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Reactivity of Isocyanides with $(C_5Me_5)_2Sm(THF)_2$: Synthesis and Structure of Trimeric $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$[1]

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$(C_5Me_5)_2Sm(THF)_2$ (1) reacts with cyclohexyl isocyanide and *tert*-butyl isocyanide to form the trimetallic complexes $[(C_5Me_5)_2Sm(CNR)(\mu\text{-}CN)]_3$ [R = C_6H_{11} (2); R = $t\text{-}C_4H_9$ (3)]. Complex 2 crystallizes from toluene at −34 °C with three toluene molecules of crystallization in space group $P2_1/c$ with a = 26.425 (13) Å, b = 13.870 (10) Å, c = 27.206 (19) Å, β = 91.93 (5)°, and D_{calcd} = 1.30 g cm^{-3} for Z = 4 (trimers). Least-squares refinement on the basis of 6825 observed reflections led to a final R value of 0.074. 2 is comprised of three $(C_5Me_5)_2Sm(CNR)$ units which are connected by CN bridges. The three Sm atoms define a nearly equilateral triangle which has Sm–C–N–Sm edges. The $[Sm(\mu\text{-}CN)]_3$ unit is planar to within 0.1 Å. The Sm–C–N and Sm–N–C angles range from 167 to 178°, the Sm–CN and Sm–NC distances average 2.57 (2) Å, the Sm–C(CNR) lengths average 2.58 (2) Å, and the Sm–C(C_5Me_5) average is 2.75 (2) Å.

Introduction

Recent studies of the chemistry of the soluble organometallic Sm(II) complex $(C_5Me_5)_2Sm(THF)_2$ (1)[2] have shown that this compound is capable of unusual transformations of multiply bonded substrates. For example, 1 can reductively homologate three CO molecules to a $O_2CC{=}C{=}O^{2-}$ ketenecarboxylate unit[3] and can activate azobenzene such that double insertion of CO into the N=N bond occurs to form a $(C_6H_5N)OCCO(NC_6H_5)^{2-}$ moiety.[4] To fully exploit the reactivity of 1 with unsaturated substrates, we need to know more about the reactivity of 1 with CO. This system is difficult to study mechanistically, however. In addition to the ketenecarboxylate complex, the 1/CO reaction generates a mixture of several air- and moisture-sensitive paramagnetic products that cannot be chromatographically separated.[3]

One approach to probing the Sm(II)/CO chemistry was to substitute isocyanides for CO. Isocyanides are isoelectronic with CO and often provide useful information when substituted for CO in transition-metal systems.[5-8] Replacement of CO by isocyanide in the above Sm(II) systems could provide some insight into the mechanisms of these transformations. We also considered the possibility that, as an unsaturated substrate, the isocyanide could demonstrate interesting reactivity with 1 independent of any CO related chemistry. Hence, to probe previous reaction systems and to learn more about the chemistry of $(C_5Me_5)_2Sm(THF)_2$, we have studied reactions with isocyanides as described here.

Experimental Section

The complexes described in this paper are air- and moisture-sensitive. Therefore, all syntheses and subsequent manipulations were conducted under nitrogen by using Schlenk, vacuum line and glovebox (Vacuum Atmospheres HE-553 DRI-LAB) techniques. Solvents and $(C_5Me_5)_2Sm(THF)_2$ were prepared as previously described.[2] Cyclohexyl isocyanide and *tert*-butyl isocyanide (Aldrich) were dried over molecular sieves and degassed before use. Physical measurements were obtained as previously described.[9]

$[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$ (2). In the glovebox, excess CNC_6H_{11} (175 mg, 1.6 mmol) in 10 mL of toluene was added dropwise to $(C_5Me_5)_2Sm(THF)_2$ (231 mg, 0.409 mmol) in 10 mL of toluene. The solution turned from purple to red immediately. The amount of solvent was reduced by rotary evaporation, and the concentrated solution was cooled to −34 °C to yield yellow crystals of 2. As discussed below, the X-ray crystal structure of crystals mounted wet with mother liquor showed that this complex

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Table I. Crystal Data for $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3 \cdot 3C_7H_8$

compd	$Sm_3C_{105}H_{147}N_6$
mol wt	1944.56
space group	$P2_1/c$
a, Å	26.425 (3)
b, Å	13.870 (10)
c, Å	27.206 (19)
α, deg	90
β, deg	91.93 (5)
γ, deg	90
cell vol, Å^3	9966
molecules/unit cell	4
ρ(calcd), g cm^{-3}	1.30
μ(calcd), cm^{-1}	17.8
radiatn	Mo Kα
max cryst/dimens, mm	0.24 × 0.47 × 0.58
scan width, deg	−1.2 in 2θ from Kα_1 to +1.2 from Kα_2
std reflctns	004, 040, 400
reflctns measd	13078
2θ range, deg	4–45
obsd reflctns	6825
no. of paramtrs varied	805
GOF	2.12
R	0.074
R_w	0.085

crystallized with toluene of crystallization. Samples separated from the mother liquor changed from clear to opaque within 10 min. The yield, elemental analysis, and IR spectrum were obtained on samples which were dried on a rotary evaporator and which contained no toluene of crystallization. The yield of the above reaction was 108 mg (47%) which was obtained from several recrystallizations. Once the crystals of **2** formed, they were no longer very soluble in toluene. The initially isolated crystals dissolved in THF, but within an hour precipitation occurred. Anal. Calcd for $SmC_{28}H_{41}N_2$: Sm, 27.03; C, 60.48; H, 7.43; N, 5.04. Found: Sm, 27.40; C, 60.47; H, 6.85; N, 4.88. IR (KBr): 2960–2860 s, 2180 m, 2105 m, 1440 m, 1390 w, 1370 w, 1020 m, 890 w cm^{-1}; after washing with THF, 2990–2870 s, 2110 m, 1450 m, 1390 w, 1070 m, 1025 m, 910 w cm^{-1}. ^{1}H NMR (C_4D_8O): δ 1.0–1.8, variable depending on the amount of CNC_6H_{11} present, (s, C_5Me_5); other absorptions are present in the aliphatic region but could not be definitively assigned to coordinated or free CNC_6H_{11}.

