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Steric Control of Lanthanide Coordination Environment: $(\mathrm{Tp}^{\mathrm{Me}_2})_2\mathrm{Sm}(\mathrm{C{\equiv}CPh})$, a Monomeric, Base-Free Lanthanide Alkynide Complex, and Its Thermally Induced Transformation to $(\mathrm{Tp}^{\mathrm{Me}_2})\{\mathrm{HB}(\mathrm{Me}_2\mathrm{pz})_2(\mathrm{C{\equiv}CPh})\}\mathrm{Sm}(\mathrm{Me}_2\mathrm{pz})$

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*Summary: Reaction of $Sm(Tp^{Me_2})_2$ (**1**) with $Hg(C{\equiv}CPh)_2$ in THF at ambient temperature afforded the monomeric, base-free lanthanide alkynide complex $(Tp^{Me_2})_2Sm(C{\equiv}CPh)$ (**2**). Thermolysis of **2** in benzene resulted in clean transformation to the new complex $(Tp^{Me_2})\{HB(Me_2pz)_2(C{\equiv}CPh)\}Sm(Me_2pz)$ (**3**), the result of an interesting, unusual ligand rearrangement on the Sm(III) center. Complexes **2** and **3** have been fully characterized by spectroscopic methods and X-ray crystallography.*

Catalytic dimerization, oligomerization, and polymerization of alkynes by organolanthanide complexes are well-documented processes.[1] In the reaction with terminal alkynes the catalytically active species is believed to be monomeric, coordinatively unsaturated alkynides such as $(\mathrm{C}_5\mathrm{Me}_5)_2\mathrm{LnC{\equiv}CR}$,[2a−c] $(\mathrm{DAC})\mathrm{YC{\equiv}CR}$[2d] (DAC = deprotonated 4,13-diaza-18-crown-6), and $\{\mathrm{PhC}(\mathrm{NSiMe}_3)_2\}_2\mathrm{YC{\equiv}CR}$.[2e] Although the trapping of these types of compounds by Lewis bases, $(\mathrm{C}_5\mathrm{Me}_5)_2\mathrm{Ln}(\mathrm{C{\equiv}CR})\mathrm{L}$ and $\{\mathrm{PhC}(\mathrm{NSiMe}_3)_2\}_2\mathrm{Y}(\mathrm{C{\equiv}CR})\mathrm{L}$ (L = THF, $\mathrm{Et}_2\mathrm{O}$, Py), has been achieved and the solid-state structures of some representative examples have been determined,[2,3] there is only one documented example of unsolvated terminal alkynide, $[(\mathrm{C}_5\mathrm{Me}_5)_2\mathrm{Sm}(\mathrm{C{\equiv}C^tBu})]_2$.[4] The dimeric structure of the latter compound in the solid state is achieved through weak $\mathrm{Sm}\cdots\mathrm{Me}(\mathrm{C}_5\mathrm{Me}_5)$ interactions rather than a bridging alkynide linkage. However, given an opportunity, coordination of THF is possible with formation of $(\mathrm{C}_5\mathrm{Me}_5)_2\mathrm{Sm}(\mathrm{C{\equiv}C^tBu})(\mathrm{THF})$.[3a,4] Clearly, the steric bulk of the spectator ligands in the above complexes is not sufficient to prevent coordination of a solvent molecule.

Work from our laboratories has demonstrated that $\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me}_2})_2$ (**1**) is capable of trapping a series of highly reactive anionic radical species, $(\mathrm{Tp}^{\mathrm{Me}_2})_2\mathrm{SmL}$ (L = superoxy anion, azobenzene, *p*-quinone, and benzophenone ketyl radical anions).[5] We attributed the ability of **1** to stabilize such species to a felicitous combination of one-electron reduction by Sm(II) and steric protection provided by the two bulky $\mathrm{Tp}^{\mathrm{Me}_2}$ ligands. Here we wish to report that the $\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me}_2})_2$ fragment is also bulky enough to allow the isolation of the monomeric, base-free phenylacetylide complex $(\mathrm{Tp}^{\mathrm{Me}_2})_2\mathrm{Sm}(\mathrm{C{\equiv}CPh})$ (**2**), a compound which undergoes an unusual thermally induced transformation.

