_2 + PhN{=}NPh \rightarrow Cp^5_2SmN_2Ph_2 + 2THF \qquad (6)$$

Table VI. Atomic Positional Parameters for $[(C_5H_5)(THF)Yb]_2(N_2Ph_2)_2{\cdot}C_7H_8$

atom	x	y	z
Yb(01)	0.40097 (3)	0.11387 (2)	0.01671 (2)
N(01)	0.4055 (5)	-0.0779 (5)	-0.1308 (4)
N(02)	0.3395 (5)	-0.0762 (5)	-0.0047 (5)
O(01)	0.3892 (5)	0.2091 (4)	-0.1774 (5)
C(01)	0.3177 (6)	-0.0863 (5)	-0.2480 (6)
C(02)	0.3794 (7)	-0.0870 (7)	-0.3690 (6)
C(03)	0.2972 (8)	-0.0934 (7)	-0.4880 (7)
C(04)	0.1568 (9)	-0.0967 (7)	-0.4905 (6)
C(05)	0.0929 (7)	-0.0968 (7)	-0.3725 (7)
C(06)	0.1728 (6)	-0.0930 (6)	-0.2518 (6)
C(07)	0.2696 (6)	-0.1820 (5)	0.0207 (6)
C(08)	0.2664 (7)	-0.2896 (6)	-0.0651 (6)
C(09)	0.2011 (9)	-0.3920 (6)	-0.0303 (8)
C(10)	0.1377 (8)	-0.3896 (7)	0.0883 (8)
C(11)	0.1388 (7)	-0.2838 (7)	0.1697 (7)
C(12)	0.2014 (7)	-0.1806 (6)	0.1370 (6)
C(13)	0.3186 (12)	0.3204 (9)	0.1266 (10)
C(14)	0.3634 (9)	0.2605 (7)	0.2331 (8)
C(15)	0.2745 (8)	0.1585 (8)	0.2327 (8)
C(16)	0.1691 (8)	0.1587 (11)	0.1267 (11)
C(17)	0.1982 (12)	0.2585 (13)	0.0628 (10)
C(18)	0.4767 (11)	0.3048 (14)	-0.2053 (13)
C(19)	0.4173 (16)	0.3547 (16)	-0.3147 (16)
C(20)	0.2801 (20)	0.2886 (17)	-0.3496 (17)
C(21)	0.2683 (12)	0.2005 (10)	-0.2715 (10)
C(22)	0.1579 (21)	0.5281 (12)	0.4633 (16)
C(23)	0.0845 (26)	0.5863 (11)	0.5763 (19)
C(24)	-0.0551 (27)	0.5581 (15)	0.6068 (14)

$$\underset{\mathbf{1}}{Cp^5_2Sm(N_2Ph_2)(THF)} + Cp^5_2Sm(THF)_2 \rightarrow \underset{\mathbf{2}}{[Cp^5_2Sm]_2N_2Ph_2} + 3THF \qquad (7)$$

Although the green and blue colors of **1** and **2** are more characteristic of Sm(II) complexes than of Sm(III) species,[25]

Table VII. Atomic Positional Parameters for $[(C_5Me_5)_2Sm]_2[(PhN)COCO(NPh)]\cdot 2C_7H_8$

atom	x	y	z
Sm(01)	0.29333 (4)	0.0000	0.32113 (4)
O(01)	0.3841 (5)	0.0000	0.4874 (5)
N(01)	0.5331 (6)	0.0000	0.6251 (5)
C(01)	0.4740 (7)	0.0000	0.5320 (7)
C(02)	0.5002 (7)	0.0000	0.6962 (7)
C(03)	0.4057 (9)	0.0000	0.6764 (9)
C(04)	0.3869 (11)	0.0000	0.7573 (10)
C(05)	0.4563 (11)	0.0000	0.8505 (9)
C(06)	0.5480 (11)	0.0000	0.8686 (9)
C(07)	0.5722 (10)	0.0000	0.7922 (9)
C(08)	0.2888 (8)	0.1852 (8)	0.3610 (9)
C(09)	0.3031 (8)	0.1837 (8)	0.2773 (11)
C(10)	0.2181 (9)	0.1491 (10)	0.2007 (8)
C(11)	0.1550 (7)	0.1323 (8)	0.2352 (9)
C(12)	0.1988 (8)	0.1513 (8)	0.3346 (9)
C(13)	0.3590 (11)	0.2238 (11)	0.4593 (12)
C(14)	0.3921 (12)	0.2258 (12)	0.2762 (18)
C(15)	0.1965 (18)	0.1455 (16)	0.0916 (10)
C(16)	0.0481 (8)	0.1121 (12)	0.1669 (15)
C(17)	0.1539 (13)	0.1465 (12)	0.3995 (12)
C(18)	0.1948 (21)	0.0000	0.8638 (21)
C(19)	0.1674 (13)	0.0789 (13)	0.7812 (13)
C(20)	0.1310 (14)	0.0755 (15)	0.6793 (15)
C(21)	0.1072 (30)	0.0000	0.6067 (31)

magnetic, spectral, and structural data suggest that the metals are in the trivalent oxidation state. The room temperature magnetic moments of **1** and **2**, 2.2 and 1.9 μ_B, respectively, are closer to the range observed for Sm(III) organometallic complexes, 1.3–2.1 μ_B, than for Sm(II) complexes, 3.5–3.8 μ_B.[26] In the ^{13}C NMR spectra, the C_5Me_5 ring carbons are found at low field and the C_5Me_5 methyl carbons are located at high field as is characteristic of Sm(III) complexes and not Sm(II) species.[9] As discussed below, Sm–C(C_5Me_5) distances are also in the Sm(III) not Sm(II) range. These data indicate that one electron has been transferred to azobenzene in forming complex **1** and two electrons have been transferred in the formation of complex **2**. It is possible that the colors of **1** and **2** arise from the reduced azobenzene moieties. Before the structural consequences of these reductions are discussed, the synthesis of yet another type of organolanthanide azobenzene derivative which forms in this system is presented.

Synthesis and Properties of the Monocyclopentadienyl Azobenzene Derivatives $[(C_5Me_5)(THF)Sm]_2[N_2Ph_2]_2$ and $[(C_5H_5)(THF)Yb]_2[N_2Ph_2]_2$. When $[(C_5Me_5)_2Sm]_2N_2Ph_2$ is dissolved in THF a brown-green solution results, which after several days deposits orange crystalline material. This species has been isolated in low yield, characterized by analytical and spectroscopic means, and identified by X-ray crystallography as the mono-C_5Me_5 species $[(C_5Me_5)(THF)Sm]_2[N_2Ph_2]_2$ (**3**).