Separation of the yellow crystals of **2** left a red mother liquor. Removal of solvent from this solution and extraction with hexane gave a red solution. Filtration to separate residual **2** and removal of solvent gave a very soluble red product which exhibited one main singlet in its ^{1}H NMR spectrum in C_6D_6 at 1.65 ppm. Anal. Found: Sm, 24.80; C, 63.82; H, 8.48; N, 2.92. Compare Calcd for $(C_5Me_5)_2SmC_6H_{11}CNC_6H_{11}$ (see Results): Sm, 24.52; C, 64.65; H, 8.55; N, 2.28. IR (KBr); 2920 s, 2860 s, 1555 w, 1500 w, 1445 m, 1340 w, 1260 m, 1200 m, 1095 w, 1020 w, 885 w, 800 w cm^{-1}.

X-ray Crystallography of $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3 \cdot 3C_7H_8$. General procedures for data collection and reduction have been described previously.[10] A crystal measuring 0.24 × 0.47 × 0.58 mm was sealed with some mother liquor under N_2 in a glass capillary and mounted on a Syntex P2$_1$ diffractometer. Lattice parameters were determined at 24 °C from the angular settings of 15 computer-centered reflections. Data were collected by the θ–2θ scan technique in bisecting geometry. The *p* factor[11] in the expression 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 data collection, the intensities of three standard reflections measured every 100 reflections exhibited linear decay of 20%; the intensities of the data were corrected for this decay. No absorption correction was applied due to the irregular shape of the crystal and the presence of some mother liquor on the crystal. Systematic absences (0*k*0, *k* odd; *h*0*l*, *l* odd) established the space group as $P2_1/c$ (No. 14). A combination of direct methods (MULTAN[12]) and difference Fourier techniques provided the locations of all nonhydrogen atoms. All atoms except the toluene and cyclohexyl isocyanide carbon atoms were refined with anisotropic thermal parameters using full-matrix least-squares methods. The toluene and cyclohexyl isocyanide carbon atoms were refined isotropically. The largest peak in a final difference map had a height of 2.2 e Å^{-3} and was about 1 Å from the C91 and C92 atoms of one of the toluene molecules of crystallization. Final fractional coordinates are given in Table II.

$[(C_5Me_5)_2Sm(CNCMe_3)(\mu\text{-}CN)]_3$ (3). Excess Me_3CNC (190 mg, 2.29 mmol) in 10 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 turned yellow immediately. Yellow crystals of **3** (110 mg, 58%) were obtained from the concentrated reaction mixture at −34 °C. Like **2**, crystals of **3** were not very soluble in toluene and in THF began to form a precipitate after an hour. Anal. Calcd for $SmC_{26}H_{39}N_2$: Sm, 28.4. Found: Sm, 28.9. IR (KBr): 2990–2870 s, 2180 m, 2110 m, 1450 m, 1390 w, 1260 w, 1020 m, 800w cm^{-1}. ^{1}H NMR (C_6D_8O): δ 0.9–1.5, variable depending on the amount of excess $CNCMe_3$ present, (s, C_5Me_5); other absorptions are present in the aliphatic region but could not be definitively assigned to coordinated or free $CNCMe_3$.

Single crystals of $[(C_5Me_5)_2Sm(CNCMe_3)(\mu\text{-}CN)]_3$ containing two THF molecules of crystallization were obtained from THF at −34 °C and were examined by X-ray crystallography.[13,14] The quality of the data set was limited by high thermal motion primarily from the THF molecules. The X-ray data did reveal a structure essentially equivalent to that of $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$.[14]

Results

Synthesis and Spectral Characterization. The addition of CNC_6H_{11} or $CNCMe_3$ to $(C_5Me_5)_2Sm(THF)_2$ in toluene causes the originally purple Sm(II) solution to change to red or yellow, colors characteristic of Sm (III) organometallic complexes.[15] When these solutions are concentrated and cooled, the yellow products $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$ (**2**) and $[(C_5Me_5)_2Sm(CNCMe_3)(\mu\text{-}CN)]_3$ (**3**) are obtained. Complex **3** was also obtained by reacting $CNCMe_3$ with $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$.[16]

Complexes **2** and **3** each have two absorptions in the ν_{CN} region, one at 2180 and one at 2105–2110 cm^{-1}. These can be compared with the ν_{CN} absorptions of CNC_6H_{11} and $CNCMe_3$ at 2138 and 2134 cm^{-1}, respectively.[7,17] The 2180 cm^{-1} band in **2** and **3** matches the ν_{CN} absorption position found in the IR spectrum of the crystallographically characterized $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$[18] and suggests the presence of a coordinated isocyanide ligand. Increases in ν_{CN} upon coordination of isocyanides to lanthanides are normal: structurally characterized $(C_5H_5)_3Pr(CNC_6H_{11})$[19] has ν_{CN} at 2208[20] cm^{-1} and the $(C_5H_5)_3Ln(CNC_6H_{11})$ series (Ln = Y, Nb, Tb, Ho, Yb)[21] has ν_{CN} between 2203 and 2208

