

Reductive Coupling of Pyridazine and Benzaldehyde Azine and Reduction of Bipyridine by $(C_5Me_5)_2Sm(THF)_2$ ¹

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Abstract: $(C_5Me_5)_2Sm(THF)_2$ reacts with pyridazine in toluene to form in high yield the complex $[(C_5Me_5)_2Sm(THF)Sm]_2[\mu, \eta^4-(CH=NNCH=CHCH-)_2]$ (**1**), which contains a bipyridazine moiety formed by coupling two pyridazine molecules at the 4-position. The complex crystallizes from toluene with three toluene molecules of crystallization in space group $P\bar{1}$ with $a = 10.449$ (3) Å, $b = 11.018$ (2) Å, $c = 16.549$ (4) Å, $\alpha = 102.03$ (2)°, $\beta = 98.51$ (2)°, $\gamma = 97.95$ (2)°, and $D_{calcd} = 1.14$ g cm⁻³ for $Z = 1$. Least-squares refinement on the basis of 4276 unique observed reflections converged to a final $R = 0.043$. Each trivalent bent metallocene unit, $(C_5Me_5)_2Sm$, is coordinated by a THF molecule [Sm-O = 2.555 (5) Å] and the adjacent nitrogen atoms of an $N_2C_4H_4$ ring [Sm-N = 2.351 (6) and 2.430 (6) Å; N-N = 1.379 (9) Å]. Benzaldehyde azine, PhHC=NN=CHPh, is also reductively coupled via C-C bond formation by $(C_5Me_5)_2Sm(THF)_2$. The product of this reaction is $[(C_5Me_5)_2Sm]_2[\mu, \eta^4-(PhHC=NNCHPh-)_2]$ (**2**). This complex crystallizes from toluene/THF with six THF molecules and a toluene molecule of crystallization per two formula units in space group $P\bar{1}$ with $a = 14.674$ (6) Å, $b = 17.806$ (6) Å, $c = 17.757$ (6) Å, $\alpha = 90.72$ (3)°, $\beta = 114.36$ (3)°, $\gamma = 108.24$ (3)°, and $D_{calcd} = 1.28$ g cm⁻³ for $Z = 2$. Least-squares refinement on the basis of 6929 unique observed reflections converged to a final $R = 0.082$. Each trivalent $(C_5Me_5)_2Sm$ unit is coordinated by two nitrogen atoms with Sm-N distances of 2.315 (13) and 2.431 (14) Å for one Sm and 2.350 (12) and 2.411 (13) Å for the other. The N-N distances are 1.34 (2) and 1.35 (2) Å. $(C_5Me_5)_2Sm(THF)_2$ reduces bipyridine to form the Sm^{3+} bipyridyl complex $(C_5Me_5)_2Sm(\eta^2-N_2C_{10}H_8)$ (**3**) which crystallizes from toluene in space group $P\bar{1}$ with $a = 9.4667$ (12) Å, $b = 9.6784$ (16) Å, $c = 15.5870$ (19) Å, $\alpha = 81.506$ (12), $\beta = 81.033$ (10), $\gamma = 71.803$ (12), and $D_{calcd} = 1.44$ g cm⁻³ for $Z = 2$. Least-squares refinement on the basis of 5422 unique observed reflections converged to a final $R = 0.026$. The bent $(C_5Me_5)_2Sm$ unit is coordinated by the bipyridyl nitrogen atoms via 2.427 (2) and 2.436 (2) Å distances.

A recent development in the use of metal-containing reagents in organic chemistry involves the Sm(II) ion^{2,3} and $SmI_2(THF)_2$ ^{4,5} is being studied with increasing frequency in this regard.⁶ The organometallic complex $(C_5Me_5)_2Sm(THF)_2$ ⁷ is also being used to probe the range of reactivity accessible via Sm(II).^{8,9} The latter complex can display chemistry different from $SmI_2(THF)_2$ and often provides crystallographically characterizable metal-containing reaction products.

Studies of the reactivity of $(C_5Me_5)_2Sm(THF)_2$ with CO ,¹⁰ $RC\equiv CR$,¹¹ $RN=NR$,^{12,13} and $R_2C=CR_2$ ¹⁴ have revealed that

Sm(II) can effect a variety of unusual and potentially useful transformations with these unsaturated substrates. These include the reductive homologation of three molecules of CO to the ketene carboxylate $O_2CC=C=O$,¹⁰ the formation of a stereospecifically substituted indenodenediolate complex from diphenylethyne and CO,¹¹ and the double insertion of CO into the N=N bond of azobenzene¹³ and the C=C bond of bis(2-pyridyl)ethene.¹⁴

The reactions cited above, which had no precedents in organometallic chemistry, demonstrated that $(C_5Me_5)_2Sm(THF)_2$ could reduce unsaturated substrates in surprising ways. Accordingly, we felt it was appropriate to explore a wide variety of unsaturated substrates to fully define the possible reactivity patterns available to $(C_5Me_5)_2Sm(THF)_2$. In this report, we describe reactions with some substrates containing N-C double bonds. Given the strong reducing power of $(C_5Me_5)_2Sm(THF)_2$ and the reduction potentials of the substrates, reactivity was expected. However, in contrast to the two electron multiple bond reduction observed for the $RC\equiv CR$, $RN=NR$, and $R_2C=CR_2$ substrates, we find that azines are reduced by one electron per substrate to cleanly form coupled moieties not readily available via electrochemical reduction.

Experimental Section

The complexes described in this paper are air- and moisture-sensitive. Therefore, all syntheses and subsequent manipulations were conducted under nitrogen using Schlenk, vacuum-line, and glove-box (Vacuum Atmospheres HE-553 Dri-Lab) techniques. $(C_5Me_5)_2Sm(THF)_2$ and the solvents were prepared as previously described.⁷ Pyridazine, benzaldehyde azine, and bipyridine were obtained from Aldrich and degassed at room temperature before use. NMR spectra,⁷ IR spectra,⁷ magnetic susceptibility measurements,⁷ and complexometric analyses¹⁵ were obtained as previously described. UV-visible spectra were recorded on a Perkin-Elmer Lambda 4A spectrometer.

$[(C_5Me_5)_2Sm(THF)Sm]_2[\mu, \eta^4-(CH=NNCH=CHCH-)_2]$ (**1**). In the glove box, pyridazine, $N_2C_4H_4$ (36 mg, 0.44 mmol), in 5 mL of toluene was added to a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (254 mg, 0.44 mmol) in 10 mL of toluene. The solution turned yellow-orange immediately. The solution was stirred for 1 h; the solvent was removed by rotary evaporation, and crude **1** was isolated as an orange powder (250