Loss of a C_5Me_5 ring from a $(C_5Me_5)_2Sm$ unit is a rather unusual result, although ligand redistribution reactions, such as the formation of $[(C_5Me_5)(THF)_2Sm(\mu\text{-}I)]_2$ from $(C_5Me_5)_2Sm(THF)_2$ and $SmI_2(THF)_2$, are known.[9] Ligand redistribution presumably occurs in the formation of **3** and a possible reaction stoichiometry is shown in eq 8. We have not been able to definitively identify the other product(s) of this reaction. Some $(C_5Me_5)_2Sm(N_2Ph_2)$ has been observed by ^1H NMR spectroscopy in the green solution which remains, but the main product appears to be one with a ^1H NMR resonance at 1.25 ppm. In THF, **1** will also slowly form the product with the 1.25 ppm ^1H NMR resonance. Note that one stoichiometrically logical product,

$$\underset{\textbf{2}}{2[Cp^5{}_2Sm]_2N_2Ph_2} \xrightarrow{\text{THF}} \underset{\textbf{3},\ \text{orange}}{[Cp^5(THF)Sm]_2[N_2Ph_2]_2} + 6C_5Me_5^- + 2Sm^{3+} \quad (8)$$

$(C_5Me_5)_3Sm$, is predicted to be too sterically crowded to exist.[27,28]

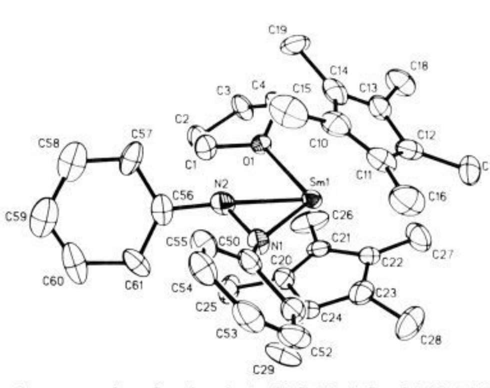

Figure 1. ORTEP plot of molecule 1 of $(C_5Me_5)_2Sm(N_2Ph_2)(THF)$ (**1**).

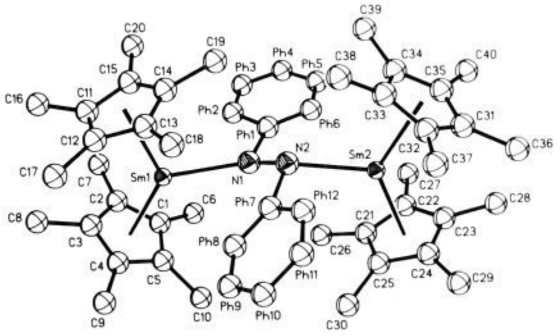

Figure 2. Molecular diagram of $[(C_5Me_5)_2Sm]_2(N_2Ph_2)$ (**2**).

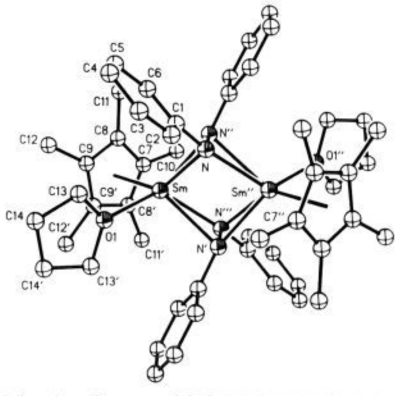

Figure 3. Molecular diagram of $[(C_5Me_5)(THF)Sm]_2[N_2Ph_2]_2$ (**3**).

The orange color of $[(C_5Me_5)(THF)Sm]_2[N_2Ph_2]_2$ is more characteristic of Sm^{3+} than the colors of **1** or **2**. Its ^{13}C NMR data as well as its Sm–C(C_5Me_5) distances are also normal for an organometallic Sm(III) complex.

To obtain ancillary data on the samarium azobenzene system and to determine if related chemistry could occur with a simple C_5H_5 (instead of C_5Me_5) complex, we examined the reaction of $(C_5H_5)_2Yb(THF)$[10,29] with azobenzene. The ytterbium complex was a reasonable choice because the samarium analogue, $[(C_5H_5)_2Sm(THF)]_n$, is insoluble.[30] In THF and in toluene, $(C_5H_5)_2Yb(THF)$ reacts immediately with azobenzene to form a green solution. Crystallization of these solutions gives a mixture of $(C_5H_5)_3Yb(THF)$ and $[(C_5H_5)(THF)Yb]_2[N_2Ph_2]_2$ (**4**), both identified by X-ray analysis of single crystals. Hence, in this

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Table VIII. Selected Bond Lengths (Å) in $Cp^5{}_2Sm(N_2Ph_2)(THF)$ (**1**), $[Cp^5{}_2Sm]_2(N_2Ph_2)$ (**2**), $[Cp^5(THF)Sm]_2[N_2Ph_2]_2$ (**3**), and $[(C_5H_5)(THF)Yb]_2[N_2Ph_2]_2$ (**4**) ($Cp^5 = C_5Me_5$; $Ph = C_6H_5$)[a]

	1	**2**	**3**	**4**
Ln-C(C_5R_5)				
av	2.76 (2)	2.74 (3)	2.76 (1)	2.63 (2)
range	2.720 (16)-2.841 (15)	2.68 (1)-2.77 (1)	2.747 (9)-2.77 (1)	2.596 (7)-2.655 (9)
Ln-O(THF)	2.532 (8) (1-1)[a] 2.557 (9) (2-2)		2.543 (9)	2.363 (5)
Ln-N	2.390 (10) (1-1) 2.426 (12) (1-2) 2.402 (11) (2-3) 2.450 (10) (2-4)	2.40 (1) (1-1) 2.41 (1) (2-2)	2.323 (8) 2.559 (7)	2.206 (5) (1-1′) 2.188 (5) (1-2) 2.487 (5) (1-1′) 2.572 (5) (1-2′)
N-N	1.388 (15) (1-2) 1.323 (14) (3-4)	1.25 (1)	1.44 (1)	1.470 (6)
Ln-Ln			3.491 (2)	3.301 (3)
N-C(Ph)	1.375 (17) (1-50) 1.448 (18) (2-56) 1.413 (16) (3-62) 1.406 (16) (4-68)	1.56 (2) (1-1) 1.61 (1) (2-7)	1.39 (1)	1.396 (7) (1-1) 1.408 (7) (2-7)
C(Ph)-C(Ph) av	1.40 (5)	1.36 (2)	1.38 (2)	1.39 (1)

[a] The two numbers connected by a hyphen following some of the distances give the numbers of the atoms involved. For example, 2.532 (8) (1-1) means the Sm(1)-O(1) distance in **1** is 2.532 (8) Å.

Table IX. Selected Bond Angles (deg) for **1-4**[a]

