Reactivity of $(C_5Me_5)_2Sm(THF)_2$ with Nitriles: C−C Bond Cleavage To Form Cyanide Complexes

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The divalent organosamarium complex $(C_5Me_5)_2Sm(THF)_2$ (**1**) reacts in toluene with Me_3CCN to form the insoluble trivalent cyanide complex $[(C_5Me_5)_2SmCN]_n$ (**2**). The Me_3CCN reaction was found to proceed through divalent $(C_5Me_5)_2Sm(NCCMe_3)(THF)_x$ (**3**). The bis(nitrile) analogue of **3**, $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (**4**), is isolable from the reaction of **1** with Me_3CCN in THF and has been characterized by X-ray crystallography. Both **3** and **4** transform via C−C bond cleavage to form the cyanide product **2** and $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (**5**). Complex **5** is the product of insertion of Me_3CCN into a Sm−H bond presumably formed by β-hydrogen elimination of a Me_3C intermediate. Complexes **2** and **5** can also be generated by the stoichiometric reaction of crystalline **4** with **1** in toluene. Complex **5** can be synthesized directly from the reaction of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ with Me_3CCN and THF. Crystallographic data on the related nitrile adducts $[(C_5Me_5)_2Sm(NCCMe_3)(\mu\text{-}CN)]_3$ (**6**) and $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (**7**) are also reported.

Introduction

The Sm^{2+} metallocenes $(C_5Me_5)_2Sm(THF)_2$[1] and $(C_5Me_5)_2Sm$[2] can effect reductive transformations on unsaturated substrates in a variety of ways.[3,4] For example, substrates such as diphenylacetylene,[5,6] azobenzene,[7] bis(2-pyridyl)ethylene,[8] N_2,[9] styrene,[10] stilbene,[10] isoprene,[6] and anthracene[11] form bimetallic complexes with the formula $[(C_5Me_5)_2Sm]_2$(substrate dianion). Substrates such as pyridazine,[12] benzaldehyde azine,[12] phosphaalkynes,[13] and CO_2[14] are reductively dimerized. Additional modes of reactivity include polymerization of ethylene[15] and R−N cleavage in isocyanides, RNC (R = CMe_3, C_6H_{11}).[16] Information on the reactivity of these divalent metallocenes with nitriles, RCN, has not yet been reported to our knowledge, however.

The reactivity of the $(C_5Me_5)_2Sm(THF)_x$ complexes with nitriles is of interest not only because these constitute another class of unsaturated substrates, but also because nitriles are potential solvents for electrochemical studies of lanthanide complexes.[17−19] Since cyanide is a pseudohalide and $(C_5Me_5)_2Sm(THF)_x$ complexes react readily with alkyl halides, RX, to form $(C_5Me_5)_2SmX(THF)$ compounds,[17,19−21] reductive cleavage of nitriles to form the cyanide complex $[(C_5Me_5)_2SmCN]_n$ seemed possible.[22] Crystallographically characterizable complexes of this type were obtained as isocyanide adducts, $[(C_5Me_5)_2Sm(CNR)(\mu\text{-}CN)]_3$[16] (R = CMe_3, C_6H_{11}), from isocyanide reactions. We have found that C−C cleavage can occur but that additional complexes are accessible depending on the particular nitrile. We report here in detail on the reactivity of Me_3CCN with $(C_5Me_5)_2Sm(THF)_2$ (**1**), which includes adduct formation, C−C bond cleavage to form cyanide products, and formation of products derived from insertion of nitriles into Sm−H bonds formed from β-hydrogen elimination of intermediate alkyl complexes.

Experimental Section

The manipulations described below were conducted under argon or nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with UHP argon and dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotope Laboratories) were dried over sodium−potassium alloy, degassed, and vacuum-transferred

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before use. Me_3CCN, PhCN, $PhCH_2CN$, and 2-pyridylnitrile (Aldrich) were dried over molecular sieves and vacuum-transferred. Anhydrous MeCN (Aldrich Sure-Seal) was used as received. $(C_5Me_5)_2Sm(THF)_2$[1] (**1**) and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$[23] were prepared according to the literature. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 spectrometer at 25 °C. Infrared spectra were recorded on Perkin-Elmer 283 and Perkin-Elmer 1620 FTIR spectrophotometers. Elemental analyses were performed by Analytische Laboratorien (Lindlar, Germany).

General Reactions of 1 with Nitriles in Toluene. When a toluene solution of **1** was mixed with a toluene solution containing an equimolar amount of the nitrile RCN (R = Me_3C, Me, Ph, $PhCH_2$, 2-pyridyl) in a glovebox, a color change to dark green was observed. Subsequent centrifugation of the reaction mixture separated an orange precipitate with an infrared spectrum that matched the spectrum of the material which forms when $[(C_5Me_5)_2Sm(\mu\text{-}CNCMe_3)(\mu\text{-}CN)]_3$ desolvates:[16] i.e., $[(C_5Me_5)_2SmCN]_n$ (**2**). The remaining yellow solution contained at least one additional (pentamethylcyclopentadienyl)samarium compound which decomposed over a 30 min to 72 h period, depending on the nitrile and the concentration of the reaction mixture, to yield other products containing $[(C_5Me_5)_2Sm]^+$ units by NMR spectroscopy. In general, (a) the presence of THF inhibits the reaction of **1** with nitriles, (b) less concentrated reactions proceed more quickly, and (c) cleaner products are obtained when solutions of the nitrile are added to solutions of **1**, in contrast to reactions in which the nitriles are syringed directly into solutions of **1**.

