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Synthesis and Reaction of $[(Tp^{iPr_2})LnH_2]_3$ (Ln = Y, Lu) with CO: Trinuclear Cluster-Bound Propenolate en Route to Selective Formation of Propene

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There is currently intense interest in the synthesis and reactivity of monoligand rare-earth dihydride complexes, "$LLnH_2$",[1−4] as they adopt structures that feature fascinating and varied cluster frameworks and mediate reaction chemistry that can be exquisitely different from their long-known bisligand rare-earth monohydride relatives, L_2LnH.[5]

Pioneering work in this area was carried out by Hou and coworkers, who showed that, depending on steric bulk of the substituted cyclopentadienyl ligands, tetranuclear, $[(C_5Me_4SiMe_3)LnH_2]_4(THF)_{0-2}$, or hexanuclear, $[(C_5Me_5)LnH_2]_6$,[1] polyhydrido clusters can be obtained. These workers also showed that the tetranuclear octahydrides exhibit unprecedented reactivity toward a variety of unsaturated small molecules,[6] most recently carbon monoxide.[7] Subsequent to this work, we reported that Trofimenko's scorpionates[8] are suitable ancillaries for the synthesis of a wide range of rare-earth dialkyls, $(Tp^{R,R'})LnR_2(THF)_{0/1}$, some of which, under suitable conditions, can be converted to the corresponding dihydrides, whose nuclearity depends on the steric bulk of the scorpionate ligand. Thus, a series of tetranuclear, $[(Tp^{Me_2})LnH_2]_4$, and hexanuclear, $[(Tp)LnH_2]_6$, polyhydrides were obtained.[2]

Although they are structurally interesting, the scorpionate-supported polyhydrides exhibited limited reactivity. In an effort to reduce the nuclearity and hence increase the reactivity, hydrogenolysis of the superbulky $(Tp^{tBu,Me})Ln(CH_2SiMe_3)_2$ complexes was investigated. The reaction proceeded by elimination of tetramethylsilane but gave a complex mixture of products, presumably from metalation of one of the methyl groups of the *t*Bu substituent of the $Tp^{tBu,Me}$ ligand; the methyl C−H bond, pointing toward the electron-deficient metal center, is poised for such a metalation reaction. To eliminate the problem-causing methyl group while maintaining the needed steric bulk, we turned our attention to the hydrotris(3,5-diisopropyl-1-pyrazolyl)borate ligand, Tp^{iPr_2}. Indeed, this ligand system has similar steric bulk as $Tp^{tBu,Me}$ but presents to the metal an interior like that in the Tp^{Me_2} ligand,[9,10] the ligand that gave the tetranuclear octahydrides.[2] Here we report that this approach led to the *exclusive* formation of *trinuclear* $[(Tp^{iPr_2})LnH_2]_3$ complexes and subsequent hydrogenation of carbon monoxide with selective formation of propene.

Protonolysis of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu) with HTp^{iPr_2} furnished the corresponding $(Tp^{iPr_2})Ln(CH_2SiMe_3)_2(THF)$ complexes in high yield (eq 1):

$$Ln(CH_2SiMe_3)_3(THF)_2 + HTp^{iPr2} \xrightarrow[\text{rt, 2h}]{\text{Pentane}} (Tp^{iPr2})Ln(CH_2SiMe_3)_2(THF) + SiMe_4 \quad (1)$$

Ln = Y (**1a**), 89%; Lu (**1b**), 84%

The compounds were characterized by the usual spectroscopic and elemental analyses, and the structures in the solid state were determined by single-crystal X-ray diffraction. The compounds, like their $(Tp^{tBu,Me})Ln(CH_2SiMe_3)_2$ relatives, are highly soluble in hydrocarbon solvents, but unlike them, they contain a coordinated THF ligand. This feature is in agreement with the observation that the interior of the ligand resembles that of Tp^{Me_2}.

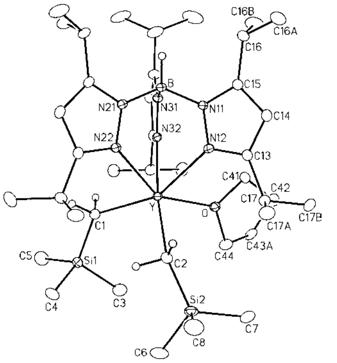

Figure 1. ORTEP plot of $(Tp^{iPr_2})Y(CH_2SiMe_3)_2(THF)$ (**1a**) with thermal ellipsoids drawn at the 20% probability level.