	1	**2**	**3**	**4**
(C_5R_5 centroid)-Ln-(C_5R_5 centroid)	135.9 137.6	133 (1)		
N-Ln-N N atoms in same N_2Ph_2	33.5 (4) (1-1-2) 31.6 (3) (3-2-4)		33.8 (3)	35.9 (3) (1-1-2) 34.8 (3) (1′-1-2′)
N-Ln-N N atoms in different N_2Ph_2			74.7 (3) (1-1-1′) 88.8 (3) (1-1-1‴)	90.8 (3) (1-1-1′) 92.6 (3) (2-1-2′) 74.6 (3) (1-1-2′) 88.5 (2) (2-1-1′)
Ln-N-C(Ph)	152.2 (9) (1-1-50) 158.2 (9) (1-2-56) 156.7 (10) (2-3-62) 154.7 (9) (2-4-68)	120.7 (7) (1-1-1) 98.3 (5) (2-2-7)	108.1 (5)	152.5 (4) (1-1-1) 158.2 (4) (1-2-7)
C(Ph)-N-N	122.7 (12) (50-1-2) 119.7 (11) (56-2-1) 122.3 (10) (62-3-4) 124.6 (11) (68-4-3)	97 (1) (1-1-2) 97 (1) (7-2-1)	116.1 (9)	117.9 (5) (7-2-1) 117.3 (4) (1-1-2)
N-N-Ln	71.8 (6) (1-2-1) 74.7 (6) (2-1-1) 76.1 (7) (3-4-2) 72.1 (6) (4-3-2)	139 (1) (2-1-1) 154.1 (9) (1-2-2)	82.2 (5) (1-1″-1) 64.1 (5) (1″-1-1)	86.4 (3) (2′-1′-1) 83.2 (3) (1-2-1) 60.9 (3) (2-1-1) 58.8 (3) (1′-2′-1)
N-C(Ph)-C(Ph)	12.4 (14) (1-50-51) 289 (14) (1-50-55) 147 (15) (2-56-57) 122.4 (16) (2-56-61) 116.8 (12) (3-62-63) 122.5 (12) (3-62-67) 116.5 (12) (4-68-69) 124.1 (13) (4-68-73)	113 (1) (1-1-2) 133 (1) (1-1-6) 132.7 (9) (2-7-8) 110.6 (8) (2-7-12)	119.8 (9) (1-1-2) 123.6 (8) (1-1-6)	123.9 (5) (1-1-6) 117.9 (5) (1-1-2) 123.2 (5) (2-7-8) 118.6 (6) (2-7-12)

[a] The three numbers connected by hyphens following some of the angles give the numbers of the atoms involved.

ytterbium case, the isolated products are consistent with reactions which parallel eq 6 and 8 as shown in eq 9 and 10 ($Cp = C_5H_5$). In the $(C_5H_5)_2Yb$ system, no evidence for analogues of **1** and **2**

$$Cp_2Yb(THF) + PhN{=}NPh \rightarrow \text{“}(Cp_2Yb)_2(N_2Ph_2)\text{” not observed} + THF \quad (9)$$

$$2\text{“}(Cp_2Yb)_2(N_2Ph_2)\text{”} + 4THF \rightarrow [Cp(THF)Yb]_2[N_2Ph_2]_2 + 2Cp_3Yb(THF) \quad (10)$$

were found, although under the appropriate conditions they may be isolable.

X-ray Crystal Structures of 1-4. ORTEP diagrams of the crystal structures of **1-4** are given in Figures 1-4, respectively. Tables VIII and IX give selected bond length and bond angle data, respectively, on **1-4**. Complete tables of these data are given in the supplementary material.

$(C_5Me_5)_2Sm(N_2Ph_2)(THF)$ crystallizes from hexane/THF with two crystallographically independent molecules in each asymmetric unit. The interatomic distances and angles in both molecules of **1** are rather similar and averages can often be used in the discussion. One main difference in the two is the relative orientation of the phenyl rings. One molecule has a 70.8° dihedral angle

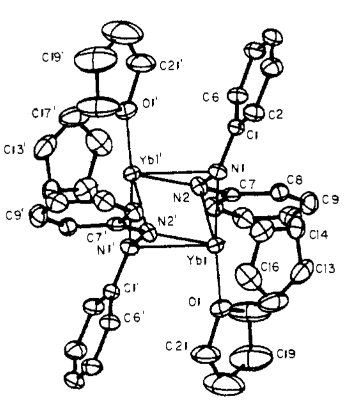

Figure 4. ORTEP plot of $[(C_5H_5)(THF)Yb]_2[N_2Ph_2]_2$ (**4**).

between the planes defined by the phenyl rings. The analogous angle in the other molecule is 63.1°. The $(C_5Me_5)_2Sm$ unit in **1** is attached to the η^2-N_2Ph_2 ligand and THF in the manner typical of bent metallocenes with three additional ligands.[31] The plane defined by the Ph_2N_2 nitrogen atoms, the metal, and the THF oxygen atom forms an average angle of 90.4° with the plane defined by the C_5Me_5 ring centroids and samarium. The samarium atom is formally nine coordinate. This coordination number is not as common as eight for trivalent $(C_5Me_5)_2Sm$ systems, but it has been observed in a few structures.[3,28,32] Consistent with the higher coordination number, the average Sm–C(ring) distance of 2.76 (2) Å is on the long end of the 2.68–2.77 Å range observed in trivalent $(C_5Me_5)_2Sm$ complexes.[28] The average Sm–O(THF) distance, 2.544 (8) Å, is also slightly longer than those in previously reported $(C_5Me_5)_2Sm(THF)(X)$ complexes (X = Cl, I, C_6H_5), 2.44 (2)–2.511 (4) Å.[33]

Upon reaction with $(C_5Me_5)_2Sm(THF)_2$, the N_2Ph_2 unit has changed shape considerably compared to free azobenzene. The phenyl rings are no longer trans and coplanar, but now they have a cis orientation with dihedral angles of 70.8° and 63.1° (in the two crystallographically independent molecules). In addition, the nitrogen atoms no longer lie in a plane defined by the two phenyl rings. In molecule 1 in Figure 1, N(1) lies 0.21 Å above and N(2) lies 0.21 Å below the plane defined by Sm(1), C(50), and C(56). In the other molecule of **1**, one nitrogen is 0.12 Å above the analogous plane and the other is 0.20 Å below.

The N–N bond distances in **1**, 1.32 (1) and 1.39 (2) Å, are intermediate between the 1.25 Å NN double bond distance typical of azobenzenes[34] and the 1.45 Å sp^3–sp^3 NN single bond distance typical of hydrazine.[34] The average N–C(Ph) distance of 1.41 (2) Å is the same as the 1.433-Å distance in *trans*-azobenzene.[35]

The Sm–N distances in **1** range from 2.390 (10) to 2.450 (10) Å and average 2.42 (2) Å. The closest structurally related system for comparison with these Sm–N distances is $(C_5Me_5)_2YN(SiMe_3)_2$,[36] which has Y–N distances of 2.253 (5) and 2.274 (5) Å. Addition of 0.06[37]–0.084[38] Å to accommodate the smaller radius of Y^{3+} compared to Sm^{3+} would give a range for an expected Sm^{3+}–NR_2 single bond of 2.31–2.35 Å. However, the Y–N distances in $(C_5Me_5)_2YN(SiMe_3)_2$ were thought to be unusually short due to a dative π-interaction between the lone pair of electrons on nitrogen and the yttrium metal. Comparisons with Y–N distances in the bridged dihapto formimidoyl complex $[(C_5H_5)_2Y(\mu\text{-}\eta^2\text{-}HCNCMe_3)]_2$[39] (Y–N = 2.325(4) Å), the bridged alkylideneamido complex $[(C_5H_5)_2Y(\mu\text{-}N{=}CHCMe_3)]_2$[40] (Y–N = 2.314 (9) and 2.382 (9) Å), and the three-coordinate $Eu[N(SiMe_3)_2]_3$[41] (Eu–N = 2.259 Å) are not as straightforward due to the differences in bonding and coordination number in these systems. These data do suggest that the Sm–N distances in **1** are slightly longer than expected for a simple Sm–NR_2 single bond.