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Table I. Crystal Data for $[(C_5Me_5)_2(THF)Sm]_2[(\mu, \eta^4-(CH=NNCH=CHCH-))_2] \cdot 3C_7H_8$ (a), $[(C_5Me_5)_2Sm]_2[(\mu, \eta^4-(PhCH=NNCHPh-))_2] \cdot 3THF \cdot 0.5C_7H_8$ (b), and $(C_5Me_5)_2Sm(\eta^2-N_2C_{10}H_8)$ (c)

	a	b	c
formula	Sm ₂ C ₇₇ H ₁₀₈ N ₄ O ₂	Sm ₂ C _{83.5} H ₁₁₂ N ₄ O ₃	SmC ₃₀ H ₃₈ N ₂
mol wt	1422.43	1520.54	577.00
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	10.449 (3)	14.674 (6)	9.4667 (12) ^a
<i>b</i> , Å	11.018 (2)	17.806 (6)	9.6784 (16)
<i>c</i> , Å	16.549 (4)	17.757 (6)	15.5870 (19)
α , deg	102.03 (2)	90.72 (3)	81.506 (12)
β , deg	98.51 (2)	114.36 (3)	81.033 (10)
γ , deg	97.95 (2)	108.24 (3)	71.803 (12)
cell vol, Å ³	1819	3960	1333
<i>Z</i>	1	2	2
<i>D</i> _{calcd} , g/cm ³	1.14	1.28	1.44
temp, °C	25	24	24
λ (Mo K α), Å	0.71073; graphite monochromator	0.71073; graphite monochromator	0.71073; graphite monochromator
(μ) cm ⁻¹	16.4	15.3	22.3
min-max transmission coeff	0.589–0.716	0.622–0.808	0.276–0.336
type of scan	θ –2 θ	θ –2 θ	θ –2 θ
scan width, deg	–1.2 in 2 θ from K α ₁ to +1.2 from K α ₂	–1.2 in 2 θ from K α ₁ to +1.2 from K α ₂	–1.2 in 2 θ from K α ₁ to +1.2 from K α ₂
scan speed, deg/min	3–16	2–16 for 3–35° in 2 θ ; 3 for 35–45° in 2 θ	4–16
bkgd counting	evaluated from 96-step peak profile	evaluated from 96-step peak profile	evaluated from 96-step peak profile
data collec range, deg	3–45	3–45	3–55
total unique data	5109	10420	6165
unique data with <i>I</i> > 3 σ (<i>I</i>)	4276	6929 (2 σ)	5422
no. of parameters	364	736	330
<i>R</i> (<i>F</i>)	0.043	0.082	0.026
<i>R</i> _w (<i>F</i>)	0.058	0.114	0.034
GOF	1.80	3.29	1.18

^aThis unit cell can be converted to one with all obtuse angles (*a* = 7.793 Å, *b* = 9.678 Å, *c* = 19.319 Å, α = 104.27°, β = 104.51°, γ = 98.49°) by the transformation matrix:

$$\begin{pmatrix} 0 & 0 & 1/2 \\ 0 & -1 & 0 \\ 2 & 0 & -1/2 \end{pmatrix}$$

mg, 98%), which was >95% pure by ¹H NMR spectroscopy. Orange crystals of **1** were obtained from a concentrated toluene solution cooled to –34 °C (144 mg, 57%). Anal. Calcd for SmC₂₈H₄₂N₂O: Sm, 26.2. Found: Sm, 25.6. ¹H NMR (C₆D₆): δ 8.53 (br s, 1 H, N₂C₄H₄), 5.64 (br s, 1 H, N₂C₄H₄), 4.24 (br s, 1 H, N₂C₄H₄), 4.19 (br s, 1 H, N₂C₄H₄), 1.29 (s, 30 H, C₅Me₅), –0.253 (s, 4 H, C₄H₈O), –0.514 (s, 4 H, C₄H₈O), the signals labeled br have line widths of 6–10 Hz at half-height. ¹³C NMR (C₆D₆): δ 111.8 (s, C₅Me₅), 67.0 (t, *J*_{CH} = 144 Hz, THF), 23.8 (t, *J*_{CH} = 132 Hz, THF), 17.5 (q, *J*_{CH} = 125 Hz, C₅Me₅). The ¹³C NMR C₅Me₅ shifts are characteristic of Sm(III) complexes.^{16,17} IR (KBr): 2980–2860 (s), 1600 (m), 1555 (w), 1535 (w), 1495 (w), 1445 (s), 1380 (m), 1315 (w), 1300 (w), 1220 (s), 1115 (m), 1025 (s), 910 (s), 875 (s), 810 (w), 730 (s), 710 (s), 695 (s), 655 (m) cm⁻¹.

X-ray Crystallography of [(C₅Me₅)₂(THF)Sm]₂[(μ, η^4 -(CH=NNCH=CHCH-))₂] \cdot 3C₇H₈. General procedures for data collection and reduction have been described previously.¹⁸ An orange crystal measuring 0.10 mm \times 0.30 mm \times 0.40 mm was sealed under nitrogen in a glass capillary and mounted on a Nicolet R3m/V diffractometer. Lattice parameters were determined at 24 °C from the angular settings of 20 computer-centered reflections. Data were collected by the θ –2 θ scan technique in bisecting geometry. The *p* factor in the expression¹⁹ for the standard deviation of the observed intensities was given a value of 0.05. Relevant crystal and data collection parameters are given in Table I. During the data collection, the intensities of three standard reflections measured every 100 reflections showed a linear decay of 7%; the intensities were corrected for this decay. An absorption correction was applied. Patterson and difference Fourier techniques were used to locate all non-hydrogen atoms. All atoms except the carbon atoms in one of the toluene molecules were

refined with anisotropic temperature parameters by use of full-matrix least-squares methods. No hydrogen atoms were located. Atomic-scattering factors were taken from ref 20. A final difference map contained no recognizable features. Fractional coordinates are given in Table II.

[(C₅Me₅)₂Sm]₂[(μ, η^4 -(PhHC=NNCHPh-))₂] **(2). In the glove box, benzaldehyde azine, C₆H₅CH=NN=CHC₆H₅ (110 mg, 0.53 mmol), in 5 mL of toluene was added to (C₅Me₅)₂Sm(THF)₂ (300 mg, 0.53 mmol) in 10 mL of toluene. The solution turned orange immediately and was stirred for 1 h. The toluene was removed by rotary evaporation and the resulting orange solid subsequently was dissolved in a minimum amount of a 1:5 THF/toluene mixture. Crystals of **2** (230 mg, 69% obtained over several recrystallizations) were grown over several days at –34 °C. Anal. Calcd for SmC₃₄H₄₂N₂: Sm, 23.91; C, 64.91; H, 6.73; N, 4.45. Found: Sm, 24.90; C, 63.67; H, 6.74; N, 4.19. mp: 140 °C dec. ¹H NMR (C₆D₆): δ 4.90 (br s, 2 H), 4.59 (br s, 2 H), 4.07 (br s, 4 H), 3.40 (vbr s, 4 H), 1.94 (s, 30 H, C₅Me₅), 1.36 (br s, 4 H), 1.30 (br s, 4 H), 0.75 (s, 30 H, C₅Me₅), –4.34 (br s, 2 H), the signals labeled br have line widths of 17–41 Hz at half-height. Given the paramagnetism of Sm(III),²¹ it is often difficult to observe and assign all of the ligand signals expected.¹² ¹³C NMR (C₆D₆): δ 118.1 (s, C₅Me₅), 117.8 (s, C₅Me₅), 21.9 (q, *J*_{CH} = 126 Hz, C₅Me₅), 21.1 (q, *J*_{CH} = 125 Hz, C₅Me₅). The ¹³C NMR C₅Me₅ shifts are characteristic of Sm(III) complexes.^{16,17} IR (KBr): 3130 (w), 2920 (s), 2860 (s), 2730 (w), 1600 (w), 1570 (w), 1520 (m), 1500 (w), 1445 (s), 1360 (m), 1290 (w), 1260 (w), 1230 (w), 1150 (s), 1020 (m), 970 (m), 895 (m), 820 (m), 745 (m), 725 (s), 690 (s) cm⁻¹.**

X-ray Crystallography of [(C₅Me₅)₂Sm]₂[(μ, η^4 -(PhHC=NNCHPh-))₂] \cdot 3THF \cdot 1/2C₇H₈. An orange crystal measuring 0.33 mm \times 0.46 mm \times 0.26 mm was handled and analyzed as described above for **1** (including the same weighting scheme). These crystals readily desolvate and had to be put in the capillary quickly. Lattice parameters were determined from 25 reflections with 20° < 2 θ < 25°. Relevant crystal and data collection parameters are given in Table I. During the