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(13) $[(C_5Me_5)_2Sm(CNCMe_3)(\mu\text{-}CN)]_3 \cdot 2THF$ crystallizes in space group $P\bar{1}$ with $a = 13.107$ (6) Å, $b = 14.018$ (9) Å, $c = 24.972$ (15) Å, $\alpha = 92.80$ (7)°, $\beta = 94.51$ (7)°, $\gamma = 95.27$ (5)°, and $D_{calcd} = 1.27$ g cm^{-3} for $z = 2$ (trimers). Least-squares refinement on the basis of 3807 observed reflections led to a final *R* value of 0.093.[14]

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Table II. Atomic Positional Parameters for $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3 \bullet 3C_7H_8$

atom	x	y	z	atom	x	y	z
Sm(1)	0.19555 (4)	0.01358 (7)	0.86103 (3)	C(53)	0.1294 (10)	−0.1686 (13)	0.6079 (10)
Sm(2)	0.11961 (4)	0.01549 (7)	0.63972 (3)	C(54)	0.1213 (11)	−0.1772 (14)	0.6584 (9)
Sm(3)	0.35232 (4)	0.05119 (7)	0.69286 (4)	C(55)	0.0454 (12)	−0.1524 (20)	0.7122 (10)
N(04)	0.0513 (6)	−0.0024 (14)	0.8553 (6)	C(56)	−0.0093 (10)	−0.1123 (18)	0.6063 (12)
N(05)	0.1818 (8)	0.0493 (13)	0.5159 (7)	C(57)	0.0759 (10)	−0.1315 (18)	0.5266 (8)
N(06)	0.4313 (7)	0.0711 (14)	0.8113 (7)	C(58)	0.1803 (9)	−0.2027 (19)	0.5846 (9)
CN(01)	0.1573 (6)	0.0134 (14)	0.7732 (6)	C(59)	0.1583 (9)	−0.2179 (15)	0.6965 (9)
CN(02)	0.1395 (7)	0.0093 (12)	0.7331 (7)	C(60)	0.0572 (11)	0.1574 (16)	0.6736 (12)
CN(03)	0.2187 (8)	0.0305 (13)	0.6529 (6)	C(61)	0.1054 (10)	0.2019 (14)	0.6671 (8)
CN(04)	0.2627 (7)	0.0386 (14)	0.6606 (6)	C(62)	0.1125 (8)	0.2067 (13)	0.6146 (9)
CN(05)	0.2994 (8)	0.0379 (13)	0.7697 (7)	C(63)	0.0702 (9)	0.1653 (15)	0.5904 (8)
CN(06)	0.2718 (7)	0.0304 (12)	0.8034 (7)	C(64)	0.0354 (10)	0.1356 (15)	0.6256 (12)
C(04)	0.0954 (9)	0.0039 (16)	0.8604 (8)	C(65)	0.0321 (10)	0.1475 (19)	0.7208 (9)
C(05)	−0.0103 (13)	−0.0112 (25)	0.8363 (13)	C(66)	0.1384 (9)	0.2473 (16)	0.7050 (9)
C(06)	−0.0336 (12)	0.0917 (22)	0.8500 (12)	C(67)	0.1575 (9)	0.2592 (16)	0.5913 (8)
C(07)	−0.0354 (12)	0.1074 (23)	0.9031 (12)	C(68)	0.0603 (9)	0.1629 (17)	0.5344 (9)
C(08)	−0.0514 (13)	0.0257 (26)	0.9363 (12)	C(69)	−0.0206 (9)	0.1082 (17)	0.6139 (13)
C(09)	−0.0267 (12)	−0.0679 (24)	0.9226 (12)	C(70)	0.3711 (9)	0.2443 (14)	0.7094 (8)
C(10)	−0.0258 (12)	−0.0911 (22)	0.8709 (12)	C(71)	0.4142 (9)	0.2094 (15)	0.6805 (10)
C(11)	0.1638 (8)	0.0329 (16)	0.5530 (8)	C(72)	0.3955 (10)	0.1883 (15)	0.6332 (9)
C(12)	0.1978 (11)	0.0870 (19)	0.4654 (10)	C(73)	0.3423 (12)	0.2069 (15)	0.6297 (8)
C(13)	0.2504 (13)	0.0644 (24)	0.4678 (11)	C(74)	0.3261 (10)	0.2378 (13)	0.6763 (9)
C(14)	0.2610 (15)	−0.0420 (29)	0.4658 (15)	C(75)	0.3726 (11)	0.2867 (18)	0.7613 (8)
C(15)	0.2364 (18)	−0.0891 (30)	0.4223 (16)	C(76)	0.4690 (8)	0.2126 (19)	0.6985 (10)