Reaction of 1 with Me_3CCN in Toluene: Formation of the Initial Adduct $(C_5Me_5)_2Sm(NCCMe_3)(THF)_x$ (3). In a glovebox, a solution of Me_3CCN (21 μL, 0.19 mmol) in toluene (2 mL) was added to a solution of **1** (109 mg, 0.193 mmol) in toluene (4 mL). The color immediately changed to dark green. Attempts to definitively characterize this product, **3**, were complicated by its limited stability at room temperature and its low solubility at low temperature. Isolated samples were contaminated with toluene that could not be removed under vacuum (10^{-4} Torr) without significant decomposition of **3** in the solid state. Low-temperature NMR spectra were not obtainable, due to the limited solubility. The ^1H NMR spectrum in C_6D_6 at room temperature contained resonances 2−3 ppm wide, due in part to the formation of insoluble material (**2**) during data collection. Complex **3** is more stable in THF, and the ^1H NMR spectrum in THF-d_8 contained resonances at δ 3.04 (s, 9H) and 2.55 (s, 30H) consistent with the presence of a $(C_5Me_5)_2Sm(NCCMe_3)(THF)_x$ unit. IR (KBr): 2860 s br, 2230 w, 2180 w, 1670 w br, 1595 w br, 1230 s, 1380 m, 1235 m, 1010 m, 870 m, 790 w, 730 m, 690 m cm^{-1}. Solutions of **3** cooled overnight to −35 °C repeatedly generated small green needles, but they were usually not suitable for X-ray diffraction. In one case, a data set was collected that showed the composition $(C_5Me_5)_2Sm(NCCMe_3)_2$, a product of ligand redistribution, but the quality of the data did not allow a discussion of metrical parameters. The crystal had the unit cell parameters $a = 18.3542$ Å, $b = 18.3542$ Å, $c = 21.5482$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 6286.528$ Å^3, and space group $P6_1$.

$(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (4). In a glovebox, Me_3CCN (78 μL, 0.72 mmol) in THF (2 mL) was added to a purple solution of **1** (203 mg, 0.36 mmol) in THF (2 mL). A black solution immediately formed. Dark brown crystals of **4** suitable for X-ray diffraction were grown by cooling the solution to −35 °C overnight (152 mg, 64%). ^1H NMR (THF-d_8): δ 3.53 ppm (s, Me_3CCN, 18H), 2.94 (s, C_5Me_5, 30H). ^{13}C NMR (THF-d_8): δ 98.2 (C_5Me_5), 43.2 (Me_3CCN), −72.3 (C_5Me$_5$). IR (KBr): 3000−2850 s, 2241 m, 1699 w, 1652 w, 1258 s, 1371 m, 1240 s, 1210 w, 1044 s, 889 m cm^{-1}. Anal. Calcd for $C_{34}H_{56}N_2OSm$: C, 61.95; H, 8.56; N, 4.25; Sm, 22.81. Found: C, 61.71; H, 8.56; N, 4.38; Sm, 23.08.

Formation of $[(C_5Me_5)_2SmCN]_n$ (2) and $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (5). In a glovebox, addition of Me_3CCN (55 μL, 0.504 mmol) in toluene (3 mL) to a solution of **1** (285 mg, 0.504 mmol) in toluene (10 mL) immediately generated a dark green solution that faded to brown-orange after 1 h. After the reaction mixture was stirred for 12 h, the brown-orange solution was evaporated to dryness, yielding an orange solid that was extracted with hexane to give a yellow solution. The orange precipitate was washed with toluene to remove residual $(C_5Me_5)_2Sm(NCCMe_3)(THF)_x$ (**3**). The remaining orange insoluble product was identified as **2** (99 mg, 44%) by its IR spectrum (KBr; 2964 sh, 2903 s, 2862 s, 2103 m, 1492 w, 1436 m, 1380 w, 1067 vw, 1021 w, 805 vw, 728 w, 692 w cm^{-1}), which matches that in the literature,[16] and by elemental analysis. (Anal. Calcd for $C_{21}H_{30}NSm$: C, 56.45; H, 6.77; N, 3.13; Sm, 33.65. Found: C, 56.14; H, 6.65; N, 3.02; Sm, 33.84.) Hexane was removed from the yellow solution under vacuum to leave **5** as a yellow solid (133 mg, 46%). ^1H NMR (C_6D_6): δ 1.94 (s, CMe_3, 9H), 1.54 (s, C_5Me_5, 30H), −0.8 and −1.0 (two broad overlapping resonances; THF, 8H). ^{13}C NMR (C_6D_6): δ 111.0 (C_5Me$_5$), 65.6 (THF), 29.4 (N=CHCMe_3), 21.8 (THF), 15.3 (C_5Me_5). IR (KBr): 2913 s, 2861 s, 2708 w, 2615 w, 2564 w, 2359 w, 1677 s, 1441 m, 1374 w, 1210 w, 1082 w, 1020 w, 913 vw, 867 m cm^{-1}. Anal. Calcd for $C_{29}H_{48}NOSm$: C, 60.36; H, 8.38; N, 2.43; Sm, 26.06. Found: C, 60.14; H, 8.27; N, 2.50; Sm, 26.42.