Treatment of a THF slurry of the insoluble, purple **1** with mercury diphenylacetylide in THF resulted in gradual dissolution of **1** and formation of a colorless solution with a black precipitate (eq 1). Removal of the precipitate (Hg), concentration of the solution, and cooling at −40 °C overnight gave $(\mathrm{Tp}^{\mathrm{Me}_2})_2\mathrm{Sm}(\mathrm{C{\equiv}CPh})$ (**2**) as a colorless crystalline solid in 75% isolated yield.[6] The formulation of the compound is based on EA, IR, and multinuclear NMR data. In particular, the ^{1}H NMR spectrum clearly showed the absence of coordinated THF ligand (Figure 1a); its simplicity also implied fluxional solution behavior which renders all six pyrazolyl groups equivalent. Although leaving no doubt as to the elemental composition, the data did not distinguish between a monomeric or dimeric structure. To resolve this ambiguity, the structure of **2** was deter-

$$2\mathrm{Sm}(\mathrm{Tp}^{\mathrm{Me}_2})_2 + \mathrm{Hg}(\mathrm{C{\equiv}CPh})_2 \xrightarrow[\text{room temp}]{\text{THF}} 2(\mathrm{Tp}^{\mathrm{Me}_2})_2\mathrm{Sm}(\mathrm{C{\equiv}CPh}) + \mathrm{Hg}(\mathrm{l}) \quad (1)$$

2: colorless, 75%

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(6) Data for **2** are as follows. IR (KBr, cm^{-1}): 2550 (ν(B−H)). MS (EI, 70 eV, 100 °C): *m/z* 746 ($\mathrm{M}^+ - \mathrm{C}_2\mathrm{Ph}$). ^{1}H NMR (benzene-$d_6$, 25 °C; δ, ppm): 9.04 (m, 2H, Ph-H_o), 7.67 (m, 2H, Ph-H_m), 7.38 (m, 1H, Ph-H_p), 5.47 (s, 6H, 4-pz-*H*), 2.94, −1.06 (s, s, 18H, 18H, 3,5-pz-CH_3). ^{13}C{^{1}H} NMR (benzene-d_6, 25 °C; δ, ppm): 149.67, 145.54 (3,5-pz-*C*), 133.79, 128.79, 125.38 (Ph-$C_{o,m,p}$), 105.36 (4-pz-*C*), 14.16, 11.47 (3,5-pz-*C*H_3). ^{11}B{^{1}H} NMR (THF-d_8, 25 °C; δ, ppm): −1.72 (s, $W_{1/2}$ = 330 Hz). Anal. Calcd for $\mathrm{C}_{38}\mathrm{H}_{49}\mathrm{B}_2\mathrm{N}_{12}\mathrm{Sm}$: C, 53.96; H, 5.84; N, 19.87. Found: C, 52.15; H, 5.60; N, 19.57.

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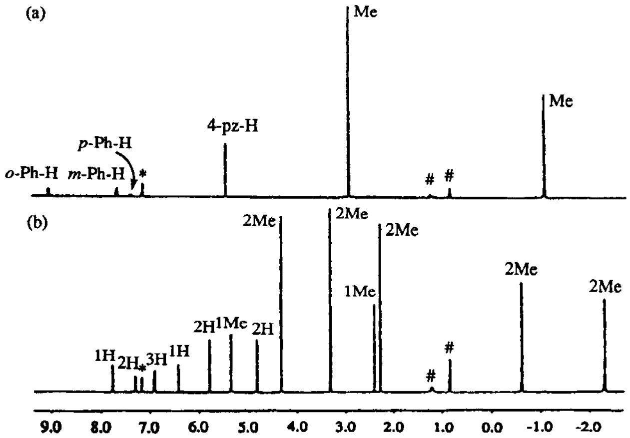

Figure 1. ^1H NMR spectra of complexes **2** (a) and **3** (b) in C_6D_6 (δ, ppm): (*) residual protons in benzene-d_6; (#) pentane contamination.