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Table II. Final Fractional Coordinates for

atom	x	y	z
Sm(1)	0.21482 (4)	0.35075 (3)	0.24662 (2)
O(1)	0.3879 (5)	0.2347 (5)	0.3066 (3)
N(1)	0.2162 (6)	0.4201 (6)	0.3909 (4)
N(2)	0.1121 (6)	0.4658 (6)	0.3535 (4)
C(1)	0.0060 (8)	0.1681 (7)	0.2436 (5)
C(2)	0.0907 (8)	0.1035 (7)	0.1991 (6)
C(3)	0.0937 (8)	0.1426 (8)	0.1232 (5)
C(4)	0.0039 (8)	0.2295 (7)	0.1198 (5)
C(5)	-0.0455 (7)	0.2447 (8)	0.1945 (6)
C(6)	-0.0268 (13)	0.1494 (11)	0.3255 (6)
C(7)	0.1570 (13)	-0.0035 (10)	0.2240 (10)
C(8)	0.1658 (11)	0.0914 (12)	0.0532 (8)
C(9)	-0.0500 (12)	0.2778 (11)	0.0458 (7)
C(10)	-0.1543 (10)	0.3209 (11)	0.2119 (9)
C(11)	0.4375 (9)	0.5169 (8)	0.2512 (5)
C(12)	0.3402 (10)	0.5923 (8)	0.2651 (6)
C(13)	0.2487 (9)	0.5678 (8)	0.1906 (6)
C(14)	0.2898 (8)	0.4807 (8)	0.1302 (5)
C(15)	0.4077 (8)	0.4471 (8)	0.1674 (5)
C(16)	0.5645 (11)	0.5168 (13)	0.3127 (8)
C(17)	0.3418 (16)	0.6922 (10)	0.3448 (8)
C(18)	0.1292 (12)	0.6320 (10)	0.1752 (8)
C(19)	0.2417 (12)	0.4482 (11)	0.0337 (6)
C(20)	0.4902 (11)	0.3656 (11)	0.1169 (7)
C(21)	0.2577 (8)	0.4746 (9)	0.4764 (5)
C(22)	0.1899 (9)	0.5451 (9)	0.5238 (5)
C(23)	0.0491 (8)	0.5506 (8)	0.4892 (5)
C(24)	0.0414 (8)	0.5332 (7)	0.3952 (5)
C(25)	0.4071 (12)	0.2249 (11)	0.3936 (6)
C(26)	0.4794 (11)	0.1696 (11)	0.2636 (7)
C(27)	0.4915 (16)	0.1243 (14)	0.3972 (9)
C(28)	0.5311 (15)	0.0905 (14)	0.3183 (8)
C(29)	0.6946 (15)	0.8079 (14)	0.1629 (7)
C(30)	0.5638 (15)	0.7526 (13)	0.1475 (9)
C(31)	0.4671 (16)	0.8120 (17)	0.1113 (10)
C(32)	0.5080 (24)	0.9316 (18)	0.0900 (10)
C(33)	0.6419 (24)	0.9745 (15)	0.1078 (11)
C(34)	0.7341 (17)	0.9204 (14)	0.1441 (9)
C(35)	0.7951 (21)	0.7417 (22)	0.1976 (11)
C(38)	-0.0131 (19)	0.9026 (15)	0.4600 (10)
C(36)	0.1830 (22)	1.0863 (20)	0.5457 (13)
C(37)	0.1129 (25)	0.9467 (23)	0.4832 (15)

data collection the intensities of three standard reflections measured every 100 reflections showed only random fluctuations within $\pm 3\%$. An empirical absorption correction was applied. Patterson and difference Fourier techniques were used to locate all non-hydrogen atoms. All atoms except those in the solvent molecules were refined with anisotropic temperature parameters by use of full-matrix least-squares methods. The solvent molecules, which were refined isotropically, were disordered and severely limited the quality of the structure. No hydrogen atoms were located. A final difference map contained no recognizable features; its largest peak was of height $4.2 \text{ e}/\text{\AA}^3$ at a distance of 1.27 \AA from Sm(2) and this reflected the poor quality of the structure. Final fractional coordinates are given in Table III.

$(C_5Me_5)_2Sm(\eta^2-N_2C_{10}H_8)$ (3). In the glove box $(C_5Me_5)_2Sm(THF)_2$ (350 mg, 0.619 mmol) and bipyridine (97 mg, 0.621 mmol) were dissolved together in toluene. The solution turned orange-brown immediately and was stirred overnight. The solvent was removed by rotary evaporation leaving 3 as a brown powder (346 mg, 97%). Dark brown crystals of 3 were grown from toluene at -34°C . Anal. Calcd for $SmC_{30}H_{38}N_2$: Sm, 26.1. Found: Sm, 26.1. ^1H NMR (C_6D_6): δ 2.49 (s, C_5Me_5), -13.4 (br, $\Delta\nu_{1/2} = 100 \text{ Hz}$), -26.0 (br, $\Delta\nu_{1/2} = 250 \text{ Hz}$). ^{13}C NMR (C_6D_6): δ 136.3 (s, C_5Me_5), 9.0 (q, $J_{CH} = 125 \text{ Hz}$, C_5Me_5). IR (KBr): 2950 (s), 1540 (m), 1500 (sh, m), 1490 (s), 1480 (s), 1440 (s), 1420 (s), 1380 (m), 1320 (w), 1290 (m), 1280 (m), 1265 (s), 1210 (m), 1150 (s), 1080 (m), 1025 (sh, m), 1015 (s), 1005 (s), 940 (s), 760 (w), 745 (w), 715 (m) cm^{-1} . $\chi_M^{298K} = 2400 \times 10^{-6}$ (cgs). $\mu_{\text{eff}}^{298K} = 2.4 \mu_B$. UV-vis ($2.4 \times 10^{-4} \text{ M}$ in toluene, λ_{max} nm, (ϵ): 524 (1700), 491 (1200), 393 (4000), 285 (6700).

X-ray Crystallography of $(C_5Me_5)_2Sm(\eta^2-N_2C_{10}H_8)$ (3). A dark brown crystal measuring $0.50 \text{ mm} \times 0.50 \text{ mm} \times 0.70 \text{ mm}$ was handled and analyzed as described above for 1 (including the same weighting scheme). Relevant crystal and data collection parameters are given in Table I. During the data collection, the intensities of three standard

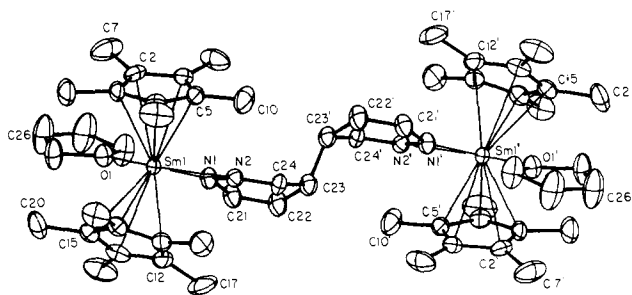


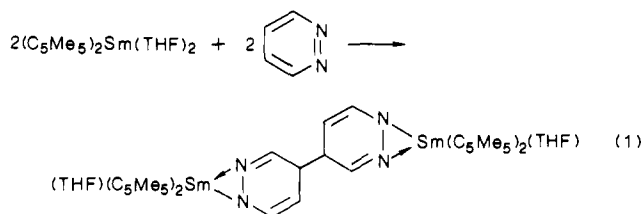
Figure 1. Molecular structure of $[(C_5Me_5)_2(THF)Sm]_2[\mu, \eta^4-(CH=NNCH=CHCH-)]_2$ (1).

reflections measured every 100 reflections showed only random variation within $\pm 1\%$. An empirical absorption correction was applied. Patterson and difference Fourier techniques were used to locate all non-hydrogen atoms which were refined with anisotropic temperature parameters by use of full-matrix least-squares methods. All hydrogen atoms were observed on a difference map. The methyl hydrogens on the pentamethylcyclopentadienyl rings were included in their idealized ($C-H = 0.95 \text{ \AA}$) positions. The hydrogen atoms of the bipyridyl rings were refined isotropically. A final difference map contained no recognizable features; its largest peak was of height $1.7 \text{ e}/\text{\AA}^3$ at a distance of 0.84 \AA from Sm. Fractional coordinates are given in Table IV.