Synthesis of 2 and 5 from 4. In a glovebox, **1** (42 mg, 0.074 mmol) in toluene was added to crystalline $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (**4**; 49 mg, 0.074 mmol). The reaction mixture gradually turned green as **4** slowly dissolved. After it was stirred for 3 h, the reaction mixture was worked up as described above to yield $[(C_5Me_5)_2SmCN]_n$ (**2**; 30 mg, 45%) and $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (**5**; 43 mg, 50%), which were identified by IR and NMR spectroscopy, respectively.

Generation of 5 from $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$. In a glovebox, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ (11.7 mg, 0.014 mmol) was dissolved in C_6D_6 in an NMR tube. Me_3CCN (3 μL, 0.028 mmol) and THF (2 μL, 0.028 mmol) were syringed into this solution. The color changed from orange to yellow as the tube was shaken thoroughly. Complex **5** was identified by NMR spectroscopy as the quantitative product.

X-ray Data Collection, Structure Determination, and Refinement Details for $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (4). A dark brown crystal of approximate dimensions 0.22 × 0.23 × 0.24 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[24] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[25] and SADABS[26] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[27] program. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group *Pbcn*, which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[28] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. The molecule was located on a 2-fold rotation axis. The tetrahydrofuran ligand was disordered. Atoms C(16) and C(17) were included using multiple components, partial site occupancy factors, and isotropic displacement parameters. At convergence, wR2 = 0.0732 and GOF

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Table 1. X-ray Data Collection Parameters for $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (4), $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (5), $[(C_5Me_5)_2Sm(NCCMe_3)(\mu\text{-}CN)]_3$ (6), and $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (7)

	4	5	6	7
empirical formula	$C_{34}H_{56}N_2OSm$	$C_{29}H_{48}NOSm$	$C_{78}H_{117}N_6\text{-}Sm_3{\cdot}3C_7H_8$	$C_{50}H_{78}N_2\text{-}Sm_2{\cdot}C_6H_6$
formula wt	659.16	577.03	1866.23	1101.95
temp (K)	163(2)	163(2)	163(2)	163(2)
cryst syst	orthorhombic	orthorhombic	hexagonal	monoclinic
space group	*Pbcn*	$P2_12_12_1$	$P6_3/m$	$P2_1/c$
a (Å)	16.4213(13)	12.5460(12)	20.3157(8)	15.335(4)
b (Å)	12.2471(10)	13.3491(12)	20.3157(8)	13.726(3)
c (Å)	16.9408(14)	16.9911(16)	14.2464(9)	26.895(7)
α (deg)	90	90	90	90
β (deg)	90	90	90	102.477(4)
γ (deg)	90	90	120	90
V (Å^3)	3407.0(5)	2845.6(5)	5092.1(4)	5527(2)
Z	4	4	2	4
ρ_{calcd} (Mg/m^3)	1.285	1.347	1.217	1.324
μ (mm^{-1})	1.749	2.083	1.750	2.140
R1[a] ($I > 2.0\sigma(I)$)	0.0262	0.0246	0.0651	0.0345
wR2[b] (all data)	0.0732	0.0604	0.2046	0.0942

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

= 1.172 for 179 variables refined against 4225 data (0.75 Å). As a comparison for refinement on *F*, R1 = 0.0262 for those 2925 data with $I > 2.0\sigma(I)$. Details are given in Table 1.

X-ray Data Collection, Structure Determination, and Refinement Details for $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (5). A yellow crystal of approximate dimensions 0.13 × 0.25 × 0.26 mm was handled as described for **4**. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$, which was later determined to be correct. At convergence, wR2 = 0.0604 and GOF = 1.070 for 303 variables refined against 7026 data. As a comparison for refinement on *F*, R1 = 0.0246 for those 5803 data with $I > 2.0\sigma(I)$. The structure was refined using the SHELXTL TWIN command (BASF = 0.405-(12)).

X-ray Data Collection, Structure Determination, and Refinement Details for $[(C_5Me_5)_2Sm(NCCMe_3)(\mu\text{-}CN)]_3$ (6). In one reaction of $(C_5Me_5)_2Sm(THF)_2$ (**1**) with Me_3CCN in toluene, yellow crystals formed over the course of 1 week. A yellow crystal of approximate dimensions 0.20 × 0.26 × 0.38 mm was handled as described above. The Laue group was 6/*m*, and the systematic absences were consistent with the hexagonal space groups $P6_3$ and $P6_3/m$. It was later determined that the correct space group was $P6_3/m$. The molecule was a trimer and was located about a site of $\bar{6}$ symmetry. Carbon atoms C(13)−C(16) were included using partial site occupancy factors to account for disorder. There were three molecules of toluene solvent present per trimeric formula unit. The solvent was located on a mirror and disordered, resulting in the methyl carbon being included with site occupancy 0.50. The ring hydrogen associated with the disordered methyl position was not included. Final least-squares analysis yielded wR2 = 0.2046 and GOF = 1.164 for 158 variables refined against 3030 data (0.85 Å). As a comparison for refinement on *F*, R1 = 0.0651 for those 2241 data with $I > 2.0\sigma(I)$.