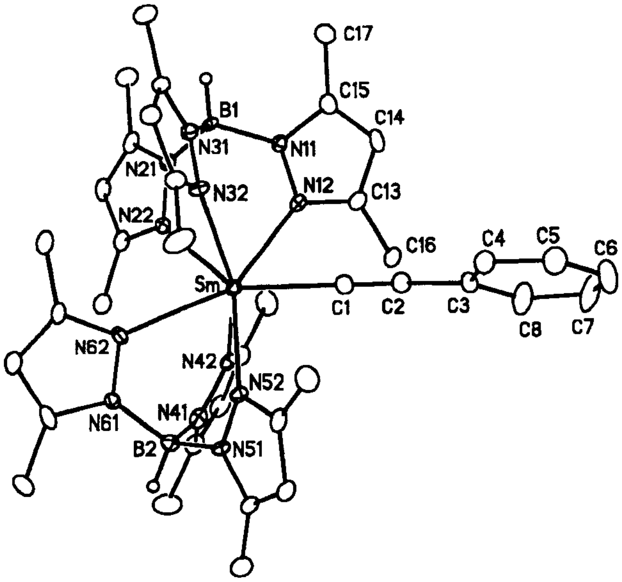

Figure 2. ORTEP drawing of molecule **2**. Selected bond distances (Å) and angles (deg): $Sm-N_{av} = 2.55$, $Sm-C1 = 2.494(9)$, $C1-C2 = 1.206(12)$, $C2-C3 = 1.4441(12)$; $Sm-C1-C2 = 176.6(8)$.

mined by single-crystal X-ray diffraction.[7] The results revealed the monomeric, solvent-free nature of **2** (Figure 2). The Sm^{3+} center is seven-coordinate with two η^3-Tp^{Me_2} ligands and the carbon of the terminal phenylacetylide ligand occupying the seventh coordination position.[8] The "$(Tp^{Me_2})_2Sm$" portion of the complex greatly resembles those in the previously characterized $(Tp^{Me_2})_2Sm(\eta^2\text{-}O_2)$[5a] and $(Tp^{Me_2})_2Sm$(azobenzene)[5b] complexes and requires no further comments. The terminal phenylacetylide ligand nestles in the cleft opened up by the two Tp^{Me_2} ligands. It is noteworthy that the Sm–C1 distance (2.494(9) Å) is longer than the corresponding Sm–C(alkynide) length (2.419(6) Å) in $[(C_5Me_5)_2Sm(C{\equiv}C^tBu)]_2$ and is the same as that observed in $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ (2.49(2) Å), which was regarded as unusually long.[3a]

An interesting feature of lanthanide alkynide chemistry is the formation, sometimes reversible, of C–C bonds via coupling of alkynide ligands.[2d,4,9] Thus, heating a toluene solution of $(C_5Me_5)_2Sm(C{\equiv}CPh)(THF)$ resulted in its transformation to dimeric $[(C_5Me_5)_2Sm]_2(\mu\text{-}PhC_4Ph)$, in which two $(C_5Me_5)_2Sm$ fragments are bridged by a trienediyl moiety.[4] It was postulated that a combination of steric unsaturation in the transient "$(C_5Me_5)_2Sm(C{\equiv}CPh)$" and steric overcrowding in the anticipated simple alkynyl-bridged dimer "$[(C_5Me_5)_2Sm(\mu\text{-}C{\equiv}CPh)]_2$" were responsible for the alkynyl coupling process.[4] In view of the more congested nature of **2**, it was of obvious interest to test its thermal behavior.