Results

The reactions of the purple complex $(C_5Me_5)_2Sm(THF)_2$ with the nitrogen-containing substrates pyridazine, benzaldehyde azine, and bipyridine are all characterized by rapid color changes to orange or orange-brown. This is consistent with a rapid oxidation of Sm(II) to Sm(III).⁹ In each case, the newly formed organo-samarium complex was characterized by complexometric analysis, ^1H and ^{13}C NMR spectroscopy, and IR spectroscopy and was identified by X-ray crystallography.

Pyridazine. The structure of complex 1, obtained from the reaction of pyridazine with $(C_5Me_5)_2Sm(THF)_2$, is shown in Figure 1. The X-ray analysis revealed that reductive carbon-carbon bond formation occurred in this reaction according to eq 1. A bipyridazine unit has been formed in which the two nitrogen



atoms of each ring coordinate to a $Sm(THF)(C_5Me_5)_2$ moiety. The molecule contains an inversion center which lies at the midpoint of the $C(23)-C(23')$ bond, which is the new C-C bond formed in the reaction. Bond distances and angles are given in Table V and in the supplementary material.

The $C(23)-C(23')$ distance of $1.545 (17) \text{ \AA}$ is typical of a C-C single bond and the bond angles around $C(23)$ are consistent with an sp^3 center. As shown in Table V, the $C(23)-C(22)$ and $C(23)-C(24)$ bond distances are clearly in the single-bond range and the $C(22)-C(21)$ distance is in the double-bond range.²² Hence, the delocalized bonding found in pyridazine, which has C-C lengths of $1.375 (1)$ and $1.393 (2) \text{ \AA}$,²³ is not present in 1. The $C(24)-N(2)$ bond of $1.29 (1) \text{ \AA}$ is shorter and the $C(21)-N(1)$ bond of $1.40 (1) \text{ \AA}$ is longer than the analogous $1.341 (2) \text{ \AA}$ C-N bond in pyridazine. These distances in 1 are consistent with a double and a single bond, respectively.²⁴ The $N(1)-N(2)$

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Table III. Final Fractional Coordinates for $[(C_5Me_5)_2Sm]_2[\mu, \eta^4-(PhHC=NNCHPh-)_2] \cdot 3THF \cdot 0.5C_7H_8$

atom	x	y	z	atom	x	y	z
Sm(1)	0.15032 (7)	0.17619 (5)	0.82061 (5)	C(44)	0.4798 (15)	0.1454 (10)	0.9944 (11)
Sm(2)	0.59098 (7)	0.26832 (5)	1.28774 (5)	C(45)	0.5630 (17)	0.1177 (12)	1.0082 (12)
N(1)	0.2671 (11)	0.1588 (8)	0.9490 (8)	C(46)	0.6019 (16)	0.0841 (12)	1.0787 (15)
N(2)	0.2028 (11)	0.0830 (8)	0.9139 (8)	C(47)	0.5599 (17)	0.0810 (12)	1.1393 (13)
N(3)	0.4690 (11)	0.2811 (7)	1.1563 (7)	C(48)	0.4807 (15)	0.1124 (10)	1.1258 (11)
N(4)	0.4881 (11)	0.3464 (7)	1.2082 (8)	C(49)	0.1311 (15)	-0.0590 (10)	0.9010 (13)
C(1)	0.2811 (16)	0.1956 (12)	0.7433 (10)	C(50)	0.1469 (18)	-0.1257 (12)	0.9390 (15)
C(2)	0.1987 (17)	0.2235 (12)	0.6921 (11)	C(51)	0.0808 (23)	-0.2050 (14)	0.8959 (20)
C(3)	0.1042 (16)	0.1575 (11)	0.6492 (10)	C(52)	-0.0011 (26)	-0.2153 (15)	0.8204 (25)
C(4)	0.1235 (17)	0.0888 (11)	0.6760 (10)	C(53)	-0.0200 (20)	-0.1500 (18)	0.7788 (17)
C(5)	0.2345 (15)	0.1100 (11)	0.7345 (11)	C(54)	0.0490 (18)	-0.0696 (13)	0.8209 (13)
C(6)	0.4018 (17)	0.2435 (14)	0.7920 (13)	C(55)	0.3803 (15)	0.2648 (9)	1.0732 (9)
C(7)	0.2176 (24)	0.3116 (14)	0.6781 (16)	C(56)	0.4387 (14)	0.3991 (10)	1.1869 (11)
C(8)	0.0062 (20)	0.1569 (15)	0.5721 (12)	C(57)	0.4120 (14)	0.3190 (9)	1.0161 (10)
C(9)	0.0443 (20)	0.0020 (12)	0.6363 (12)	C(58)	0.5171 (16)	0.3487 (10)	1.0242 (12)
C(10)	0.2916 (17)	0.0529 (12)	0.7715 (13)	C(59)	0.5417 (19)	0.4032 (12)	0.9684 (14)
C(11)	-0.0625 (16)	0.1383 (13)	0.7754 (12)	C(60)	0.4641 (24)	0.4270 (13)	0.9131 (15)
C(12)	-0.0194 (17)	0.1289 (16)	0.8631 (14)	C(61)	0.3608 (24)	0.3990 (12)	0.9041 (12)
C(13)	0.0436 (16)	0.2119 (15)	0.9052 (12)	C(62)	0.3322 (17)	0.3425 (11)	0.9567 (11)
C(14)	0.0372 (16)	0.2625 (13)	0.8489 (14)	C(63)	0.4687 (18)	0.4678 (11)	1.2502 (14)
C(15)	-0.0292 (18)	0.2196 (14)	0.7675 (13)	C(64)	0.5520 (22)	0.4846 (14)	1.3296 (15)
C(16)	-0.1479 (19)	0.0703 (16)	0.7043 (16)	C(65)	0.5675 (30)	0.5477 (19)	1.3870 (20)
C(17)	-0.0441 (21)	0.0575 (15)	0.9013 (17)	C(66)	0.5049 (40)	0.5968 (23)	1.3628 (32)
C(18)	0.0974 (20)	0.2380 (21)	1.0022 (14)	C(67)	0.4305 (39)	0.5827 (21)	1.2892 (32)
C(19)	0.0813 (20)	0.3562 (15)	0.8665 (19)	C(68)	0.4077 (23)	0.5175 (14)	1.2266 (17)
C(20)	-0.0686 (22)	0.2582 (18)	0.6918 (15)	C(71)	1.0224 (67)	0.5613 (41)	0.9540 (44)
C(21)	0.7553 (13)	0.3890 (10)	1.2777 (11)	C(72)	1.1188 (46)	0.5382 (35)	0.9900 (37)
C(22)	0.7868 (14)	0.3929 (11)	1.3672 (11)	C(73)	0.9499 (66)	0.5042 (56)	0.9642 (49)
C(23)	0.8076 (15)	0.3218 (11)	1.3941 (12)	C(74)	0.3144 (59)	0.7885 (46)	0.2570 (45)
C(24)	0.7901 (15)	0.2757 (11)	1.3210 (13)	C(75)	0.2275 (64)	0.7213 (47)	0.1942 (55)
C(25)	0.7603 (13)	0.3167 (10)	1.2515 (12)	C(76)	0.2167 (63)	0.7215 (46)	0.1114 (49)
C(26)	0.7376 (16)	0.4546 (11)	1.2268 (12)	C(77)	0.3036 (58)	0.7812 (45)	0.1302 (45)
C(27)	0.8139 (20)	0.4716 (12)	1.4261 (14)	C(78)	0.3277 (44)	0.8448 (34)	0.1982 (37)
C(28)	0.8663 (18)	0.3156 (14)	1.4837 (12)	C(79)	0.2148 (51)	0.4651 (38)	0.3412 (39)
C(29)	0.8157 (20)	0.1980 (13)	1.3238 (16)	C(80)	0.1531 (61)	0.5034 (40)	0.2972 (44)
C(30)	0.7501 (17)	0.2902 (13)	1.1645 (12)	C(81)	0.0592 (48)	0.4775 (36)	0.3134 (36)
C(31)	0.5559 (23)	0.2553 (13)	1.4284 (14)	C(82)	0.1903 (62)	0.4040 (45)	0.3632 (46)
C(32)	0.5721 (17)	0.1847 (14)	1.4147 (13)	C(83)	0.0696 (39)	0.4060 (29)	0.3565 (29)
C(33)	0.4826 (20)	0.1369 (13)	1.3385 (13)	C(84)	0.3509 (61)	0.0860 (43)	0.4691 (44)
C(34)	0.4144 (17)	0.1788 (14)	1.3058 (13)	C(85)	0.2665 (36)	0.0784 (27)	0.5466 (27)
C(35)	0.4537 (23)	0.2497 (16)	1.3609 (17)	C(86)	0.2532 (41)	0.1421 (30)	0.5201 (31)
C(36)	0.6152 (22)	0.3157 (17)	1.5071 (15)	C(87)	0.4799 (85)	0.1277 (66)	0.5409 (66)
C(37)	0.6542 (23)	0.1543 (17)	1.4745 (16)	C(88)	0.2676 (68)	0.1054 (51)	0.4516 (50)
C(38)	0.4640 (24)	0.0479 (13)	1.3095 (16)	C(89)	0.3879 (61)	0.0821 (47)	0.5607 (44)
C(39)	0.3000 (19)	0.1494 (19)	1.2343 (16)	C(90)	0.3705 (84)	0.1784 (58)	0.5231 (64)
C(40)	0.3966 (27)	0.3077 (20)	1.3587 (23)	C(91)	0.2903 (62)	0.0373 (45)	0.4897 (48)
C(41)	0.3447 (13)	0.1717 (9)	1.0387 (9)	C(92)	0.4178 (97)	0.1440 (76)	0.5436 (79)
C(42)	0.2102 (15)	0.0209 (10)	0.9484 (10)	C(93)	0.3579 (68)	0.1615 (49)	0.5838 (52)
C(43)	0.4377 (13)	0.1442 (9)	1.0516 (9)				