X-ray Data Collection, Structure Determination, and Refinement Details for $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (7). In one attempt to crystallize **5** from benzene, decomposition to the oxide $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (**7**) occurred. Oxide formation of this type is common.[29,30] A yellow crystal of approximate dimensions 0.20 × 0.23 × 0.33 mm was handled as described for **4**. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$, which was later determined to be correct. There was one molecule of benzene solvent present per formula unit. Carbon atoms C(42)−C(45) and the solvent molecule were disordered. These atoms were included using multiple components, partial site occupancy factors, and isotropic displacement parameters. Carbons C(42)−C(45) were assigned the same isotropic displacement parameters (EADP). The benzene solvent was refined as a regular hexagon. At convergence, wR2 = 0.0942 and GOF = 1.082 for 510 variables refined against 13 136 data (0.76 Å). As a comparison for refinement on *F*, R1 = 0.0345 for those 11 071 data with $I > 2.0\sigma(I)$.

Results

General Reactivity of 1 with Nitriles in Toluene. When a solution containing an equimolar amount of RCN (R = Me_3C, Me, Ph, $PhCH_2$, and 2-pyridyl) in toluene is added to a purple solution of $(C_5Me_5)_2Sm(THF)_2$ (**1**) in toluene, an immediate color change to dark green is observed. This color fades within 20 s to 24 h, depending on the nitrile and the concentration of the solution, and a precipitate forms. The analytical and infrared data on this insoluble product match those of $[(C_5Me_5)_2SmCN]_n$ (**2**), which has previously been observed when the crystallographically characterized cyanide complexes $[(C_5Me_5)_2Sm(RNC)(\mu\text{-}CN)]_3$ (R = CMe_3, C_6H_{11}) desolvate.[16] Accompanying the formation of **2** is at least one other samarium-containing product that is unstable under the reaction conditions. This is presumably derived from the alkyl group of the cleaved RCN. It is well-known that complexes of the type $[(C_5Me_5)_2SmR]_n$ are highly reactive.[17,19,21,31−33] In the $PhCH_2CN$ and Me_3CCN reactions, the insoluble cyanide product is observed within 1 h. For the other nitriles, observable amounts of insoluble product are formed after 12 h. The reaction of **1** with Me_3CCN has been studied in detail and the results are presented below.

Reactivity of 1 with Me_3CCN in THF. The reaction of **1** with Me_3CCN in THF is described first, since it gives an adduct which could be definitively identified by X-ray crystallography. One equivalent of **1** in THF reacts with 2 equiv of Me_3CCN to form a black solution, which can be stirred for 3 days in THF with no observable change. Dark brown crystals can be obtained from THF at −35 °C that were identified by X-ray crystallography as $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (**4**) (eq 1, Figure 1).

$$(C_5Me_5)_2Sm(THF)_2 + 2Me_3CCN \xrightarrow[-THF]{} \underset{\mathbf{4}}{(C_5Me_5)_2Sm(NCCMe_3)_2(THF)} \quad (1)$$

When a 1:1 mixture of **1** with Me_3CCN is stirred in THF and recrystallized, the bis(nitrile) adduct **4** is again isolated, rather than a mono(nitrile) adduct such as $(C_5Me_5)_2Sm(NCCMe_3)(THF)$ or $(C_5Me_5)_2Sm(NCCMe_3)(THF)_2$.

The intense color and the ^{13}C NMR spectrum of **4** are consistent with the presence of Sm^{2+}.[34] The infrared spectrum contained an absorption at 2241 cm^{-1} that is similar to the ν_{CN} 2246 cm^{-1} band in $[Sm(\mu\text{-}I)_2(NCCMe_3)_2]_n$, and is close to the absorption for free Me_3CCN at 2231 cm^{-1}.[35] Previous examples of nitriles coordinated to lanthanides have given infrared

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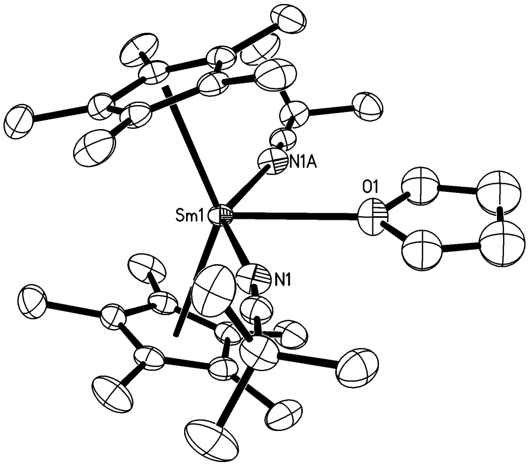

Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (**4**), with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been excluded for clarity.