C(16)	0.1823 (14)	−0.0627 (27)	0.4219 (12)	C(77)	0.4299 (11)	0.1797 (19)	0.5883 (11)
C(17)	0.1702 (11)	0.0359 (23)	0.4243 (11)	C(78)	0.3087 (9)	0.2008 (18)	0.5831 (8)
C(18)	0.4112 (8)	0.0642 (16)	0.7743 (8)	C(79)	0.2729 (8)	0.2743 (16)	0.6894 (9)
C(19)	0.4600 (10)	0.0897 (19)	0.8609 (9)	C(80)	0.3860 (11)	−0.1316 (15)	0.7113 (9)
C(20)	0.4502 (10)	0.1809 (19)	0.8782 (10)	C(81)	0.4277 (9)	−0.0895 (17)	0.6886 (10)
C(21)	0.4713 (13)	0.1918 (25)	0.9327 (13)	C(82)	0.4102 (11)	−0.0726 (16)	0.6397 (9)
C(22)	0.4516 (11)	0.1172 (21)	0.9634 (10)	C(83)	0.3605 (12)	−0.1042 (19)	0.6323 (10)
C(23)	0.4583 (12)	0.0179 (23)	0.9484 (12)	C(84)	0.3418 (11)	−0.1414 (16)	0.6795 (9)
C(24)	0.4341 (11)	0.0021 (20)	0.8905 (11)	C(85)	0.3852 (11)	−0.1714 (18)	0.7640 (8)
C(30)	0.2230 (11)	−0.1732 (14)	0.8541 (9)	C(86)	0.4798 (9)	−0.0772 (19)	0.7090 (10)
C(31)	0.2523 (10)	−0.1497 (17)	0.8949 (11)	C(87)	0.4485 (10)	−0.0526 (20)	0.5978 (10)
C(32)	0.2182 (13)	−0.1224 (16)	0.9324 (10)	C(88)	0.3308 (9)	−0.1025 (19)	0.5837 (8)
C(33)	0.1653 (10)	−0.1461 (16)	0.9170 (9)	C(89)	0.2930 (9)	−0.1917 (15)	0.6848 (10)
C(34)	0.1729 (11)	−0.1895 (14)	0.8679 (9)	C(90)	0.1794 (12)	0.5124 (21)	0.6828 (11)
C(35)	0.2413 (10)	−0.2076 (16)	0.8053 (10)	C(91)	0.233 (2)	0.523 (3)	0.636 (2)
C(36)	0.3104 (10)	−0.1283 (19)	0.8974 (9)	C(92)	0.257 (2)	0.542 (3)	0.682 (2)
C(37)	0.2387 (13)	−0.1082 (21)	0.9867 (9)	C(93)	0.261 (2)	0.538 (3)	0.732 (2)
C(38)	0.1243 (11)	−0.1518 (20)	0.9481 (10)	C(94)	0.225 (2)	0.524 (3)	0.769 (2)
C(39)	0.1282 (11)	−0.2197 (16)	0.8369 (11)	C(95)	0.174 (2)	0.514 (3)	0.744 (2)
C(40)	0.2121 (11)	0.2061 (15)	0.8608 (8)	C(96)	0.600 (2)	0.135 (2)	0.865 (2)
C(41)	0.2461 (8)	0.1711 (14)	0.8976 (9)	C(97)	0.618 (2)	0.122 (3)	0.915 (2)
C(42)	0.2170 (12)	0.1429 (15)	0.9367 (9)	C(98)	0.630 (2)	0.006 (3)	0.936 (2)
C(43)	0.1654 (10)	0.1545 (16)	0.9239 (10)	C(99)	0.609 (2)	−0.025 (3)	0.880 (2)
C(44)	0.1626 (11)	0.1984 (15)	0.8756 (10)	C(100)	0.592 (2)	−0.009 (3)	0.835 (2)
C(45)	0.2266 (10)	0.2543 (16)	0.8119 (9)	C(101)	0.580 (2)	0.094 (3)	0.806 (2)
C(46)	0.3040 (10)	0.1770 (18)	0.8966 (10)	C(102)	0.576 (2)	0.070 (4)	0.555 (2)
C(47)	0.2361 (12)	0.1208 (19)	0.9884 (9)	C(103)	0.592 (2)	−0.023 (4)	0.560 (2)
C(48)	0.1227 (10)	0.1368 (18)	0.9580 (10)	C(104)	0.613 (2)	−0.051 (3)	0.612 (2)
C(49)	0.1149 (9)	0.2307 (18)	0.8488 (10)	C(105)	0.613 (2)	0.039 (4)	0.643 (2)
C(50)	0.0699 (11)	−0.1487 (15)	0.6663 (10)	C(106)	0.597 (2)	0.134 (3)	0.614 (2)
C(51)	0.0494 (9)	−0.1232 (15)	0.6173 (11)	C(107)	0.567 (2)	0.188 (4)	0.557 (2)
C(52)	0.0853 (10)	−0.1365 (14)	0.5827 (9)				