distance of 1.379 (9) Å is larger than the 1.330 (1) Å length in pyridazine and suggests that the double-bond character present in pyridazine has been lost after the reductive coupling and complexation by samarium.

These distances and normal valence considerations suggest the following formal bonding arrangements between the nitrogen atoms and the samarium atoms. N(1) can bind to samarium via a single bond of the Sm-NR₂ type. N(2) coordinates to samarium via its lone pair in a Sm←:NR₃ type donor bond. Consistent with this the Sm-N(1) bond of 2.351(6) Å is very close to the Sm-NR₂ single-bond distance of 2.333 (9) Å in $[(C_5Me_5)(THF)Sm]_2[\mu, \eta^2, \eta^2-PhNNPh]_2$ ²⁵ and agrees with the Y-NR₂ single-bond distances of 2.253 (5) and 2.274 (5) Å in $(C_5Me_5)_2YN(SiMe_3)_2$ ²⁶ after adding 0.06²⁷-0.084 Å²⁸ to account for the radial difference in the metals. The Sm-N(2) length of 2.430 (6) Å is longer than

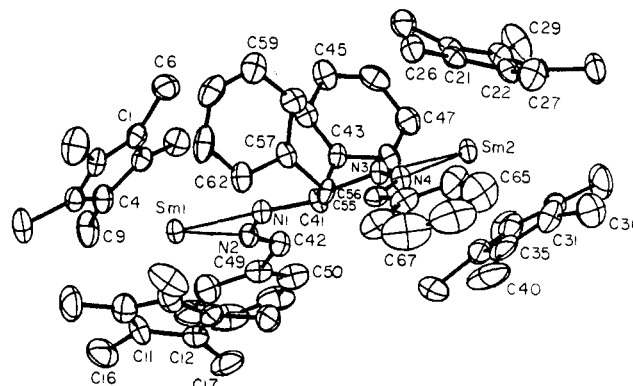


Figure 2. Molecular structure of $[(C_5Me_5)_2Sm]_2[\mu, \eta^4-(PhCH=NNCHPh-)]_2$ (2).

a typical Sm-NR₂ single bond, but it is shorter than the range expected for Sm←:NR₃ donor bonds: 2.5-2.8 Å.^{25,29} A specific example of this in a complex which is similarly ligated is the 2.539

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Table IV. Final Fractional Coordinates for $(C_5Me_5)_2Sm(\eta^2-N_2C_{10}H_8)$ (3)

atom	x	y	z
Sm(1)	0.132257 (14)	0.238670 (14)	0.246348 (8)
N(1)	0.2599 (3)	0.4230 (3)	0.1925 (2)
N(2)	0.2799 (3)	0.2719 (3)	0.3514 (2)
C(1)	0.2597 (4)	-0.0536 (3)	0.2474 (2)
C(2)	0.1634 (4)	-0.0169 (3)	0.1816 (2)
C(3)	0.2217 (4)	0.0674 (3)	0.1122 (2)
C(4)	0.3563 (4)	0.0801 (4)	0.1345 (2)
C(5)	0.3802 (4)	0.0049 (4)	0.2175 (2)
C(6)	0.2379 (6)	-0.1453 (4)	0.3325 (3)
C(7)	0.0396 (5)	-0.0823 (4)	0.1791 (3)
C(8)	0.1597 (6)	0.1228 (5)	0.0260 (3)
C(9)	0.4625 (5)	0.1512 (5)	0.0757 (3)
C(10)	0.5162 (5)	-0.0220 (6)	0.2641 (4)
C(11)	-0.0946 (4)	0.4666 (3)	0.3078 (2)
C(12)	-0.1055 (4)	0.3443 (4)	0.3671 (2)
C(13)	-0.1503 (3)	0.2499 (4)	0.3239 (2)
C(14)	-0.1684 (3)	0.3146 (4)	0.2379 (2)
C(15)	-0.1334 (4)	0.4482 (4)	0.2277 (2)
C(16)	-0.0574 (5)	0.5976 (5)	0.3278 (3)
C(17)	-0.0900 (5)	0.3289 (6)	0.4629 (3)
C(18)	-0.1867 (5)	0.1140 (5)	0.3677 (4)
C(19)	-0.2319 (5)	0.2626 (6)	0.1701 (4)
C(20)	-0.1500 (5)	0.5588 (5)	0.1485 (3)
C(21)	0.3496 (3)	0.4520 (3)	0.2449 (2)
C(22)	0.4239 (4)	0.5595 (4)	0.2129 (3)
C(23)	0.4101 (5)	0.6317 (5)	0.1330 (3)
C(24)	0.3210 (5)	0.6006 (4)	0.0794 (3)
C(25)	0.2496 (4)	0.4970 (4)	0.1114 (2)
C(26)	0.3591 (3)	0.3735 (3)	0.3300 (2)
C(27)	0.4438 (5)	0.3929 (5)	0.3921 (3)
C(28)	0.4490 (5)	0.3154 (6)	0.4705 (3)
C(29)	0.3721 (5)	0.2087 (6)	0.4913 (3)
C(30)	0.2906 (4)	0.1926 (4)	0.4305 (2)