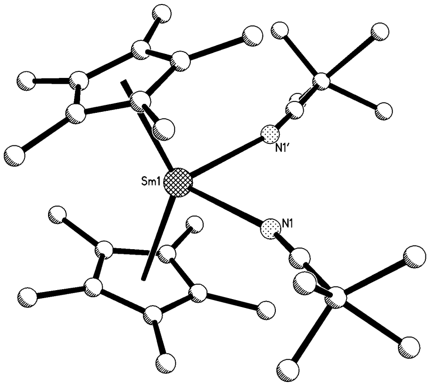

Figure 2. Ball and stick plot of $(C_5Me_5)_2Sm(NCCMe_3)_2$.

absorptions slightly higher than those of the free nitrile. For example, $(C_5Me_5)_2CeI(NCMe)_2$ has ν_{CN} 2299 and 2267 cm^{-1}, compared to ν_{CN} 2293 and 2257 cm^{-1} for free MeCN.[36]

Reactivity of 1 with Me_3CCN in Toluene. As in the THF reaction, addition of Me_3CCN to **1** in toluene causes an immediate color change, but in this solvent, a dark green compound $(C_5Me_5)_2Sm(NCCMe_3)(THF)_x$ (**3**), is formed. Characterization of **3** has been hindered by the fact that it is not very soluble and quickly decomposes in solution. The ^1H NMR spectrum of **3** in THF-d_8 contains resonances for C_5Me_5 and Me_3CCN in a 30:9 ratio which suggest the composition $(C_5Me_5)_2Sm(NCCMe_3)(THF)_x$, a composition closely related to that of divalent **4**. The infrared spectrum of **3** contains an absorption at 2230 cm^{-1}, which is very similar to the ν_{CN} band for the coordinated nitrile of **4**, as well as absorptions characteristic of coordinated THF. The dark green color is indicative of Sm^{2+}.[37] Clusters of thin green needles can be obtained from toluene solutions of **3** at −35 °C, but they do not diffract X-rays very well. In one case, they revealed the ligand redistribution product $(C_5Me_5)_2Sm(NCCMe_3)_2$ (Figure 2), but the data were too poor to allow a detailed discussion.

When **3** is not isolated, it transforms within 24 h to the insoluble orange species $[(C_5Me_5)_2SmCN]_n$ (**2**) and a yellow material, $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (**5**). The ^1H NMR spectrum of **5** in C_6D_6 contains one C_5Me_5 resonance, two THF resonances, and a resonance at 1.94 ppm attributable to the $(N{=}CHCMe_3)^-$ ligand. The ^{13}C NMR spectrum is consistent with the trivalent oxidation state of this complex[34] as well as the presence of THF. Although the ^{13}C resonance for the methyl groups of the $(N{=}CHCMe_3)^-$ ligand was found, neither of the other carbon resonances could be located. Since these spectroscopic data were not structurally definitive, a sample of **5** was recrystallized from hexane at −35 °C and characterized by X-ray crystallography as $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (**5**) Figure 3.

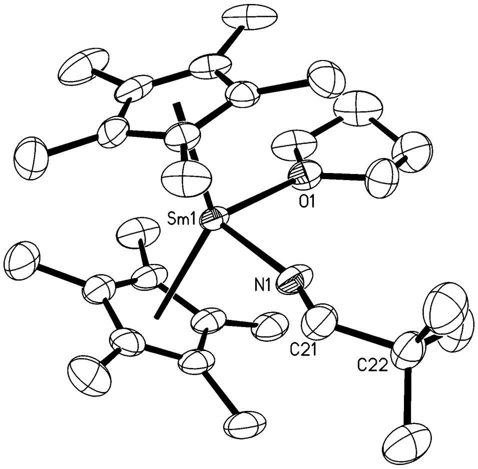

Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (**5**), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been excluded for clarity.

Complex **5** can be formally viewed as a THF adduct of the product of inserting Me_3CCN into the Sm−H bond of a $[(C_5Me_5)_2Sm(\mu\text{-H})]_2$ unit. Indeed, **5** can be independently generated in an NMR-scale experiment by this route (eq 2). Since

$$[(C_5Me_5)_2Sm(\mu\text{-H})]_2 + 2Me_3CCN + 2THF \rightarrow \underset{\mathbf{5}}{2(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)} \quad (2)$$

formation of a cyanide from Me_3CCN would leave a Me_3C group which could eliminate a β-hydrogen to form a hydride, a reasonable route for the formation of **5** is shown in Scheme 1. Attempts to identify isobutene in the reaction mixtures by ^1H NMR spectroscopy were complicated by the fact that the products are paramagnetic and complex **2** readily precipitates during analysis, but resonances at 4.71 and 1.72 ppm in toluene-d_8 were observed that are close to the resonances of isobutene in a diamagnetic solution.[38]

Complexes **2** and **5** also form from **4** in toluene. Complex **4** forms **2** and **5** very slowly in THF (only after 10 days or more), but crystalline samples of **4** decompose quickly in toluene to form a dark green material which reacts as it dissolves to form **2** and **5**.