cm^{-1}. $[(Me_3Si)_2N]_3Nd(CNCMe_3)$[22] has ν_{CN} at 2195 cm^{-1}. If samples of **2** and **3** are washed with THF, they lose solubility and their IR spectra no longer contain the 2180 cm^{-1} absorption in the ν_{CN} region. Only the 2105–2110 cm^{-1} absorptions are observed. Their assignment will be discussed after the X-ray data are presented.

Useful NMR data on **2** and **3** were difficult to obtain. Once the crystals precipitated from toluene, they were no longer very soluble in arene solvents. As described above, THF induced changes in the complexes and made them less soluble. The NMR data we could obtain together with the IR data suggest that the decrease in solubility is due to the loss of coordinated isocyanide ligands (see below). If freshly obtained crystals were thoroughly dried by rotary evaporation, they exhibited very low solubility. NMR data could be obtained on crystals that had not been fully dried, but the positions of the C_5Me_5 shifts were variable due to the presence of varying amounts of CNR and toluene. Hence, only a range of C_5Me_5 resonance positions can be reported: 1.0–1.8 ppm for **2** and 0.9–1.5 ppm for **3** in THF-d_8. In all cases just a single C_5Me_5 peak is observed, and after 1–2 days the sample had precipitated from solution completely.

Structural Analysis. Given the dearth of spectroscopic information, X-ray crystallographic characterization was attempted. Although the X-ray data on the $CNCMe_3$ complex **3** established the basic structure,[13,14] the quality of the X-ray data did not allow as good a refinement as desired. Hence, the CNC_6H_{11} complex was also studied. Tables III and IV contain data on bond distances and angles.

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Table III. Selected Interatomic Distances (Å) for $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$

Sm(1)–CN(06)	2.60 (2)	Sm(2)–C(63)	2.79 (2)
Sm(1)–CN(01)	2.57 (2)	Sm(2)–C(64)	2.82 (2)
Sm(1)–C(04)	2.67 (2)	Sm(3)–CN(04)	2.49 (2)
Sm(1)–C(30)	2.70 (2)	Sm(3)–CN(05)	2.56 (2)
Sm(1)–C(31)	2.74 (2)	Sm(3)–C(18)	2.66 (2)
Sm(1)–C(32)	2.75 (2)	Sm(3)–C(70)	2.76 (2)
Sm(1)–C(33)	2.83 (2)	Sm(3)–C(71)	2.76 (2)
Sm(1)–C(34)	2.77 (2)	Sm(3)–C(72)	2.78 (2)
Sm(1)–C(40)	2.70 (2)	Sm(3)–C(73)	2.77 (2)
Sm(1)–C(41)	2.72 (2)	Sm(3)–C(74)	2.72 (2)
Sm(1)–C(42)	2.78 (2)	Sm(3)–C(80)	2.73 (2)
Sm(1)–C(43)	2.74 (2)	Sm(3)–C(81)	2.81 (2)
Sm(1)–C(44)	2.73 (2)	Sm(3)–C(82)	2.75 (2)
Sm(2)–CN(02)	2.59 (2)	Sm(3)–C(83)	2.73 (2)
Sm(2)–CN(03)	2.64 (2)	Sm(3)–C(84)	2.70 (2)
Sm(2)–C(11)	2.68 (2)	CN(02)–CN(01)	1.16 (2)
Sm(2)–C(50)	2.74 (2)	CN(03)–CN(04)	1.18 (2)
Sm(2)–C(51)	2.74 (2)	CN(06)–CN(05)	1.17 (2)
Sm(2)–C(52)	2.75 (2)	N(04)–C(04)	1.17 (2)
Sm(2)–C(53)	2.71 (2)	N(04)–C(05)	1.68 (4)
Sm(2)–C(54)	2.71 (2)	N(05)–C(11)	1.15 (2)
Sm(2)–C(60)	2.76 (2)	N(05)–C(12)	1.56 (3)
Sm(2)–C(61)	2.73 (2)	N(06)–C(18)	1.12 (2)
Sm(2)–C(62)	2.75 (2)	N(06)–C(19)	1.54 (3)

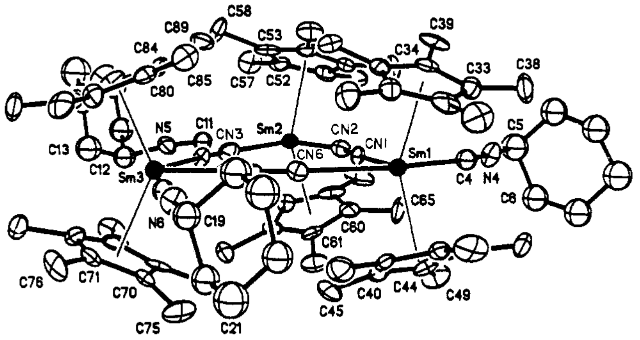

Figure 1. Molecular structure of $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$ (**2**).

X-ray crystallography established that both **2** and **3** are trimeric complexes with the formula $[(C_5Me_5)_2Sm(CNR)(\mu\text{-}CN)]_3$ (**2**, R = C_6H_{11}; **3**, R = CMe_3). As shown in Figure 1, the three $(C_5Me_5)_2Sm(CNR)$ units are connected via μ-CN bridges. The presence of the cyanide ligand explains the origin of the other ν_{CN} absorption at 2105–2110 cm^{-1} in the infrared spectra of **2** and **3**. This band can be attributed to the bridging cyanide ligand and is close to the ν_{CN} absorptions found in the infrared spectrum of $Sm(CN)_3$[23] at 2130 and 2115 cm^{-1}. As is common in X-ray studies of cyanide complexes,[24] the X-ray data did not differentiate between C and N in these bridges. Moreover, there was no clear pattern of distances that would indicate the relative orientation of the CN bridges with respect to each other around the triangle, i.e., Sm(1)–C–N–Sm(2) or Sm(1)–N–C–Sm(2) etc. Accordingly, the cyanide bridge atoms have been called CN(1), CN(2), CN(3), etc. rather than arbitrarily labeling one a carbon and another a nitrogen. Hence, CN(X), where X is a number, in the following discussion always refers to a single atom.

The three samarium atoms in **2** define a triangle which is equilateral within experimental error (Sm–Sm distances of 6.28, 6.29, and 6.30 Å). Each side of this triangle contains a bridging cyanide ligand. The Sm–CN(X)–CN(Y) angles in these sides approach linearity with a range of 166.8 (16) to 177.4 (16)° and an average of 172 (2)°. The CN(X)–Sm–CN(Y) angles of the triangle are 72.5 (14), 74.2 (15), and 75.2 (14)°. The nine atoms in the $[Sm(\mu\text{-}CN)]_3$ unit comprise a nine-membered ring which is planar to within 0.04 Å.