Complex **2** is stable at ambient temperature both in the solid state and in solution. However, heating a benzene-d_6 solution of **2** at 105 °C for 36 h led to clean, exclusive, and quantitative conversion to a new complex (**3**; Figure 1b). Although the elemental compositions of compounds **2** and **3** are identical, the complicated appearance of the ^1H and ^{13}C NMR spectra and the presence of two ^{11}B NMR signals at −7.96 and −12.11 ppm,[10] indicating two different boron environments, are clearly not in accord with a simple dimeric alkynyl-coupled product and suggest a more extensive ligand rearrangement in the transformation of **2** to **3**. The prediction was confirmed by single-crystal X-ray crystallography, which revealed the nature of the rearrangement.[11] As can be seen in Figure 3, one of the Tp^{Me_2} ligands remained intact during thermolysis and is still bonded to samarium via the classic, tridentate fashion. However, the other ligand underwent an interesting and unusual change in which one of the pyrazolyl groups has been replaced by the phenylacetylide moiety. The displaced pyrazolate is coordinated to Sm^{3+} as an η^2-chelating ligand, a bonding mode that recently is proving to be quite common in lanthanide complexes with bulky 3,5-substituted pyrazolates.[12] The η^2-bidentate bonding of the modified $HB(3,5\text{-}Me_2pz)_2(C{\equiv}CPh)$ ligand with additional Sm–HB interaction is emerging also as a recurrent feature in related Ln(III) complexes where steric congestion forces a $Tp^{R,R'}$ ligand to adopt an η^2-bidentate bonding mode.[13] The Sm–N distances are normal. In particular, the stronger inter-

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[7] X-ray data for **2**: triclinic, $P\bar{1}$ (No. 2), $a = 11.6181(7)$ Å, $b = 11.6681(7)$ Å, $c = 15.1635(6)$ Å, $\alpha = 98.998(4)°$, $\beta = 94.478(5)°$, $\gamma = 100.326(6)$, $V = 1985.5(2)$ Å^3, $Z = 2$, $T = -60$ °C, R1 = 0.0559, wR2 = 0.1563, GOF = 1.046. For further details, see the Supporting Information.

[8] The ^1H NMR spectra of **2** in benzene-d_6, toluene-d_8, and thf-d_8 are very similar. A VT ^1H NMR study in thf-d_8 between 60 and −100 °C showed no change except for the temperature dependence of the chemical shifts; plots of chemical shifts versus $1/T$ were linear, consistent with simple Curie–Weiss behavior. These observations indicate that the simple, monomeric solid-state structure is maintained in solution and that the molecular rearrangement which renders the pyrazolyl groups equivalent has a low activation barrier.

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[10] Data for **3** are as follows. ^1H NMR (benzene-d_6, 25 °C; δ, ppm): 7.74 (s, 1H, 4-pz-*H*), 7.28 (m, 2H, Ph-*H*), 6.89 (m, 3H, Ph-*H*), 6.41 (s, 1H, 4-pz-*H*), 5.77 (s, 2H, 4-pz-*H*), 5.34 (s, 3H, 1 *Me*), 4.81 (s, 2H, 4-pz-*H*), 4.32 (s, 6H, 2 *Me*), 3.31 (s, 6H, 2 *Me*), 2.42 (s, 3H, 1 *Me*), 2.30 (s, 6H, 2 *Me*), −0.58 (s, 6H, 2 *Me*), −2.27 (s, 6H, 2 *Me*). $^{13}C\{^1H\}$ NMR (benzene-d_6, 25 °C; δ, ppm): 154.50, 148.65, 147.75, 145.79, 144.17, 143.76, 141.87 (3,5-pz-*C*), 131.36, 127.06, 126.32 (Ph-$C_{o,m,p}$), 110.42, 106.11, 105.30, 102.93 (4-pz-*C*), 34.39, 22.66 ($PhC{\equiv}C$), 16.28, 15.50, 14.27, 14.20, 13.60, 12.98, 10.60 (3,5-pz-CH_3). $^{11}B\{^1H\}$ NMR (benzene-d_6, 25 °C; δ, ppm): −7.96 (s, $W_{1/2} = 350$ Hz), −12.11 (s, $W_{1/2} = 220$ Hz).