In one reaction of $(C_5Me_5)_2Sm(THF)_2$ with Me_3CCN in toluene, the Me_3CCN adduct of **2**, namely $[(C_5Me_5)_2Sm(NCCMe_3)(\mu\text{-CN})]_3$ (**6**), was isolated and crystallographically characterized (Figure 4). Although the connectivity of the complex was established, the data were not good enough to discuss metrical parameters. Complex **6** is similar to the isocyanide analogue $[(C_5Me_5)_2Sm(CNCMe_3)(\mu\text{-CN})]_3$ isolated earlier.[16]

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Scheme 1

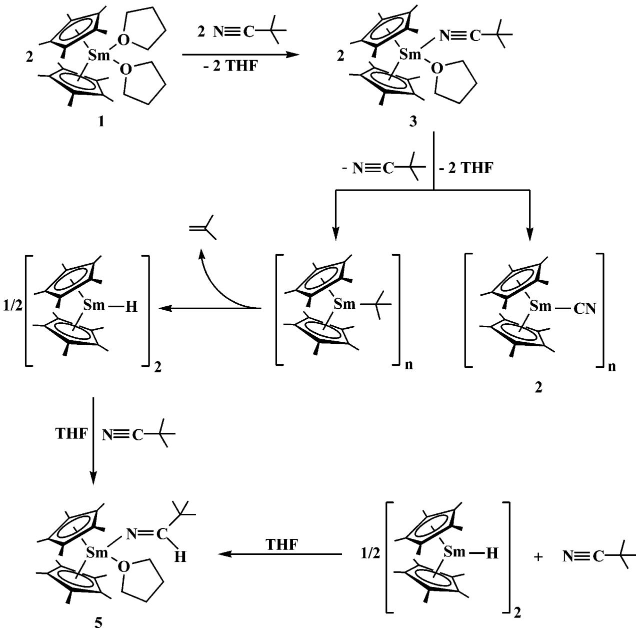

Table 2. Selected Bond Distances (Å) and Angles (deg) in $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (4)

Sm(1)−Cnt	2.598	Sm(1)−O(1)	2.716(3)
Sm(1)−C(C_5Me_5) av	2.86(3)	N(1)−C(11)	1.145(4)
Sm(1)−N(1)	2.735(3)	C(11)−C(12)	1.481(4)
Cnt1−Sm(1)−Cnt2	139.3	Cnt−Sm(1)−O(1)	110.3
Cnt−Sm(1)−N(1)	95.6	O(1)−Sm(1)−N(1)	73.52(6)

In one attempt to crystallize **5** from benzene, the oxide decomposition product $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (**7**) was isolated and crystallographically characterized (Figure 5). Formation of oxides of this type is common in this metallocene chemistry of these oxophilic metals.[29,30]

Structural Results. $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (4). Complex **4** (Figure 1) has a typical bent-metallocene structure, but it is the first structurally characterized nine-coordinate divalent $(C_5Me_5)_2Sm$-containing complex. Although the average Sm−C(C_5Me_5) distance of 2.86(3) Å (Table 2) is identical with the 2.86(3) Å distance in eight-coordinate $(C_5Me_5)_2Sm(THF)_2$ (**1**),[1] the 2.716(3) Å Sm−O(THF) distance in **4** is longer than the 2.64(2) Å distance in **1**, as anticipated. As expected for a high-coordinate complex, the 2.735(3) Å Sm−N distance in **4** is much longer than the 2.596(8) Å Sm−N bond in six-coordinate $[Sm(\mu\text{-}I)_2(NCCMe_3)_2]_n$.[35] The Sm−N distance in **4** is comparable to the 2.586(7) and 2.544(6) Å Yb−N distances in divalent $(C_5Me_5)_2Yb(NC_5H_5)_2$[39] and the 2.55(3) Å distance in $(C_5Me_5)_2Yb(NH_3)(THF)$,[40] when the 0.18 Å difference in radius of eight-coordinate Yb^{2+} and nine-coordinate Sm^{2+} is considered.[41] The THF ligand is located between the two nitriles in the equatorial plane of the bent metallocene. The samarium center and the oxygen and two nitrogen donor atoms are coplanar.

$(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (5). Complex **5** has a structure typical of trivalent eight-coordinate $(C_5Me_5)_2SmZL$ complexes (Z = monoanionic monodentate ligand, L = neutral monodentate ligand). The average Sm−C(C_5Me_5) distance of 2.73(8) Å and the Sm−O distance of 2.495(3) Å are within the normal range (Table 3).[42] The Sm−N distance of 2.204(3) Å is nearly 0.1 Å shorter than the 2.301(3) Å Sm−N bond in $(C_5Me_5)_2Sm[N(SiMe_3)_2]$[43] and the shortest Sm−N distance in $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}HNNH)$[44] (2.313(4) Å). This short distance is accompanied by a 158.3(3)° Sm(1)−N(1)−C(21) angle. The 1.254(4) Å C−N bond distance in **5** is comparable to the 1.275(6) Å distance in $[(C_5H_5)_2Y(\mu\text{-}\eta^2\text{-}HC{=}NCMe_3)]_2$[45] and is, as expected, longer than the 1.145(4) Å distance in **4**. The 126.8(4)° N(1)−C(21)−C(22) angle is in the range expected.