Each samarium atom in **2** and **3** is attached to two C_5Me_5 rings, one terminal isocyanide ligand, and two bridging cyanide units for a formal coordination number of nine. Eight is the more common coordination number for complexes containing trivalent $(C_5Me_5)_2Sm$ units,[18] although a number of nine-coordinate structures recently have been described.[3,18,25,26] All of the nine-coordinate $(C_5Me_5)_2SmL_3$ complexes have at least two of the L groups connected in the form of a bidentate or tridentate ligand and frequently one of the L groups has a rather long Sm–L distance. Complexes **2** and **3** also formally fit this description since the two cyanide ligands attached to a given samarium atom are connected (by a $[(C_5Me_5)_2Sm]_2CN$ link) and the isocyanide samarium distances are long (see below).

The Sm–C(C_5Me_5) average distance in **2** is 2.75 (2) Å. This average is on the long end of the range of values previously observed for trivalent $(C_5Me_5)_2Sm$ complexes, 2.68 (1)[27]–2.80 (1) Å.[18] The (ring centroid)–Sm–(ring centroid) angles of 133.0–135.1° are well within the normal range, 130–138°.[2]

The average Sm–C(isocyanide) bond distance in **2** is 2.58 (2) Å. This distance is comparable to the 2.62 (1) and 2.66 (1) Å Sm–C($CNCMe_3$) distances found in the eight-coordinate complex $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$ (**4**)[18] and the 2.65 (1) Å Pr–C(CNC_6H_{11}) distance in ten-coordinate $(C_5H_5)_3Pr(CNC_6H_{11})$ (**5**).[19] Since the size of ten-coordinate Pr^{3+} is significantly larger than that of eight- or nine-coordinate Sm^{3+},[28] it appears that the similar Pr–CNR distance is consistent with a stronger interaction in **5** than is present in **2** and **4**. This is consistent with the IR data: the ν_{CN} stretch for **5** is 70 cm^{-1} greater than that in the free isocyanide compared to a 36–46 cm^{-1} increase in ν_{CN} for **2** and **4**. The longer distance and lower ν_{CN} in **4** were attributed to steric crowding,[18] and the same is likely in **2**.

The CN(X)–CN(Y) distances of the ambidentate cyanide ligands in **2** average 1.17 (2) Å. These distances are consistent with the presence of a triple bond in a cyanide ligand.[24] The Sm–CN(X) distances in **2** range from 2.49 (2) to 2.64 (2) Å and average 2.57 (2) Å. To our knowledge there are no structurally characterized lanthanide cyanide complexes with which to compare these distances.[29] In fact, very few organolanthanide cyanide complexes are known.[30] Within the 3σ error range, the average Sm–CN(X) distance is comparable to typical Sm–C σ bond distances, such as those in $(C_5Me_5)_2Sm(C_6H_5)$ (THF),[31] 2.511 (8) Å, and $(C_5Me_5)_2Sm(CH_2C_6H_5)(THF)$,[32] 2.528 (8) Å. The average Sm–CN(X) distance is longer than typical

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Table IV. Selected Interatomic Angles (deg) for $[(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)]_3$

CN(01)–Sm(1)–C(04)	68.4 (14)	Sm(1)–CN(06)–CN(05)	166.8 (16)	Sm(2)–C(11)–N(05)	173.7 (16)
CN(01)–Sm(1)–CN(06)	74.2 (15)	Sm(1)–C(04)–N(04)	173.4 (16)	C(13)–C(12)–C(17)	113.1 (26)
CN(06)–Sm(1)–C(04)	142.5 (15)	C(04)–N(04)–C(05)	168.8 (22)	C(13)–C(12)–N(05)	99.5 (23)
CN(02)–Sm(2)–C(11)	142.2 (15)	C(11)–N(05)–C(12)	168.3 (24)	C(17)–C(12)–N(05)	111.2 (23)
CN(02)–Sm(2)–CN(03)	72.5 (14)	C(18)–N(06)–C(19)	178.2 (24)	C(12)–C(13)–C(14)	114.2 (30)
CN(03)–Sm(2)–C(11)	69.6 (14)	C(10)–C(05)–C(06)	112.1 (26)	C(15)–C(14)–C(13)	112.0 (34)
CN(04)–Sm(3)–CN(05)	75.2 (14)	C(10)–C(05)–N(04)	98.3 (24)	C(16)–C(15)–C(14)	107.2 (37)
CN(04)–Sm(3)–C(18)	144.4 (15)	C(06)–C(05)–N(04)	104.0 (24)	C(17)–C(16)–C(15)	117.2 (34)
CN(05)–Sm(3)–C(18)	69.4 (14)	C(07)–C(06)–C(05)	112.3 (27)	C(16)–C(17)–C(12)	112.5 (28)
Sm(1)–CN(01)–CN(02)	177.3 (16)	C(06)–C(07)–C(08)	119.8 (29)	Sm(3)–C(18)–N(06)	172.3 (16)
CN(01)–CN(02)–Sm(2)	167.3 (16)	C(09)–C(08)–C(07)	112.2 (29)	C(20)–C(19)–C(24)	114.1 (23)
CN(04)–CN(03)–Sm(2)	177.4 (16)	C(10)–C(09)–C(08)	116.3 (29)	C(20)–C(19)–N(06)	105.0 (21)
Sm(3)–CN(04)–CN(03)	169.6 (16)	C(09)–C(10)–C(05)	117.5 (29)	C(24)–C(19)–N(06)	101.2 (21)
Sm(3)–CN(05)–CN(06)	175.4 (16)				