The Sm–N distances in **1** are clearly shorter than typical $R_3N{:}\rightarrow Ln$ donor bond distances. The range expected for a $R_3N{:}\rightarrow Sm^{3+}$ bond based on a recent survey of seven $R_3N{:}\rightarrow Ln^{3+}$ distances (adjusted for differences in radii) is 2.53–2.77 Å.[39] The 2.539 (14) Å Sm–N distance in $(C_5Me_5)_2SmI(tetrazole)$ is a typical example.[33]

The structure of **1** is similar to that of $(C_5H_5)_2TiN_2Ph_2$ (**10**)[42] except for the absence of the THF of solvation in the titanium complex. In the diamagnetic **10**, the 1.339 (8) N–N distance, the 1.395 (10) average N–C distance, and the orientation of the phenyl rings are similar to those in **1**. In both **1** and **10**, electron density has been transferred to the N_2Ph_2 unit.

The structure of **1** is consistent with the spectroscopic and magnetic data given above. In this complex, a Sm^{3+} center is interacting with a $N_2Ph_2^-$ anion. The Sm–N interactions are somewhat longer than that expected from a simple Sm–NR_2 single bond and they are much shorter than that expected for a $Sm\leftarrow{:}NR_3$ donor bond. Considerable delocalization must be present in the ligand.

It is best to describe the structure of $[(C_5Me_5)(THF)Sm]_2(N_2Ph_2)_2$ (**3**) next. As shown in Figure 3, this highly symmetric structure has a mirror plane which contains Sm, O(1), C(7) and C(10), as well as a perpendicular C_2 axis which bisects the N–N″ and Sm–Sm″ vectors. The four nitrogen atoms are coplanar and this plane makes a 77° angle with the Sm–Sm″ vector. Each samarium atom is formally eight coordinate and the Sm–C(C_5Me_5) average distance 2.76 (1) Å and Sm–O(THF) distance 2.543 (9) Å are in the range observed for Sm^{3+} complexes. Both of these values are similar to those for **1** and are on the high end of the observed range.

The N–N″ distance in **3**, 1.44 (1) Å, is considerably longer than that in **1** and is in the N–N single bond range. The dihedral angle between the planes of the phenyl rings is 76°, and the angles around each nitrogen atom are consistent with an sp^3 center. These data suggest the presence of a $N_2Ph_2^{2-}$ ligand.

There are two distinct Sm–N distances in **3**. The Sm–N″ distance of 2.323 (8) Å is in the range expected for a Sm^{3+}–NR_2 single bond on the basis of the data presented above. The Sm–N distance of 2.559 (7) Å is in the range of a $Sm^{3+}\leftarrow{:}NR_3$ donor bond (see above). Each samarium atom is involved in two single bonds (one to each N_2Ph_2 unit) and two donor bonds (one to each N_2Ph_2 unit). Each N_2Ph_2 ligand is involved in two single bonds (to two different Sm atoms) and two donor bonds (to two different Sm atoms). Hence, this structure contains two fully reduced $N_2Ph_2^{2-}$ ligands, each complexed to two Sm^{3+} ions.

An unusual feature in the structure of **3** is that the Sm atoms are close: Sm–Sm″ = 3.491 (2) Å. This is the closest Sm⋯Sm distance yet observed in any crystallographically characterized organosamarium complex and is 0.4 Å shorter than the closest previous distance of 3.9 Å in $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$.[5]

The structure of $[(C_5H_5)(THF)Yb]_2(N_2Ph_2)_2$ (**4**), shown in Figure 4, is similar to that of **3** in many respects. The overall geometry is the same and the ligand parameters are similar. Hence, each N_2Ph_2 ligand binds to two metal centers as in **3**, the four nitrogen atoms define a plane which forms a 71.1° angle with the Yb(1)–Yb(1)′ vector, the 1.470 (6) Å N(1)–N(2) bond is again in the single bond range, there is a significant dihedral angle between the planes of the phenyl rings, 45.7°, and the angles around each nitrogen atom are those of an sp^3 center. Complex **4** is less symmetric than **3** and has only an inversion center between the ytterbium atoms rather than a mirror plane and a C_2 axis. As a result, there are four distinct metal–nitrogen distances instead of the two in **3**. However, these distances are similar in that the four Yb–N distances fall into two sets, one set consistent with an Yb–NR_2 single bond and one set consistent with an $Yb\leftarrow NR_3$ donor bond. As in **3**, each N_2Ph_2 unit forms one short and one long Yb–N interaction with a given ytterbium atom.

It was expected that the ytterbium ligand distances in **4** would be shorter than those in **3** due to the smaller size of the metal. However, several of these distances are much shorter than the difference in ionic radii of 0.094[37]–0.106[38] Å. Compared to **3**, the Yb–C(C_5H_5) average distance of 2.635 (5) Å is 0.125 Å shorter, the Yb–O(THF) distance of 2.363 (5) Å is 0.177 Å

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shorter, and the single bond Yb–N distances of 2.188 (5) and 2.206 (5) Å are 0.127–0.145 Å shorter. One of the Yb$\leftarrow$:N donor bond distances, 2.487 (5) Å, is in the range expected based on radial size differences. The other donor bond length, 2.572 (5) Å, is longer than expected! These deviations from values expected by comparing ionic radii may occur in part due to the difference in substitution of the cyclopentadienyl rings.

Like **3**, the arrangement of ligands in **4** brings the two metal centers much closer together, 3.301 (3) Å, than is typical for late lanthanide dimers (Ln–Ln distances are usually 3.5–3.7 Å).[43,44]

The last structure to be considered in this series is that of $[(C_5Me_5)_2Sm]_2N_2Ph_2$ (**2**). Considering the magnetic data, which indicated that Sm^{3+} was present, and the synthetic route to **2**, which involved a further reduction of the $N_2Ph_2^-$ ligand in **1** with an additional mole of $(C_5Me_5)_2Sm(THF)_2$, complex **2** could reasonably be expected to contain an $N_2Ph_2^{2-}$ ligand as was found in **3** and **4**. This is not the result which was determined by X-ray crystallography. Instead, a structure unusual in several respects is found.

As shown in Figure 2, each samarium atom appears to be seven coordinate, an unusual coordination number for trivalent $(C_5Me_5)_2Sm$ systems unless a very bulky ligand is present.[4,45,46] The Sm–C(C_5Me_5) average distance, 2.74 (3) Å, is in the normal range for trivalent $(C_5Me_5)_2Sm$ complexes. The Sm–N lengths of 2.40 (1) and 2.41 (1) Å are close to those in **1**, i.e., they are somewhat longer than the simple Sm–NR_2 single bonds in **3** and they are much shorter than a typical $Sm^{3+}\leftarrow:NR_3$ donor bond.

The N–N distance is 1.25 (1) Å, a value almost identical with the 1.247-Å distance in *trans*-azobenzene.[35] This short N–N distance is consistent with a double bond between the nitrogen atoms with sp^2 hybridization at each nitrogen center. A perfectly sp^2 hybridized nitrogen atom would be coplanar with the three atoms to which it connects, i.e., the phenyl carbon, the samarium, and the other nitrogen atom. Within each set of such atoms N(1), N(2), Ph(1), and Sm(1) and N(1), N(2), Ph(7), and Sm(2) the atoms are roughly coplanar, but deviations as large as 0.18 Å are present.[47] The two planes are not coincident, however, and have a 10° dihedral angle between them.