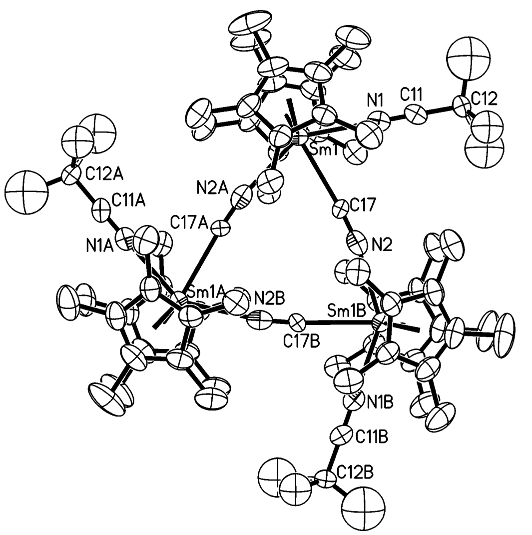

Figure 4. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm(NCCMe_3)(\mu\text{-}CN)]_3$ (**6**), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been excluded for clarity.

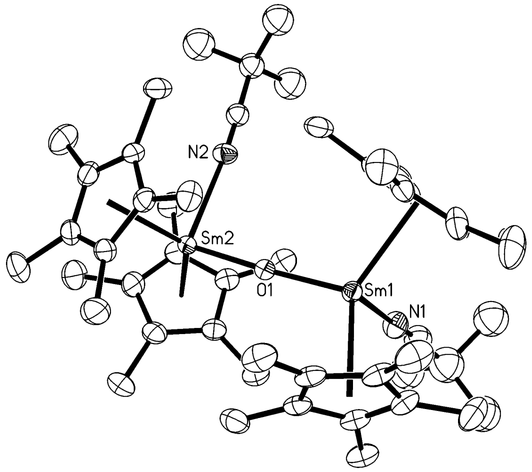

Figure 5. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (**7**), with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms have been excluded for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) in $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (5)

Sm(1)−Cnt	2.453/2.455	Sm(1)−O(1)	2.495(3)
Sm(1)−C(C_5Me_5) av	2.73(8)	N(1)−C(21)	1.254(4)
Sm(1)−N(1)	2.204(3)	C(21)−C(22)	1.537(5)
Cnt1−Sm(1)−Cnt2	138.5	N(1)−Sm(1)−O(1)	97.36(10)
Cnt−Sm(1)−N(1)	102.2/103.2	C(21)−N(1)−Sm(1)	158.3(3)
Cnt−Sm(1)−O(1)	104.1/104.5	N(1)−C(21)−C(22)	126.8(4)

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Table 4. Selected Bond Distances (Å) and Angles (deg) in $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (7) and $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$ (8)

	7	8
Sm−Cnt	2.504/2.513 2.502/2.518	2.516/2.538 2.517/2.545
Sm(1)−C(C_5Me_5) av	2.78(2)	2.80(1)
Sm−O(1)	2.107(2)/2.115(2)	2.101(7)/2.117(7)
Sm−N($NCCMe_3$)	2.530(3)/2.545(3)	n/a[a]
Sm−C($CNCMe_3$)	n/a	2.62(1)/2.66(1)
N−$CCMe_3$	1.139(6)/1.144(5)	n/a
C−$NCMe_3$	n/a	1.13(2)/1.12(2)
Cnt1−Sm−Cnt2	132.3/133.1	133.5/131.9
Sm(1)−O(1)−Sm(2)	173.03(13)	174.3(4)
O(1)−Sm−N($NCCMe_3$)	97.49(10)/99.30(11)	n/a
O(1)−Sm−C($CNCMe_3$)	n/a	98.7(4)/100.7(4)

[a] n/a = not applicable.

$[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (7). The structure of $[(C_5Me_5)_2Sm(NCCMe_3)]_2(\mu\text{-}O)$ (**7**) is very similar to that of $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$[46] and matches well with the data compiled on $[(C_5R_5)_2LnL]_2(\mu\text{-}O)$ complexes in general.[30] Crystals of complex **7** were obtained with one benzene per molecule in the lattice, whereas $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$ had one molecule of toluene in the lattice. Both structures crystallize in $P2_1/c$, and the unit cell constants of **7** parallel those of $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$, but they are smaller by 0.17, 0.22, and 0.37 Å in *a*, *b*, and *c*, respectively.

The metrical parameters in the two structures are very similar, as shown in Table 4. The main difference is that the 2.530(3) and 2.545(3) Å Sm−N(nitrile) distances are shorter than the 2.62(1) and 2.66(1) Å Sm−C(isocyanide) distances. This shows that *tert*-butyl cyanide and *tert*-butyl isocyanide adducts of lanthanide complexes can form nearly identical molecules, despite the difference in Ln−donor atom distances. This is consistent with the fact that little back-bonding to the isocyanide would be expected from a lanthanide such that these two different types of ligands bind similarly to the metal in this case.