As is typical in other complexes with Tp^{iPr_2} ligands,[9,10] the C−H bonds of the Tp-isopropyl groups in **1a** point toward the B and Y atoms (Figure 1), thus leaving enough interior room for the THF molecule to coordinate to the yttrium center, just as in the analogous complex $(Tp^{Me_2})Y(CH_2SiMe_3)_2(THF)$. Indeed, the bond distances in **1a** [Y−O = 2.397(2) Å, $Y-N_{ave}$ = 2.463(2) Å, and $Y-C_{ave}$ = 2.415(2) Å] are similar to those in the Tp^{Me_2} complex.[2]

To our delight, hydrogenolysis of the dialkyl complexes proceeded well and after simple workup gave the corresponding dihydrides in very good yield (eq 2):

$$(Tp^{iPr2})Ln(CH_2SiMe_3)_2(THF) \xrightarrow[\text{rt, 18~27h}]{H_2\text{ (75 atm), Pentane}} [(Tp^{iPr2})LnH_2]_3 + SiMe_4 \quad (2)$$

Ln = Y (**2a**), 86%; Lu (**2b**), 81%

The dihydrides are soluble and stable in hydrocarbon, aromatic, and ether-type solvents under an inert atmosphere. The ^1H NMR spectra show the hydride signals at 7.62 and 11.27 ppm for the Y (**2a**) and Lu (**2b**) complexes, respectively. The quartet appearance of the former signal ($^1J_{Y-H}$ = 15.6 Hz) and its temperature-invariant nature down to −80 °C indicate coupling of the hydrides to three equivalent yttrium atoms as a result of very rapid hydrogen exchange and suggest a trinuclear cluster structure. The hydride chemical shifts in **2a** and **2b** are at slightly higher field than in the analogous complex $[(Tp^{Me_2})LnH_2]_4$ (Y, 8.22 ppm; Lu, 12.19 ppm), and as expected, the average $^1J_{Y-H}$ is larger than the one observed in $[(Tp^{Me_2})YH_2]_4$ (12.1 Hz).

The trinuclear cluster structure was corroborated by single-crystal X-ray diffraction (Figure 2). Each Y is bonded to a κ^3-Tp^{iPr_2} ligand, and the Y atoms are bridged by hydrides, which were found and isotropically refined.

There are two different types of bridging hydrides: one hydride is triply bridging (μ_3-H3) and located above the Y_3 triangular plane, and the remaining five hydrides are doubly bridging (μ_2-H) and

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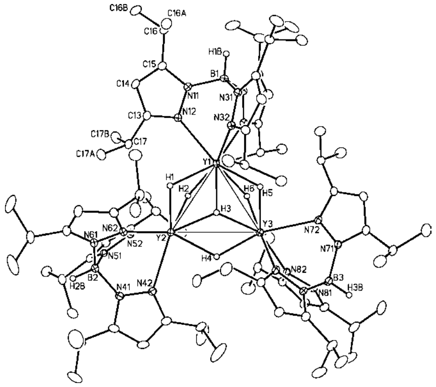
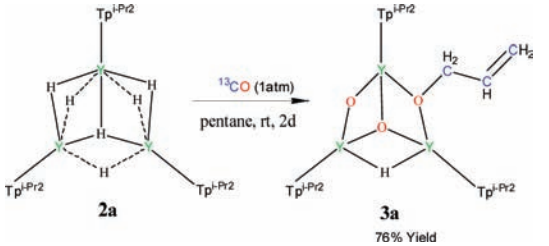


Figure 2. ORTEP plot of $[(Tp^{iPr_2})YH_2]_3$ (**2a**) with thermal ellipsoids drawn at the 20% probability level.