Given the Sm–N and N=N bonding already discussed, it is perhaps not surprising that the N–C(Ph) bonds have lengthened. The 1.56 (2) and 1.61 (2) Å lengths are quite long compared to the normal 1.42 Å length found in azobenzene compounds and the 1.37–1.45 Å distances found in **1**, **3**, and **4**.

Another unusual aspect of this complex is the asymmetric arrangement of the $(C_5Me_5)_2Sm$ units. Both metallocene groups are closer to phenyl ring 7–12 than to ring 1–6 as is evident from the Sm(1)–N(1)–Ph(1) angle of 120.8° versus the Sm(2)–N(2)–Ph(7) angle of 98.4 (5)°. This arrangement brings Sm(1) to within 2.29 Å of the ortho hydrogen atom attached to Ph(8); Sm(2) is within 2.34 Å of the hydrogen on Ph(12). In contrast, Sm(1) is 2.70 Å away from the ortho hydrogen on Ph(2) and Sm(2) is 2.42 Å away from the ortho hydrogen in Ph(6). The angular relationship of the phenyl rings to the samarium centers also is such that the hydrogen atoms are close to the metal.[48]

These samarium ortho hydrogen distances are within a few percent of the distance expected for a bridging Sm–H bond and within 15% of an expected terminal Sm–H bond distance.[49] Both of the short Sm–H distances are within the range cited as typical for agostic hydrogen interactions by Brookhart and Green.[50]

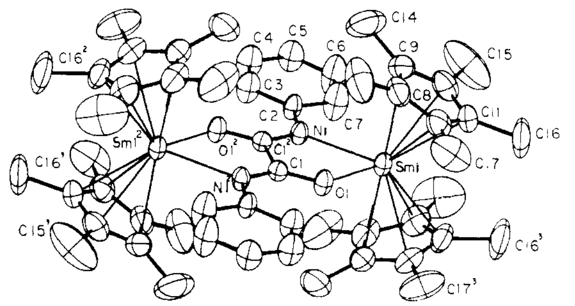

Figure 5. ORTEP plot of $[(C_5Me_5)_2Sm]_2[(PhN)OCCO(NPh)]$ (**5**).

Table X. Selected Bond Lengths (Å) and Angles (deg) for $[(C_5Me_5)_2Sm]_2[(PhN)OCCO(NPh)]$ (**5**)

Sm(01)–O(01)	2.30 (1)	O(01)–Sm(01)–N(01)	67.1 (2)
Sm(01)–N(01)	2.49 (1)	C(01)–O(01)–Sm(01)	124.6 (6)
Sm(01)–C(12)	2.69 (1)	C(01)–N(01)–C(02)	121.7 (8)
Sm(01)–C(10)	2.71 (1)	C(01)–N(01)–Sm(01)	118.7 (6)
Sm(01)–C(08)	2.71 (1)	C(02)–N(01)–Sm(01)	119.6 (6)
Sm(01)–C(09)	2.72 (1)	O(01)–C(01)–N(01)	130.4 (10)
Sm(01)–C(11)	2.72 (1)	O(01)–C(01)–C(01)	116.9 (10)
O(01)–C(01)	1.26 (1)	N(01)–C(01)–C(01)	112.7 (11)
N(01)–C(01)	1.31 (1)	N(01)–C(01)–N(01)	142.9 (7)
N(01)–C(02)	1.43 (1)	C(03)–C(02)–C(07)	119.8 (10)
C(01)–C(01²)	1.57 (2)	C(03)–C(02)–N(01)	125.7 (10)
		C(07)–C(02)–N(01)	114.5 (10)

Hence, although it appears that two Sm^{2+} ions have transferred one electron each to azobenzene in **2**, the result is not a simple PhÑ–ÑPh ion. The N–N bond has remained short, the N–C bonds are drastically stretched, and SmH(Ph) interactions exist. The electron density is much more delocalized in this system than in **3** or **4**.

Reactivity of 2 with CO. The crystal structure of **2** provides a reasonable paradigm for the intermediate $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$ (**11**) discussed in the introduction. The connectivity of the atoms in **2** is consistent with the possible structure for **11** shown in Scheme I, and the structure of **2** shows that this structure is sterically reasonable. Moreover, the close approach of the samarium atoms to ortho phenyl hydrogen atoms is consistent with the step in Scheme I in which the ortho CH bonds are activated by a carbene-like center near the metal.

Given the possible similarity between **2** and **11**, the reaction of **2** with CO was of great interest to see if it would parallel that of **11**. If the reaction proceeded in an analogous fashion it would generate a tetracyclic hydrocarbon containing two central nitrogen atoms. Complex **2** does react with CO and forms a product which has incorporated two CO molecules, i.e., the reaction has the same stoichiometry as the reaction of CO with **11** (eq 3). However, the reaction product, $[(C_5Me_5)_2Sm]_2O_2N_2C_{14}H_{10}$, is green not orange-brown like $[(C_5Me_5)_2Sm]_2O_2C_{16}H_{10}$ and it has a very different structure.

X-ray Crystal Structure of $[(C_5Me_5)_2Sm]_2[\mu$-η^4-(PhN)OCCO(NPh)] (5). As shown in Figure 5, the N=N bond in **2** has been completely cleaved in the CO reaction product, **5**. The CO molecules have been inserted into the N–N bond and coupled. Apparently, neither the long N–C(Ph) bonds nor the agostic phenyl hydrogen atoms have been sufficiently activated for a reaction with CO.

Bond distance and angle data for the rather symmetric **5** are given in Table X. The molecule has C_{2h} symmetry with the mirror

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(47) Deviations from planarity within each set in Å: set 1, Sm(1), –0.035; N(1), 0.13; Ph(1), –0.035; N(2), –0.059; set 2, Sm(2), 0.052; N(2), –0.178; Ph(7), 0.025; N(1), 0.102.

(48) Let M(1) be the midpoint of the vector between the centroids of the C_5Me_5 rings bonded to Sm(1) and let M(2) relate similarly to Sm(2). A torsional angle of ±180° (or 0°) would ideally be expected for a Sm–H bond. M(1)–Sm(1)–N(1)–H(48; on Ph 8) = –164°. M(1)–Sm(1)–N(1)–H(42; on Ph 2) = –22°. M(2)–Sm(2)–N(2)–H(52; on Ph 12) = –177°. M(2)–Sm(2)–N(2)–H(46; on Ph 6) = –22°.

(49) On the basis of the X-ray diffraction structure of $[(CH_3C_5H_4)_2Y(\mu$-$H)(THF)]_2$ (Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008–2014) and the neutron diffraction structure of $[(C_5Me_5)_2ThH(\mu$-$H)]_2$ (Broach, R. W.; Schultz, A. J.; Williams, J. M.; Brown, G. M.; Manriquez, J. M.; Fagan, P. J.; Marks, T. J. *Science (Washington, D.C.)* **1979**, *203*, 172–174) after correcting for the different radial sizes of the metals.