Table V. Selected Interatomic Bond Distances (Å) and Angles (deg) for $[(C_5Me_5)_2(THF)Sm]_2[\mu, \eta^4-(CH=NNCH=CHCH-)]_2$ (1)

Sm(1)-N(1)	2.351 (6)	N(1)-Sm(1)-O(1)	79.8 (2)
Sm(1)-N(2)	2.430 (6)	N(2)-Sm(1)-O(1)	112.9 (2)
Sm(1)-O(1)	2.555 (5)	C(25)-O(1)-C(26)	109.6 (7)
Sm(1)-C(12)	2.737 (8)	N(2)-N(1)-C(21)	114.2 (6)
Sm(1)-C(11)	2.739 (8)	N(2)-N(1)-Sm(1)	76.4 (4)
Sm(1)-C(13)	2.740 (8)	C(21)-N(1)-Sm(1)	162.2 (6)
Sm(1)-C(5)	2.743 (7)	C(24)-N(2)-N(1)	123.4 (6)
Sm(1)-C(3)	2.743 (7)	C(24)-N(2)-Sm(1)	166.4 (6)
Sm(1)-C(1)	2.746 (8)	C(22)-C(21)-N(1)	124.5 (8)
Sm(1)-C(2)	2.750 (7)	C(21)-C(22)-C(23)	119.6 (7)
Sm(1)-C(14)	2.772 (7)	C(22)-C(23)-C(24)	105.4 (7)
Sm(1)-C(15)	2.775 (7)	C(22)-C(23)-C(23)	112.0 (9)
Sm(1)-C(4)	2.775 (8)	C(24)-C(23)-C(23)	112.1 (8)
O(1)-C(25)	1.454 (10)	N(2)-C(24)-C(23)	122.9 (7)
O(1)-C(26)	1.455 (11)	O(1)-C(25)-C(27)	105.0 (9)
N(1)-N(2)	1.379 (9)	O(1)-C(26)-C(28)	106.2 (8)
N(1)-C(21)	1.395 (10)	C(28)-C(27)-C(25)	108.4 (10)
N(2)-C(24)	1.290 (9)	C(27)-C(28)-C(26)	108.8 (9)
		Cn ^a -Sm-Cn	134.2

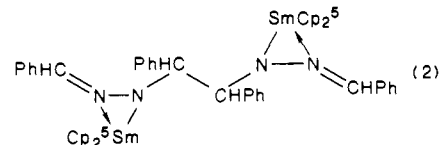
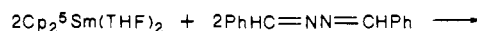
^a Cn is the centroid of the C_5Me_5 ring.(14) Å Sm-N length in $(C_5Me_5)_2SmI$ (tetrazole).³⁰

The samarium atom in complex **1** is formally nine coordinate. Organosamarium(III) complexes containing the $(C_5Me_5)_2Sm$ unit are most commonly eight coordinate, but a few nine-coordinate species are known.^{10,16,25,30,31} In **1**, the average Sm-C(ring) distance of 2.752 (8) Å is typical of bis(pentamethylcyclopentadienyl)Sm(III) complexes as is the (ring centroid)-Sm-(ring centroid) angle of 134.2°. The Sm-O(THF) bond distance of 2.555 (5) Å is slightly longer than the 2.44 (2)-2.511 (4) Å distances found in $(C_5Me_5)_2Sm(THF)(X)$ compounds previously characterized by X-ray crystallography³⁰ (X = Cl, I, C_6H_5 , OR).

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Sm(1)-N(1)	2.315 (13)	N(1)-Sm(1)-N(2)	32.7 (5)
Sm(1)-N(2)	2.431 (14)	N(3)-Sm(2)-N(4)	33.0 (5)
Sm(1)-C(2)	2.73 (2)	N(2)-N(1)-C(41)	116.3 (12)
Sm(1)-C(11)	2.73 (2)	N(2)-N(1)-Sm(1)	78.4 (8)
Sm(1)-C(1)	2.73 (2)	C(41)-N(1)-Sm(1)	163.3 (10)
Sm(1)-C(14)	2.76 (2)	C(42)-N(2)-N(1)	125.3 (13)
Sm(1)-C(13)	2.77 (2)	C(42)-N(2)-Sm(1)	165.7 (11)
Sm(1)-C(15)	2.78 (2)	N(1)-N(2)-Sm(1)	68.8 (8)
Sm(1)-C(5)	2.77 (2)	N(4)-N(3)-C(55)	116.2 (12)
Sm(1)-C(12)	2.78 (2)	N(4)-N(3)-Sm(2)	75.9 (7)
Sm(1)-C(4)	2.80 (2)	C(55)-N(3)-Sm(2)	163.8 (9)
Sm(1)-C(3)	2.82 (2)	C(56)-N(4)-N(3)	125.1 (13)
Sm(2)-N(3)	2.350 (12)	C(56)-N(4)-Sm(2)	163.0 (11)
Sm(2)-N(4)	2.411 (13)	N(3)-N(4)-Sm(2)	71.0 (7)
Sm(2)-C(24)	2.69 (2)	N(1)-C(41)-C(43)	113.0 (13)
Sm(2)-C(25)	2.70 (2)	N(1)-C(41)-C(55)	105.9 (11)
Sm(2)-C(34)	2.73 (2)	C(43)-C(41)-C(55)	113.7 (13)
Sm(2)-C(31)	2.75 (2)	N(2)-C(42)-C(49)	118.4 (16)
Sm(2)-C(21)	2.75 (2)	N(3)-C(55)-C(41)	106.4 (11)
Sm(2)-C(35)	2.76 (2)	N(3)-C(55)-N(1)	141.2 (11)
Sm(2)-C(23)	2.77 (2)	C(57)-C(55)-C(41)	112.6 (12)
Sm(2)-C(32)	2.78 (2)	N(4)-C(56)-C(63)	119.0 (16)
Sm(2)-C(33)	2.78 (2)		
Sm(2)-C(22)	2.78 (2)		
N(1)-N(2)	1.34 (2)		
N(1)-C(41)	1.48 (2)		
N(2)-C(42)	1.28 (2)		
N(3)-N(4)	1.35 (2)		
N(3)-C(55)	1.45 (2)		
N(4)-C(56)	1.32 (2)		
C(41)-C(43)	1.52 (2)		
C(41)-C(55)	1.60 (2)		
C(42)-C(49)	1.48 (2)		

Benzaldehyde Azine. The structure of complex **2** (Figure 2) revealed another example of reductive coupling effected by $(C_5Me_5)_2Sm(THF)_2$ as shown in eq 2 ($Cp^5 = C_5Me_5$, Ph = C_6H_5).



As in the synthesis of **1**, a bimetallic complex is obtained in which each $(C_5Me_5)_2Sm$ unit is coordinated to two adjacent nitrogen atoms. In contrast to **1**, **2** crystallizes without a THF coordinated to the samarium atom; hence, the metal is eight coordinate.