bridge two yttrium atoms. The $Y2\cdots Y3$ distance of 3.6841(3) Å, supported by the μ_3-H3 and μ_2-H4 bridges, is significantly longer than the $Y1\cdots Y2$ and $Y1\cdots Y3$ distances (average 3.3601(3) Å), which are bridged by the same μ_3-H3 but two μ_2-H bridges. Thus, the three yttrium atoms form a slightly distorted isosceles triangle. As such, the structure is subtly different from that of $[Y(Me_3TACD)H_2]_3$, in which all six hydrides are μ_2-H bridges.[3,11]

The reaction with CO was chosen as a test case to investigate the reactivity differences between the trinuclear hexahydrides **2** and the tetranuclear octahydrides reported by Hou et al.[7] and us.[2] Stirring a pentane solution of the yttrium hydride, **2a**, under an atmosphere of ^{13}CO for 2 days resulted in clean conversion of **2a** into a pale-yellow crystalline solid, **3a** (Scheme 1).

Scheme 1. Reaction of **2a** with ^{13}C-Enriched Carbon Monoxide



2a **3a**

The $^{13}C\{^1H\}$ NMR spectrum of **3a** revealed a *three*-^{13}C unit by prominent resonances at 67.36 (d, $J_{C-C} = 46$ Hz), 109.08 (d, $J_{C-C} = 70$ Hz), and 141.25 (dd, $J_{C-C} = 70, 46$ Hz) ppm; these appeared in the ^1H-coupled spectrum as "td" ($-CH_2-$), "td" ($=CH_2$), and "ddd"' ($-CH=$), respectively, due to $^1J_{C-H}$ and J_{C-C} coupling, accounting for five of the original six hydrogens. The sixth hydrogen was seen as a signal of intensity 1 in the ^1H NMR spectrum at 7.35 (dd, 1H, $J_{Y-H} = 38.4, 33.2$ Hz) ppm. The nature of the three-^{13}C unit in **3a** was established by X-ray crystallography as a cluster-bound propenolate fragment resulting from hydrogenation and coupling of *three* carbon monoxides (Figure 3).[12,13] Heating a tolune-d_8 solution of **3a** overnight released ^{13}C-propene ($^{13}C_3H_6$), as verified by its ^{13}C NMR signatures (chemical shifts and J_{C-H} and J_{C-C} values).[14]

Preliminary ^{13}C NMR monitoring of the reaction and short reaction time at low temperature revealed that **3a** already forms at −50 °C, but attempts to clearly identify or isolate further intermediates have to date been hampered by the overlapping natures of the reaction steps. Work to fully map out the mechanism that leads to the formation of **3a** is continuing.[15]

In summary, the use of the Tp^{iPr_2} ligand led to the straightforward and high-yield synthesis of rare examples of trinuclear monoligand lanthanide dihydrides, $[(Tp^{iPr_2})LnH_2]_3$ (Ln = Y, Lu). The Y complex was found to mediate the hydrogenation and coupling of carbon monoxide with exclusive formation of propene. The reactions of the dihydrides with small, unsaturated substrates are under investigation.

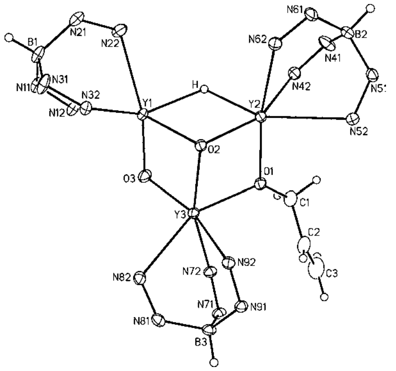


Figure 3. ORTEP plot of the core structure of **3a** with thermal ellipsoids drawn at the 20% probability level. Except for the bridging hydride, the B−H moieties, and the propenolate group, all of the other H and C atoms have been omitted for clarity. Selected bond distances (Å): Y1−H, 2.20(3); Y2−H, 2.22(3); Y2−O1, 2.221(2); Y3−O1, 2.308(2); Y1−O2, 2.233(2); Y2−O2, 2.127(2); Y3−O2, 2.2678(19); Y1−O3, 2.054(2); Y3−O3, 2.048(2); O1−C1, 1.418(4); C1−C2, 1.509(6); C2−C3, 1.290(7)

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Supporting Information Available: Synthesis, spectroscopic, and X-ray diffraction (CIF) details. This material is available free of charge via the Internet at http://pubs.acs.org.

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