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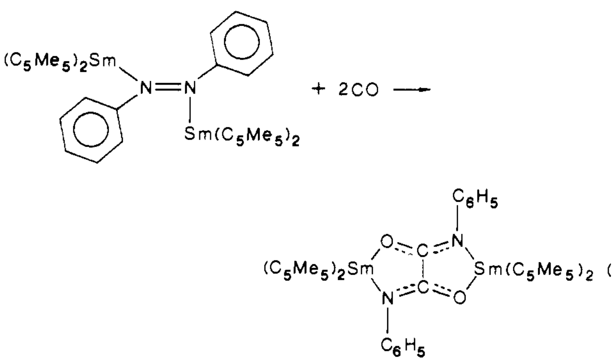
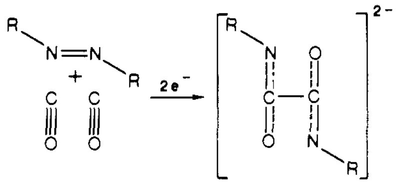
plane containing C(1), N(2), O(1), Sm(1) and the phenyl rings and the C_2 axis bisecting the C(1)–C(1²) bond. The average Sm–C(ring) distance, 2.71 (1) Å, and the (ring centroid)–Sm–(ring centroid) angle of 138.6° are typical for eight-coordinate $(C_5Me_5)_2Sm(X)(Y)$ complexes. The eclipsed orientation of the C_5Me_5 rings is unusual, although recently several $(C_5Me_5)_2Ln$ complexes with eclipsed rings have been structurally characterized.[51-53] The C(1)–C(1²) distance of 1.57 (2) Å is that of a single bond and the C(1)–O(1) and C(1)–N(1) distances, 1.26 (1) and 1.31 (1) Å, respectively, are consistent with one multiple bond delocalized over the N–C–O⁻ unit.[54,55] The Sm(1)–N(1) distance, 2.49 (1) Å, is intermediate between a Sm–NR_2 bond and a Sm←:NR_3 donor bond (see discussion of **1–4**). The Sm(1)–O(1) bond, 2.30 (1) Å, is longer than Sm–OR bonds, which range[46] from 2.094 (1)[45] to 2.25 (1)[3] Å in $(C_5Me_5)_2Sm(OR)$ complexes, and is shorter than Sm←:OR_2 donor bonds which range from 2.44 (2) to 2.56 (1) Å (see discussion of **1–4**). Hence, the $[(PhN)OCCO(NPh)]^{2-}$ dianion (formally related to *N,N′*-diphenyloxamide by double deprotonation) attaches to the samarium atoms via a partial single bond–partial donor bond interaction with both nitrogen and both oxygen atoms. Equation 11 shows the synthesis and bonding in the product.



(11)

Mechanistic Studies of the 2/CO System. The overall transformation accomplished by treating azobenzene with $(C_5Me_5)_2Sm(THF)_2$ and then CO is shown in eq 12. Before mechanisms for such a reaction can be considered, one must



(12)

determine if the two RN moieties in the product orginate from a single azobenzene molecular or if separate RN containing moieties are present in the reaction which later couple into the diphenyloxamide ligand. The formation of NPh moieties from azobenzene is known to occur in some transition-metal azobenzene systems.[56-59]

To test this aspect of the reaction of **2** with CO, two phenyl-substituted derivatives of **2** were prepared from 3,3′-azotoluene ($3\text{-}MeC_6H_4N{=}NC_6H_4Me\text{-}3'$) and methyl yellow ($C_6H_5N{=}NC_6H_4NMe_2\text{-}4$). The reaction of these two azobenzene derivatives with $(C_5Me_5)_2Sm(THF)_2$ gave blue $[(C_5Me_5)_2Sm]_2[N_2(C_6H_4Me\text{-}3)_2]$ (**6**) and green $[(C_5Me_5)_2Sm]_2[N_2(C_6H_4)(C_6H_4NMe_2\text{-}4)]$ (**8**) which have NMR spectra very similar to those of **2**. The green color of **8** is presumably due to the presence of the methyl yellow chromophore with the inherently blue complex. Complex **6** was treated with CO to form the 3-methyl-substituted analogue of **5**, $[(C_5Me_5)_2Sm]_2[(3\text{-}MeC_6H_4N)CO]_2$ (**7**), which had spectroscopic properties very similar to those of **5**.

With these complexes in hand the reaction of a 1:1 mixture of **2** and **6** with CO was conducted (eq 13) in the same manner as the synthesis of **5** (eq 11). The ¹H NMR spectrum of the green

$$[Cp^5{}_2Sm]_2N_2Ph_2 + [Cp^5{}_2Sm]_2N_2(C_6H_4Me\text{-}3)_2 + \text{excess CO} \rightarrow \underset{\mathbf{5}}{[Cp^5{}_2Sm]_2[(PhN)CO]_2} + \underset{\mathbf{7}}{[Cp^5{}_2Sm]_2[(3\text{-}MeC_6H_4N)(CO)]_2} \quad (13)$$

product mixture contained C_5Me_5 resonances at δ 1.91 and 1.94 only. This was consistent with the formation of **5** and **7** only and none of the crossover product $[(C_5Me_5)_2Sm]_2[(PhN)OCCO(NC_6H_4Me\text{-}3)]$ (**12**), assuming that **12** had a C_5Me_5 resonance distinct from those of **5** and **7**. The latter assumption, although likely, was not proven. Further evidence for lack of crossover was sought by hydrolyzing the products of reaction 13 and examining their mass spectra. These mass spectra contained parent ions for $(MeC_6H_4NH)OCCO(NHC_6H_4Me)^+$, 268, the expected crossover product, $(PhNH)OCCO(NHC_6H_4Me)^+$, 254, and $(PhNH)OCCO(NHPh)^+$, 240. This was inconsistent with the ¹H NMR results. Since these mass spectra were obtained on the products from a secondary hydrolysis reaction, it was possible that crossover was occurring after reaction 13 was complete, i.e., during hydrolysis or in the mass spectrometer. Fortunately, despite problems with air-sensitivity and low volatility, mass spectroscopy of the actual product mixture was successfully accomplished. Peaks for the parent ions of **5** and **7** and their fragments were observed with no evidence for the presence of **12**.

The reaction of CO with the methyl yellow substituted complex **8** was then carried out to see if N–N cleavage could be detected in a monosubstituted azobenzene complex (eq 14). The ¹H NMR

$$\underset{\mathbf{8}}{[Cp^5{}_2Sm]_2[PhN_2(C_6H_4NMe_2\text{-}4)]} + \text{excess CO} \rightarrow \underset{\mathbf{9}}{[Cp^5{}_2Sm]_2[(PhN)OCCO(NC_6H_4NMe_2\text{-}4)]} \quad (14)$$

spectrum of the dark-brown product **9** contained C_5Me_5 resonances at δ 1.99 and 2.02 and an NMe_2 peak with an integration consistent with **9** and not $[(C_5Me_5)_2Sm]_2[(4\text{-}Me_2NC_6H_4N)_2(CO)_2]$ (**13**). No evidence for the formation of $[(C_5Me_5)_2Sm]_2[(PhN)OCCO(NPh)]$ (**5**) was found. The reaction of **2** and **8** with CO was also examined and found to give only **5** and **9** with no evidence of **13** in either the ¹H NMR or mass spectrum. All of these results indicate that the two (aryl)N parts in the $[(C_5Me_5)_2Sm]_2\{[(aryl)N]_2(CO)_2\}$ products (**5**, **7**, and **9**) originated from the same (aryl)N=N(aryl) starting material.