Since crystals of **2** readily desolvated and the solvent in the lattice was disordered, the quality of the structural data on **2** is not optimum. However, the connectivity of the atoms is well-defined and the bond distances and angles (Table VI) are similar to those for complex **1**. The average Sm-C(ring) distance of 2.76 (2) Å, the average (ring centroid)-Sm-(ring centroid) angle of 133°, the Sm-N distances, and the N-N distances are equivalent to those in **1**. The N-C distances are either in the single- or double-bond range,²⁴ not in between, and eq 2 shows their arrangement in **2**. The C(41)-C(55) bond of 1.60 (2) Å which links the two benzaldehyde azines is in the single-bond range.²²

Bipyridine. The reaction of $(C_5Me_5)_2Sm(THF)_2$ with bipyridine differs from the reactions discussed above. With bipyridine a monometallic complex, $(C_5Me_5)_2Sm(\eta^2-N_2C_{10}H_8)$ (**3**), is isolated. The room temperature magnetic susceptibility of this complex, $\chi_M = 2400 \times 10^{-6}$ (cgs), is in between the $(700-1500) \times 10^{-6}$ (cgs) range observed for trivalent $(C_5Me_5)_2Sm$ systems and the $(4800-6000) \times 10^{-6}$ (cgs) range observed for divalent complexes containing the $(C_5Me_5)_2Sm$ unit.²¹ The ¹³C NMR shifts for the C_5Me_5 carbon atoms are characteristic of Sm(III) complexes rather than Sm(II) systems.^{16,17} Specifically, we have observed that for trivalent $(C_5Me_5)_2Sm$ complexes, the ring carbons resonate in the range 113-121 ppm and the methyl carbons in the range 18-28 ppm.^{13,14,16} For divalent $(C_5Me_5)_2Sm$ complexes, the ring

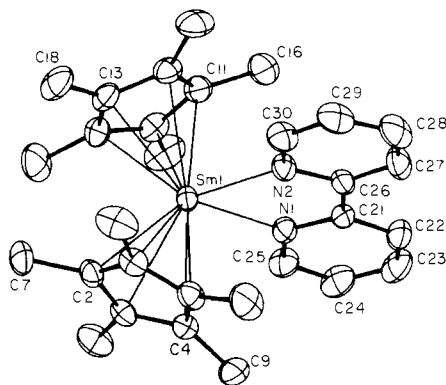


Figure 3. Molecular structure of $(C_5Me_5)_2Sm(\eta^2-N_2C_8H_{10})$ (**3**).

carbons are found from -73 to -99 ppm and the methyl carbons are at 94 – 100 ppm.^{7,17}

Consistent with this apparent oxidation of samarium, the infrared spectrum of **3** exhibits absorptions more typical of a bipyridyl anion³² than of a neutral bipyridine ligand.^{32,33} In particular, the infrared spectrum of **3** has a strong band in the 900 – 1000 - cm^{-1} region and several strong to medium intensity bands in the 1490 – 1575 - cm^{-1} range. These are two characteristic features of reduced bipyridyl systems which differ from neutral bipyridine complexes.³² In addition, the strong absorption in the 755 - cm^{-1} region attributed to an out of plane CH bending mode³⁴ in bipyridine and neutral bipyridine complexes³³ is absent from the spectrum of **3**. The infrared spectrum of $Li(bipy)^{32}$ similarly lacks this absorption.

The UV-visible spectrum of **3** shows four main peaks (with several shoulders) in three different wavelength regions. The spectrum is not similar to that of free bipyridine³⁵ or bipyridyl dianion.^{36,37} The presence of three regions of absorption in the spectrum of **3** is similar to spectra of bipyridyl monoanion^{36,37} and complexes of bipyridyl monoanion.^{37–39}

The structure of **3** is shown in Figure 3, and bond distances and angles are given in Table VII. The overall geometry of **3** is typical of both divalent and trivalent $(C_5Me_5)_2Sm(X)(Y)$ complexes. The plane defined by Sm and the two nitrogen atoms forms a 90.5° dihedral angle with the plane defined by Sm and the two C_5Me_5 ring centroids. The Sm–C(ring) average distance of 2.724 (3) Å is consistent with a trivalent-metal center. The range of Sm–C(ring) averages for trivalent $(C_5Me_5)_2Sm$ complexes is 2.68 – 2.77 Å compared to 2.79 (1)– 2.86 (1) Å for divalent $(C_5Me_5)_2Sm$ species.^{16,17} The Sm–N distances of 2.427 (2) and 2.436 (2) Å are somewhat longer than the 2.31 – 2.36 Å typical for simple Sm(III)–NR₂ bonds (see above) and shorter than the 2.5 – 2.8 Å range typical for Sm(III)–NR₃ bonds. This is consistent with a one-electron reduction of bipyridine in **3**.

Comparisons of these Sm–N distances with the Nd–N distances in the lanthanide bipyridine complex $Nd(TTA)_3(N_2C_{10}H_8)$ ⁴⁰ (**4**) (TTA = thenoyltrifluoroacetato) also support this idea. Eight-coordinate **4** has an average Nd–N distance of 2.71 (2) Å. Since eight-coordinate Nd(III) is larger than eight-coordinate Sm(III) by 0.03 Å,²⁷ a Sm(III)–N(neutral bipyridine) bond of 2.68 Å would be expected. The bond length in **3** is considerably shorter. Ln–N bond length comparisons with $La(\eta^2-NO_3)_3(N_2C_{10}H_8)_2$ ⁴¹ (**5**) are less direct since the bipyridine ligand in **5**

Table VII. Selected Interatomic Bond Distances (Å) and Angles (deg) for $(C_5Me_5)_2Sm(\eta^2-C_{10}H_8N_2)$ (**3**)

Sm(1)–N(2)	2.427 (2)	N(2)–Sm(1)–N(1)	67.05 (9)
Sm(1)–N(1)	2.436 (2)	C(25)–N(1)–C(21)	118.0 (3)
Sm(1)–C(1)	2.705 (3)	C(25)–N(1)–Sm(1)	122.7 (3)
Sm(1)–C(15)	2.719 (3)	C(21)–N(1)–Sm(1)	119.3 (2)
Sm(1)–C(2)	2.723 (3)	C(30)–N(2)–C(26)	118.0 (3)
Sm(1)–C(11)	2.724 (3)	C(30)–N(2)–Sm(1)	122.4 (2)
Sm(1)–C(3)	2.726 (3)	C(26)–N(2)–Sm(1)	119.6 (2)
Sm(1)–C(14)	2.728 (3)	N(1)–C(21)–C(22)	118.9 (3)
Sm(1)–C(12)	2.733 (3)	N(1)–C(21)–C(26)	117.3 (2)
Sm(1)–C(13)	2.735 (3)	C(22)–C(21)–C(26)	123.8 (3)
Sm(1)–C(5)	2.736 (3)	C(23)–C(22)–C(21)	121.6 (4)
Sm(1)–C(4)	2.738 (3)	C(22)–C(23)–C(24)	119.4 (3)
N(1)–C(25)	1.359 (4)	C(25)–C(24)–C(23)	118.2 (4)
N(1)–C(21)	1.378 (4)	N(1)–C(25)–C(24)	123.8 (4)
N(2)–C(30)	1.353 (4)	N(2)–C(26)–C(27)	119.1 (3)
N(2)–C(26)	1.388 (4)	N(2)–C(26)–C(21)	116.7 (2)
C(21)–C(22)	1.421 (4)	C(27)–C(26)–C(21)	124.2 (3)
C(21)–C(26)	1.429 (4)	C(28)–C(27)–C(26)	121.3 (4)
C(22)–C(23)	1.339 (6)	C(27)–C(28)–C(29)	119.6 (4)
C(23)–C(24)	1.397 (7)	C(30)–C(29)–C(28)	118.0 (4)
C(24)–C(25)	1.372 (5)	N(2)–C(30)–C(29)	123.9 (4)
C(26)–C(27)	1.416 (4)	Cent–Sm(1)–Cent	138.0
C(27)–C(28)	1.335 (7)		
C(28)–C(29)	1.414 (7)		
C(28)–C(30)	2.382 (6)		
C(29)–C(30)	1.365 (5)		

has C–C distances different from free bipyridine (see below). The La–N distance in **5** is 2.66 (1) Å and the metal is ten coordinate. Since ten-coordinate La(III) is larger than eight-coordinate Sm(III) by 0.19 Å,²⁷ this would predict a Sm(III)–N(neutral bipyridine) bond of 2.47 Å, if the bipyridine ligand in **5** is neutral. This Ln–N length is much closer to that in **3**.