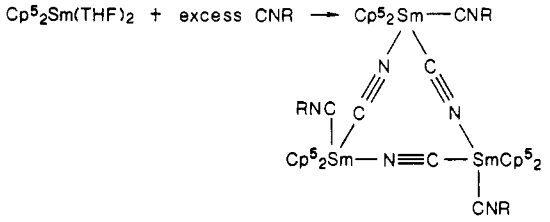
Sm-NR_2 σ bonds, such as those in $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$,[16] 2.40 (1) Å, and $[(C_5Me_5)(THF)Sm]_2[N_2(C_6H_5)_2]_2$,[33] 2.333 (9) Å. However, the Sm–CN(X) averages are in the range of Sm←:NR_3 donor bonds,[33] 2.5–2.8 Å, as well as the range of Sm←:CNR donor bonds, 2.58 (2)–2.66 (1) Å (see above). Hence, these distances are reasonable for a CN^- anion bridging through both the carbon and nitrogen atoms.

Discussion

Replacement of CO by isocyanides in reactions 1[3] and 2[4] ($Cp^5 = C_5Me_5$; Ph = C_6H_5) does not give analogous products. Instead of participating in a reductive homologation as in eq 1, reductive cleavage of the isocyanide is effected to give cyanide ligands as shown in eq 3.

$$4Cp^5_2Sm(THF)_2 + 6CO \rightarrow [(Cp^5_2Sm)_2(\mu\text{-}\eta^4\text{-}O_2CC{=}C{=}O)(THF)]_2 + 6THF \quad (1)$$

$$[Cp^5_2Sm]_2N_2Ph_2 + 2CO \rightarrow [Cp^5_2Sm]_2[\mu\text{-}\eta^4\text{-}(PhN)OCCO(NPh)] \quad (2)$$



(3)

Despite the propensity of isocyanides to undergo insertion reactions,[5-8] $CNCMe_3$ does not react with $[(C_5Me_5)_2Sm]_2N_2(C_6H_5)_2$ via an insertion route. Instead this samarium reagent also reductively cleaves the N–C single bond in the isocyanide to form **3**.

Cleavage of the N–C single bond in isocyanides to form cyanide ligands has been described previously in the literature but only under rather harsh conditions. For example, reductive cleavage of isocyanides can be effected by alkali metals in liquid ammonia as shown in eq 4 (M

$$CNR + 2M + NH_3 \rightarrow MCN + MNH_2 + RH \quad (4)$$

= Li, Na, or K).[34] Phosphorus[35] and tin[36] radicals generated by treating organophosphorus and organotin hydrides with azobis(isobutyronitrile) or di-*tert*-butyl peroxide are also known to accomplish this cleavage (eq 5 and 6). A number of cationic transition-metal polyisocyanide

$$R^\bullet + R'_2PH \xrightarrow{-RH} R'_2P^\bullet \xrightarrow{CNR''} R'_2PCN + R''^\bullet \quad (5)$$

$$R^\bullet + R'_3SnH \xrightarrow{-RH} R'_3Sn^\bullet \xrightarrow{CNR''} R'_3SnCN + R''^\bullet \quad (6)$$

complexes, $M(CNR)_xL_y^{n+}$ ($x = 4$–7; y = variable), thermally decompose to cyanide species[37-42] and thermolysis of $Ru(Me_2PCH_2CH_2PMe_2)_2$(naphthyl)H at 60 °C for 22 h in the presence of $CNCMe_3$ gives the cyanide complex $Ru(Me_2PCH_2CH_2PMe_2)_2(CN)_2$ plus Me_3CCN, naphthalene, isobutene, and isobutane.[43] The transition-metal-based isocyanide dealkylation most closely related to this samarium system is the thermolysis of the complexes $(C_5Me_5)_2V(CNR)$ and $(C_5Me_5)_2V(CNR)(CO)$ to form $(C_5Me_5)_2V(CN)(CNR)$ and $(C_5Me_5)_2V(CN)$.[44]

The fact that $(C_5Me_5)_2Sm(THF)_2$ can accomplish this reductive cleavage rapidly under mild conditions attests to the powerful reactivity of this divalent samarium complex. Parallels between $(C_5Me_5)_2Sm(THF)_2$ and the alkali metals and radicals have been previously noted.[3,15,26,45,46] However, $(C_5Me_5)_2Sm(THF)_2$ has some advantages compared to alkali metals and radicals. It is soluble in a variety of solvents, in contrast to the alkali metals which require liquid ammonia, and it is readily prepared, in contrast to the radicals described above which must be generated in situ by radical initiators.

This $(C_5Me_5)_2Sm(THF)_2$ reaction provides an unusual example of a trimeric cyanide-bridged complex. Although dimeric[39] and polymeric bridged cyanide complexes are known,[24] relatively few discrete polymetallic cyanide-bridged complexes have been structurally characterized. One rare example of this is the tetramer [*closo*-3-PPh_3-3-(μ-CN)-3,1,2-$RhC_2B_9H_{11}]_4$ (**6**).[47] This complex is similar to **2** and **3** in that each metal is connected to two nearly linear (170–176°) cyanide bridges to make a figure (in this case four-sided) with metal–C–N–metal sides. Simply stated, the Sm(III) fragment, $(C_5Me_5)_2Sm$, and the Rh(III) fragment, $Ph_3PRhC_2B_9H_{11}$, are binding to two bridging

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cyanide ligands in a similar way. Given the marked differences between Sm(III) and Rh(III), it is unusual to find them in such similar bonding situations.