Discussion

Azobenzene Sm(II) Systems. Azobenzene is known to undergo two one-electron reductions in nonaqueous solvents such as acetonitrile, pyridine, and dimethylformamide in the ranges −1.35 to −1.41 V and −1.75 to −2.03 V (versus SCE) depending on the solvent.[60] Given the large reducing potential of Sm(II),[61,62] it is reasonable that $(C_5Me_5)_2Sm(THF)_2$ should be able to reduce azobenzene to both the monoanion and the dianion. The synthetic details and the structure of $(C_5Me_5)_2Sm(N_2Ph_2)(THF)$ (**1**) are consistent with Sm(II) reduction of azobenzene to form a trivalent

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samarium complex of the anion $N_2Ph_2^-$. The reaction is rapid and must be done by keeping the azobenzene in excess to avoid further reduction. Both nitrogen atoms of the $N_2Ph_2^-$ anion coordinate to the samarium atom to form an η^2-complex. The similar Sm–N distances indicate that the system is delocalized and that each Sm–N interaction has partial single and donor bond character.

On the basis of synthesis and stoichiometry, the formation of $[(C_5Me_5)_2Sm]_2N_2Ph_2$ (**2**) is consistent with a two-electron reduction of azobenzene to form the $N_2Ph_2^{2-}$ dianion. Hence, **2** is obtained when the samarium reducing agent is in excess and alternatively can be generated from **1** by adding additional $(C_5Me_5)_2Sm(THF)_2$. The presence of trivalent $(C_5Me_5)_2Sm$ moieties would be consistent with the presence of a N–N single-bonded $PhN{-}NPh^{2-}$ species which could form single Sm–N bonds to each samarium and still have a nitrogen lone pair available on each nitrogen atom for further coordination to samarium. This is not the structure observed for **2**, however. The N–N distance is as short as a typical N═N double bond. The samarium Sm–N bonds are comparable to those in **1**, but each samarium atom makes only one Sm–N linkage. The N–C(Ph) bonds are extraordinarily long and Sm–H agostic interactions are present.

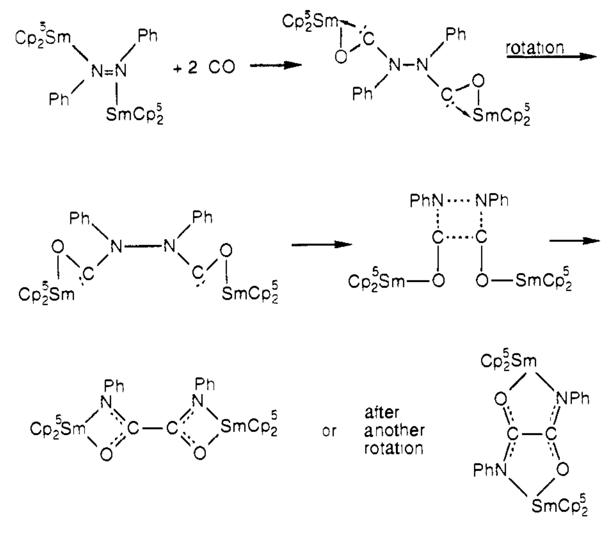
Before evaluating these features in **2**, consider the fact that the structure of **3** demonstrates that the above description of a $PhN{-}NPh^{2-}$ ligand is reasonable. In **3**, each $Ph_2N_2^{2-}$ unit makes a single bond to each of the two samarium atoms and also uses the lone pairs on the nitrogen atoms for two additional donor bonds to the samarium atoms. The Sm–N bond lengths are reasonable for distinct $Sm{-}NR_2$ and $Sm \leftarrow :NR_3$ bonds and the N–N distance is that of a single bond. Obviously, the $PhN{-}NPh^{2-}$ ligand can exist in an organosamarium complex.

Since **3** is formed from **2** by a non-redox ligand redistribution reaction, both **2** and **3** have N_2Ph_2 ligands in an equivalent state of reduction. Moreover, the structure of **3** shows that this ligand can coordinate to two samarium atoms. Hence, one must ask why **2** does not adopt a structure related to that of **3**. If one replaced the two THF ligands and the "bottom" $Ph_2N_2^{2-}$ ligand in Figure 3 with two $C_5Me_5^-$ groups (one on each Sm atom), one would have such a structure. If a C_5Me_5 group takes up more room on a samarium center than the THF and the "bottom" η^2-$N_2Ph_2^{2-}$ ion, then steric crowding would be the answer. However, the structure of **1** shows that a $(C_5Me_5)_2Sm$ unit can η^2-coordinate to a N_2Ph_2 ligand *and* still have room for THF to coordinate.

Some of the unusual features of **2** can be explained given the presence of an N═N double bond and roughly coplanar phenyl rings in the $N_2Ph_2^{2-}$ ligand. Figure 2 shows that with the azobenzene ligand in this orientation, η^2-coordination to each samarium atom is not possible sterically. Each samarium atom can make only one bond to each nitrogen and each will make the strongest bond possible. With a short N–N bond and a substantial Sm–N bond, the N–C(Ph) bond lengthens. The agostic hydrogen interactions arise because the seven-coordinate samarium center is still electron deficient. The nearest available electron density with which to coordinate is found in the ortho CH bond.

It is also possible that some of the features discussed in the previous paragraph help cause the roughly planar orientation of the $N_2Ph_2^{2-}$ ligand to form. Consider the reduction of **1** by a molecule of $(C_5Me_5)_2Sm(THF)_2$. The divalent reducing agent cannot initially get close to the nitrogen atoms because they are coordinated to the Sm^{3+} ion in **1**. Initial contact of $(C_5Me_5)_2Sm(THF)_2$ with **1** may occur via the phenyl rings. Hence, Sm–H(Ph) interactions actually may be established early in the course of the reaction rather than later (as subsequent attempts by the Sm atom to increase its coordination number). As the Sm^{2+} center transfers electron density to the $N_2Ph_2^-$ ligand in **1** and begins to coordinate to a nitrogen atom, e.g., N(2) in Figure 1, the N(2)–C(56) length may stretch, N(2) may pull away from the Sm^{3+} center to which it was originally bonded, and its lone pair may become involved in a double bond to N(1). This would cause the phenyl rings to flatten such that the samarium centers cannot η^2-coordinate. This scenario could form a molecule locked into the structure found in **2**. The fact that **2** can be converted to **3** under mild conditions (addition of THF) shows that this structure is not enormously favored thermodynamically.

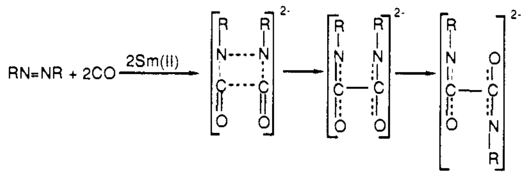
Scheme II



Cp^5 = C$_5$Me$_5$

Azobenzene/Yb(II) System. The fact that $(C_5H_5)_2Yb(THF)$ reacts with azobenzene to form the analogue of **3** directly with no evidence for analogues of **1** or **2** is interesting especially considering that Yb^{2+} is a weaker reducing agent than Sm^{2+}.[61,62] This may be another indication that **2** is a rather special type of complex. The sterically less demanding $(C_5H_5)_2Yb$ unit may be more readily able to reduce a $(C_5H_5)_2Yb(N_2Ph_2)$ precursor analogous to **1** to form **4** directly. Hence, the formation of **2** may be a special result of the steric bulk of the $(C_5Me_5)_2Sm$ unit.