[11] X-ray-quality single crystals were grown from pentane solution. The analysis revealed that the compound crystallized with a pentane molecule of solvation. X-ray data for **3**·(pentane): triclinic, $P\bar{1}$ (No. 2), $a = 11.8627(12)$ Å, $b = 13.4162(8)$ Å, $c = 16.2980(6)$ Å, $\alpha = 79.852(3)°$, $\beta = 68.796(6)°$, $\gamma = 70.675(7)°$, $V = 2277.3(3)$ Å^3, $Z = 2$, $T = -60$ °C, R1 = 0.0660, wR2 = 0.1551, GOF = 1.048. For further details, see the Supporting Information.

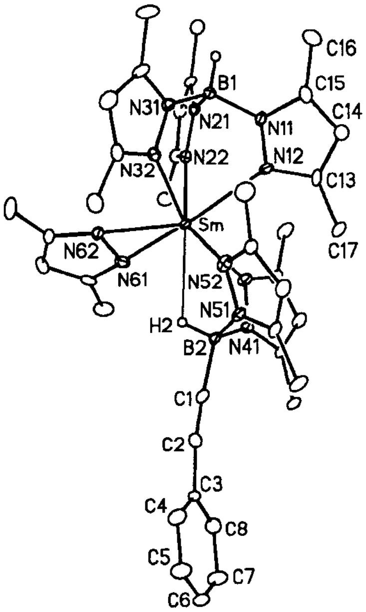

Figure 3. ORTEP drawing of molecule **3**. Selected bond distances (Å) and angles (deg): Sm$-$N$_{av}$(N12,N22,N32, N42,N52) = 2.53, Sm$-$N$_{av}$(N61,N62) = 2.38, N61$-$N62 = 1.402(11), C1$-$B2 = 1.578(14), C1$-$C2 = 1.176(13); B2$-$C1$-$C2 = 175.3(11), C1$-$C2$-$C3 = 171.7(11).

action with the η^2-pyrazolate ligand is reflected in the shorter Sm$-$N61/N62 bond lengths. Complex **3** has approximate C_s symmetry which is retained in solution and accounts nicely for the number and ratio of the ^{1}H and ^{13}C NMR signals.

The most plausible mechanism for the transformation of **2** to **3** involves intramolecular nucleophilic substitution of a pyrazolyl group at boron by the phenylacetylide ligand.[14] Indeed, the views shown and the numbering schemes utilized in Figures 2 and 3 were chosen to indicate the nice alignment of the pyrazolyl ring N61$-$C65 and the phenylacetylide moiety that leads to smooth backside attack of B2 by the latter group and displacement of the pyrazolyl ring. Preliminary kinetic data, which show that the reaction is first order in **2**, and the unusually long Sm$-$C$\equiv$CPh bond distance are consistent with the proposed mechanism and with the suggestion that the rate-determining step of the transformation is heterolytic Sm$-$C$\equiv$CPh bond cleavage.

In conclusion, we have shown that the use of the sterically demanding Tp^{Me_2} ligand allows the isolation and X-ray characterization of a base-free, monomeric lanthanide phenylacetylide complex.[15] The relatively facile thermal rearrangement of complex **2** represents the second example of an unusual transformation of the Tp^{Me_2} ligand within the coordination sphere of a Sm(III) center.[16]

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Supporting Information Available: Details of X-ray structure determinations of **2** and **3**, including final coordinates, thermal parameters, bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The steric demand of the two Tp^{Me_2} ligands that secures the monomeric, solvent-free nature of **2** also hampers its reactivity. Compound **2** proved unreactive toward excess HC$\equiv$C^{t}Bu and HC$\equiv$CSiMe$_3$.

(16) We recently reported that thermolysis of (η^3-Tp^{Me_2})(η^2-Tp^{Me_2})-Sm(η^5-Cp) in the solid state results in the formation of Sm(η^3-Tp^{Me_2}){HB(Me$_2$pz)$_2$(C$_5$H$_4$)}.[13b]