Discussion

$(C_5Me_5)_2Sm(THF)_2$ (**1**) reacts with nitriles, RCN, to form the cyanide complex $[(C_5Me_5)_2SmCN]_n$ (**2**) and reactive byproducts. The overall reaction of **1** with nitriles has parallels with the reaction of **1** with alkyl halides.[20,21] When **1** reacts with alkyl halides, the R−X bond is cleaved to give $(C_5Me_5)_2SmX(THF)$ complexes as products (eq 3). The complexity of these RX

$$(C_5Me_5)_2Sm(THF)_2 + RX \rightarrow (C_5Me_5)_2SmX(THF) + R^{\bullet} + THF \quad (3)$$

reactions varies with R,[17,19,21] but when R is *tert*-butyl and X = Cl, $(C_5Me_5)_2SmCl(THF)$ is produced in greater than 95% yield.[20]

When **1** reacts with Me_3CCN, the nitrile-cleaved cyanide product **2** is obtained in no greater than 50% yield. This along with the presence of the $(N{=}CHCMe_3)^-$ complex **5** indicate that not all of the nitrile was cleaved according to eq 3. This suggested that the 1:1 stoichiometry employed when X = Cl may not be optimal for X = CN and that an additional 1 equiv of **1** may be needed. However, even when excess **1** is used, the yield of **2** is not increased. Instead, excess starting material is observed by ^1H NMR spectroscopy.

The reaction of **1** with *tert*-butyl cyanide also differs from the *tert*-butyl chloride reaction in that divalent coordination complexes of the nitrile can be isolated. Evidence for several divalent nitrile adducts was obtained: namely, $(C_5Me_5)_2Sm(NCCMe_3)(THF)_x$ (**3**), $(C_5Me_5)_2Sm(NCCMe_3)_2$, and $(C_5Me_5)_2Sm(NCCMe_3)_2(THF)$ (**4**). Only in the case of **4** were high-quality X-ray data obtainable, but the interconversion chemistry of these species suggests that the nitrile is a ligand comparable to THF. The isolation of these nitrile coordination complexes prior to the reductive cleavage is consistent with the mechanism postulated for the reactions of alkyl halides with divalent metallocenes, which are considered to be inner-sphere redox reactions.[17,19,21] Ephritikhine has shown with the trivalent uranium reductant $(C_5H_5)_3U$ that the adducts $(C_5H_5)_3U(NCR)$ can also be isolated and subsequently thermolyzed to $(C_5H_5)_3U(CN)$ and $(C_5H_5)_3UR$, both of which can be isolated for R = Me, ^nPr.[22]

Since THF inhibits the nitrile cleavage reaction, the first step is likely to be dissociation of THF in $(C_5Me_5)_2Sm(THF)_2$ to make $(C_5Me_5)_2Sm(THF)$. This process has been well documented in solution[47] and by the structure of $(C_5Me_5)_2Sm(THF)$.[48] Subsequently, the nitrile coordinates, as shown by **3** and **4**. The isolation of $[(C_5Me_5)_2SmCN]_n$ (**2**) and $(C_5Me_5)_2Sm(N{=}CHCMe_3)(THF)$ (**5**) is consistent with a two-electron reduction of Me_3CCN to form "$(C_5Me_5)_2Sm(CN)$" and "$(C_5Me_5)_2Sm(CMe_3)$" as intermediates. The former precipitates as oligomeric $[(C_5Me_5)_2SmCN]_n$, a product which has soluble, base-adduct, trimeric analogues of the type $[(C_5Me_5)_2SmL(\mu\text{-}CN)]_3$, where L = Me_3CNC,[16] $C_6H_{11}NC$,[16] Me_3CCN (**6**). "$(C_5Me_5)_2Sm(CMe_3)$" would be expected to be highly reactive both in metalation[31] and in β-hydrogen elimination chemistry. Isolation of **5** is consistent with β-hydrogen elimination to make $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[23] which adds to the Me_3CCN present. The latter step has been independently confirmed. It is conceivable that the presence of Me_3CCN with the "$(C_5Me_5)_2Sm(CMe_3)$" moiety inhibits σ-bond metathesis of the solvent[31,33] such that β-hydrogen elimination and addition of the Sm−H bond to the coordinated nitrile predominates.

Reductive decyanation of alkyl cyanides has been observed with alkali metals as the reducing agent.[49−51] However, only the free alkanes were isolated after workup. In this case, the cyanide portion of the molecule has been isolated as discrete organometallic species, while the alkyl portion undergoes subsequent β-hydrogen elimination and addition to the nitrile.

Conclusion

The facile Sm^{2+}-based reduction of nitriles to cyanide complexes shows that nitriles can be more than innocent bases and solvents for lanthanide complexes of this reductive capacity. In this metallocene case, the reduction of the nitrile is easily monitored, since it forms an insoluble cyanide with a distinctive infrared absorption.

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Supporting Information Available: CIF files giving X-ray diffraction data for **4**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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