CO Chemistry. Each of the above samarium azobenzene complexes **1**–**3** have been reacted with CO. Complex **1** does not react with CO at 70 psi in benzene over a 2-day period. Complex **3** gives a complicated product mixture, from which single, well-defined products have not yet been isolated. The reaction of **2** with CO is clean and unusual. The studies with the substituted azobenzene derivatives suggest that the reaction may be concerted. The multiple bond breaking and bond making which occurs is reminiscent of olefin metathesis[63] and possibly could have a four-center transition state (eq 15) like that proposed as a possible intermediate in some metathesis mechanisms.



(15)

Scheme II shows one reaction sequence which could occur via a four-center intermediate. The first step in the scheme is analogous to that given in Scheme I for the PhC≡CPh analogue. In this case, CO inserts into a Sm–N bond instead of a Sm–C bond. Insertion of CO into an f element–N bond has previously been demonstrated with Th and U dialkylamide complexes.[64] Once CO has inserted into the two Sm–N bonds in **2**, rotation around the N–N bond is necessary to get the two carbon atoms together to form the four-center intermediate. Considerable bond reorganization is necessary and complexation of the samarium centers to the nitrogen atoms must occur to give **5**. However, in Scheme II, complexation of the closest nitrogen atoms gives

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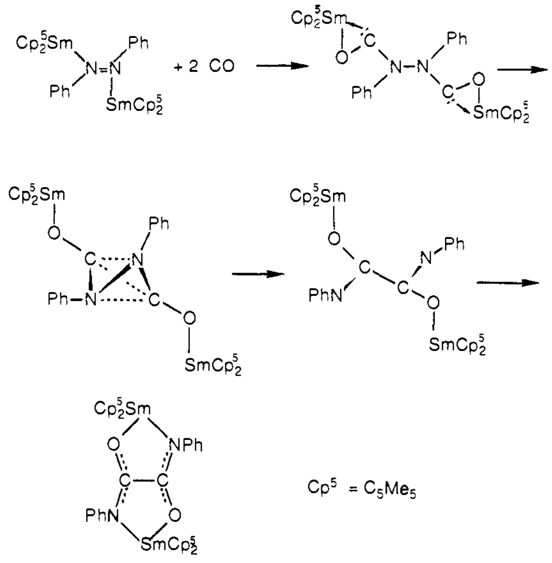
(63) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983. Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley Interscience: New York, 1985.

(64) Fagan, P. J.; Manriquez, J. M.; Vollmer, S. H.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220.

Scheme III



four-membered rings not the five-membered rings observed in **5**. To get to **5**, a second rotation of the molecule is necessary.

A major drawback in Scheme II is that two rotations are required. As Figure 5 shows, this system is sterically bulky. A sequence which does not involve rotations of such large fragments would be more desirable. Scheme III shows such an alternative. The first part of Scheme III is the same as in Scheme II. However, rather than rotate the CO inserted intermediate to bring the carbon atoms together in a planar four-center transition state, Scheme III shows the formation of a tetrahedral intermediate. Once the multiple bonds are reorganized in this intermediate, the nitrogen atoms are in the proper position to coordinate to the samarium atoms without any rotation. In terms of simplicity, Scheme III is more appealing and it is possible that a tetrahedral rather than square-planar intermediate is present in this reaction.

Conclusion

$(C_5Me_5)_2Sm(THF)_2$ reduces azobenzene to form both mono- and dianionic species. At both levels of reduction, complexes containing η^2-coordination of two adjacent nitrogen atoms can be formed. In addition, an unusual η^1,η^1-$Ph_2N_2^{2-}$ complex can be obtained. The complex containing the $Ph_2N_2^-$ monoanion is not activated for reaction with CO, but the dianion-containing complexes are reactive with CO. The product obtained from the $[(C_5Me_5)_2Sm]_2(\mu$-η^1:η^1-$N_2Ph_2)$ reaction shows an unusual reorganization of the multiple bonds in CO and azobenzene. This example shows that $(C_5Me_5)_2Sm(THF)_2$ can generate unusual multiple bond "metathesis" reactions with heteroatomic unsaturated substrates and should be considered as a possible reagent when multiple bond cleavage and activation is desirable. This system also suggests that tetrahedral intermediates may provide viable pathways for reactions of this type.

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Registry No. 1, 114251-64-8; **1**·0.5THF, 114251-71-7; **2**, 105140-21-4; **3**, 114251-65-9; **3**·2THF, 114251-72-8; **4**, 114251-66-0; **4**·C_7H_8, 114273-26-6; **5**, 105140-22-5; **5**·$2C_7H_8$, 114251-73-9; **6**, 114251-67-1; **7**, 114251-68-2; **8**, 114251-69-3; 9, 114251-70-6; $(C_5Me_5)_2Sm(THF)_2$, 79372-14-8; $(C_5H_5)_2Yb(THF)$, 99593-36-9; $C_6H_5N{=}NC_6H_4$-NMe_2-4, 60-11-7; CO, 630-08-0; azobenzene, 103-33-3; 3,3′-azotoluene, 588-04-5.

Supplementary Material Available: Tables of bond distances and angles and thermal parameters (17 pages); a listing of observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

Cocomplexation of Neutral Guests and Electrophilic Metal Cations in Synthetic Macrocyclic Hosts[1]

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Abstract: A novel method for the cocomplexation of neutral guest molecules by macrocyclic hosts, using an electrophilic metal cation, "immobilized" within a Schiff base moiety of a macrocyclic ligand, is described. The synthesis, IR and NMR spectral data, and X-ray crystal structures of the complexes are discussed. In 2,6-pyrido-27-crown-9·$LiClO_4$·urea (1:1:2) Li^+ and one urea are encapsulated by the host molecule, and urea is coordinated to the lithium ion via the oxygen atom. In the $Ba(ClO_4)_2$ and $Ba(CF_3SO_3)_2$ complexes of two Schiff base macrocycles, **11c**·MeOH and **12a**, the barium cation is coordinated in the polyether moiety of the ligand. In the $Ni^{(II)}$–H_2O and $Ni^{(II)}$–urea complexes of two Schiff base macrocycles, **19a**·H_2O and **16e**·urea, the nickel ion is complexed in the Schiff base moiety, whereas the neutral molecule is complexed in the polyether cavity, without short contact between the metal ion and the neutral guest. In the UO_2–urea complexes, the coordination of the neutral guest with the uranyl cation, located in the Schiff base moiety, was proven by IR spectroscopy and X-ray crystallography in the case of **20e**·urea. Similar complexes were obtained with substituted amides and ureas.

The synthesis of tailor-made receptor molecules is one of the main aims in host–guest chemistry. Although most of the efforts in this field used to be focussed on the complexation of cations,[2] more recently also the complexation of neutral guest species has become a rapidly growing field of interest.[3] Whereas relatively stable complexes have been reported when cations are the guest species, the interaction of macrocyclic ligands and neutral guests is generally very weak, especially when the host–guest interaction is the result of hydrogen bonding.[4] We are particularly interested

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