To our knowledge, complex 2 represents the first crystallographically characterized molecular lanthanide cyanide complex.[29] Although simple lanthanide cyanides have been known since 1972[23] and organometallic lanthanide cyanides such as $(C_5H_5)_2NdCN$ and $(C_5H_5)_2YbCN$ are reported in the literature,[30] no other molecular species have been studied by diffraction techniques.

These samarium-based isocyanide dealkylation reactions (eq 3) also produce organosamarium byproducts which may incorporate the R groups cleaved from the isocyanide ligands. In the cyclohexyl isocyanide system, a byproduct is isolated which has a complete elemental analysis consistent with the formula $(C_5Me_5)_2Sm(C_6H_{11}CNC_6H_{11})$. No evidence for cyclohexane, cyclohexene, or bicyclohexyl was found in the reaction mixture (in contrast to the $(C_5Me_5)_2V/CNC_6H_{11}$ system that forms cyclohexane[44]). An iminoacyl complex such as $(C_5Me_5)_2Sm(C_6H_{11}CNC_6H_{11})$ is a reasonable byproduct of reaction 3 based on the mechanism postulated for the dialkyl phosphorus and trialkyltin reactions (eq 5 and 6) and the isocyanide intermediates isolated in the $(C_5Me_5)_2V$ system. Hence, the isocyanide reagent could displace one or two THF molecules from $(C_5Me_5)_2Sm(THF)_2$ to form $(C_5Me_5)_2Sm(THF)(CNR)$ or $(C_5Me_5)_2Sm(CNR)_2$. Electron transfer would give the radical $(C_5Me_5)_2LSm^{III}\dot{C}{=}NR$ (L = THF or CNR) which could fragment to $(C_5Me_5)_2LSm(CN)$ and $R^{\cdot}$. A $(C_5Me_5)_2Sm(CNR)(CN)$ complex (analogous to the structurally characterized $(C_5Me_5)_2V(CNR)(CN)$[44]) could trimerize to **2** or **3**. $R^{\cdot}$ could combine with the $(C_5Me_5)_2LSm\dot{C}{=}NR$ intermediate to form $(C_5Me_5)_2Sm(RC{=}NR)$ plus L. Consistent with this, the byproduct of the cyclohexyl isocyanide reaction has an infrared absorption at 1555 cm^{-1} which is in the range observed for early-transition-metal iminoacyl complexes.[48–50] However, definitive identification by X-ray crystallography of the extremely soluble organosamarium byproduct of eq 3 has not yet been accomplished.

Conclusion

$(C_5Me_5)_2Sm(THF)_2$ has been found to promote facile cleavage of the C–N single bond in isocyanides to form the trimeric cyanide complexes $[(C_5Me_5)_2Sm(CNR)(\mu\text{-}CN)]_3$ (R = CMe_3, C_6H_{11}). This reaction demonstrates the potential of $(C_5Me_5)_2Sm(THF)_2$ for selective bond-breaking reactions that require strongly reducing conditions. In addition, this reaction provides an interesting trimeric cyanide-bridged species.

Acknowledgment. We thank the National Science Foundation for support of this research, Professor Robert J. Doedens for helpful discussions regarding the crystallography at UCI, and Professor Jerry L. Atwood and Hongming Zhang for providing the first X-ray data on a system of this type.[13,14] Access to the Cambridge Structural Database was provided by the San Diego Supercomputer Center with the support of the National Science Foundation.

Registry No. 1, 79372-14-8; 2, 112041-54-0; 2·3C_7H_8, 112041-55-1; 3, 112068-62-9; 3·2THF, 112068-63-0; CNC_6H_{11}, 931-53-3; Me_3CNC, 7188-38-7; $(C_5Me_5)_2SmC_6H_{11}CNC_6H_{11}$, 112021-60-0.

Supplementary Material Available: Tables of complete interatomic distances and angles and thermal parameters (6 pages): a listing of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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Studies on Rare Earth–Indenyl Compounds. 2. Synthesis and Crystal Structure of Hexakis(tetrahydrofuran)sodium (μ-Chloro)bis(triindenylneodymate)

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By the reaction of lanthanide trichloride with indenylsodium in THF solution the title complex $[Na(C_4H_8O)_6][Nd(\eta^5\text{-}C_9H_7)_3(\mu\text{-}Cl)Nd(\eta^5\text{-}C_9H_7)_3]$ was synthesized and characterized by elemental analysis, infrared spectrum, molar conductivity, and X-ray diffraction analysis. The compound crystallized in the triclinic space group $P\bar{1}$ with a = 10.701 (2) Å, b = 12.697 (3) Å, c = 12.838 (2) Å, α = 92.55 (2)°, β = 97.95 (2)°, γ = 88.28 (2)°, and Z = 1. The structure was determined by direct methods and refined by full-matrix least squares to the final R = 0.046 for 6843 observed reflections.

Introduction

Although a series of lanthanide–indenyl compounds, $Ln(C_9H_7)_3{\cdot}THF$, were synthesized and studied by Tsutsui et al. in 1969 (where Ln = La, Sm, Gd, Tb, Dy, Yb)[1] and by Huang et al. in 1985 (where Ln = Ce, Nd, Y),[2] the related crystal structural research has been rather limited.[3]

Here we report the preparation and structural characterization of the first lanthanide–indenyl compound con-

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