The Sm–N distances in **3** are shorter than those expected for a Sm(II)–NR₂ or Sm(II)←NR₃ interaction. The bond lengths in **3** are less than the Sm(II)–NR₂ single bond distances found in formally four-coordinate $[(Me_3Si)_2N]_2Sm(THF)_2$, 2.43 (1) Å, and formally six-coordinate $\{[(Me_3Si)_2N]Sm(THF)(DME)(\mu-I)\}_2$, 2.455 (7) Å,⁴² after taking into account the difference in coordination number.²⁷ The Sm–N distances in **3** are also shorter than the Sm(II)←NR₃ donor bond distance of 2.596 (8) Å found in six-coordinate $[SmI_2(NCCMe_3)_2]_n$.⁴³

The metrical parameters in the bipyridyl ligand also suggest the presence of a reduced bipyridyl ligand. The greatest difference among the bipyridyl ligand in **3**, free bipyridine,^{44,45} and bipyridine in **4** and **5** is the C–C length connecting the pyridine rings. In **3** it is 1.429 (4) Å compared to 1.490 (3) Å in the free ligand, 1.50 (3) Å in **4** and 1.450 (17) Å in **5**. The C–N and C–C average lengths in **3**, 1.37 (1) and 1.38 (3) Å, respectively, do not differ greatly from those in free bipyridine [1.344 (2) and 1.387 (2) Å], **4** [1.38 (3) and 1.42 (4) Å], and **5** [1.34 (1) and 1.41 (1) Å]. However, the arrangement of the long and short C–C and C–N bonds in **3** is regular and different from that in bipyridine, **4**, and **5**. The bonding in the bipyridyl ligand in **3** apparently has increased contributions from resonance structures containing double bonds between C(21) and C(26), N(1) and C(25), C(25) and C(24), and C(22) and C(23) (and the corresponding atoms on the other ring). This pattern is very similar to that observed in $Mo(OPr-t)_2(C_{10}H_8N_2)_2$ ⁴⁵ and $(\eta^6-toluene)Fe(C_{10}H_8N_2)_2$,⁴⁶ both of which contain reduced bipyridyl ligands. All of the above structural data agree with the magnetic data in suggesting that Sm(II) has transferred almost a full electron to bipyridine to form

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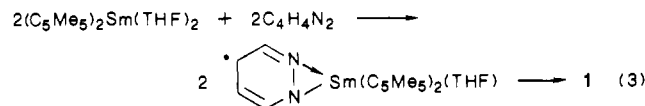
a complex which is most closely described as a Sm^{3+} bipyridyl⁻ compound.

Discussion

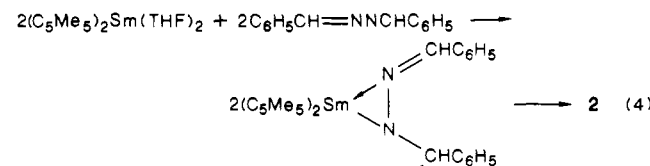
As a result of the large reduction potential of $Sm(II)$,⁴⁷ $(C_5Me_5)_2Sm(THF)_2$ reacts rapidly with pyridazine, benzaldehyde azine, and bipyridine by transferring an electron to the substrate and forming a Sm^{3+} species. Given the reduction potentials of these substrates (pyridazine, -2.30 V vs SCE in DMF;⁴⁸ benzaldehyde azine, -0.72 V vs SCE;⁴⁹ and bipyridine, -1.55 V vs SCE),⁵⁰ an electron-transfer reaction of this type is expected. In contrast to $(C_5Me_5)_2Sm(THF)_2$ reduction of other previously studied unsaturated substrates,^{10,11,13,14} these reactions of C=N-containing molecules do not result in a two-electron reduction of the multiple bond with formation of a Sm_2 (substrate) product. Instead, with pyridazine and benzaldehyde azine, C-C bond formation occurs, a reaction which is best discussed following a summary of substrate-reduction chemistry.

The reduction of pyridazine has previously been studied in liquid ammonia. A stable radical anion, $C_4N_2H_4^-$, is observed which can be further reduced to a dianion.⁵¹ Hydrolysis produces dihydropyridazine. The latter product is also obtained when pyridazine is reduced in DMF containing 2–4% H_2O .⁵² 3,6-Disubstituted pyridazines are similarly reduced to dihydro species.^{49,53,54} Reduction of benzaldehyde azine in the presence of a proton source gives either $PhCH=NNH_2CH_2Ph^+$ or the cleavage product $PhCH=NH_2^+$.⁴⁹ Polarographic studies of bipyridine^{50,54} show two reduction waves. The radical anion initially formed can be readily reoxidized to bipyridine.⁵⁰

With $(C_5Me_5)_2Sm(THF)_2$ as a reductant, pyridazine does not form a dianion $C_4N_2H_4^{2-}$ which is bound to two Sm^{3+} ions. Instead, the one electron reduction product couples at the 4-position to form **1**. This is consistent with Hückel calculations which place the most electron density in the radical anion at the 1- and 4-positions.⁵⁵ The probable sequence is shown in eq 3.



The formation of the coupled benzaldehyde azine product **2** could occur in a similar fashion (eq 4). In both cases, the



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$(C_5Me_5)_2Sm^+$ cation may stabilize the radical anion by coordinating to the two nitrogen positions. The soluble radical intermediate may have a sufficiently long lifetime to give the observed coupled products in high yield.⁵⁶ Such radical coupling is well-established in pyrimidine reductions.⁵⁶ The formation of radicals by the $Sm(II)$ reagent $SmI_2(THF)_2$ is also well preceded.^{2–4}

In the bipyridine reaction, this coupling does not occur presumably because this substrate can readily delocalize the added electron density. Coordination of the bipyridyl anion to the metal can occur without generating a radical at one specific carbon atom, hence coupling does not occur. Reduced bipyridyl systems of this type have been extensively studied.^{32,39,45,46,57–60}

Conclusion

The reaction of $(C_5Me_5)_2Sm(THF)_2$ with the C=N-containing substrates discussed in this paper expands the range of substrates which can be reductively activated in special ways by this organosamarium(II) reducing agent. For the azine substrates, a selective high-yield reduction occurs which provides dimeric products not readily accessible using other reducing agents. This example of $(C_5Me_5)_2Sm(THF)_2$ activation of unsaturated substrates differs from previous studies^{10–14} in that the intermediate radicals formed in these reductions dimerize rather than undergo further reduction. The initial one-electron reduction, which is likely to occur in the pyridazine and benzaldehyde azine reactions and which occurs in the bipyridine reaction, is consistent with the reductive chemistry previously observed for $(C_5Me_5)_2Sm(THF)_2$. The formation of coupled products rather than doubly reduced species such as $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$ ⁶¹ and $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$ ¹² may be related to the specific nature of the radical intermediate which is formed. Hence, in designed activation of unsaturated substrates by $(C_5Me_5)_2Sm(THF)_2$, the stability and location of the initial radical must be considered in order to predict the likely mode of organosamarium activation. Another feature which emerges from this study is the preference for the $(C_5Me_5)_2Sm^{III}$ unit to η^2 -coordinate to two adjacent nitrogen atoms. It is too early to assess the importance of this tendency in guiding the course of $(C_5Me_5)_2Sm(THF)_2$ activation reactions, but this type of $(\eta^2-N,N)Sm(C_5Me_5)_2$ moiety is becoming increasingly common.^{25,30}

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Supplementary Material Available: Tables of complete bond distance and angle data and thermal parameters (9 pages); a listing of observed and calculated structure factor amplitudes (75 pages). Ordering information is given on any current masthead page.

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