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Efficient Hydride and Pyrazolyl Redistribution upon Thermolysis of a Calcium Complex Containing Dihydrobis(pyrazolyl)borate Ligands

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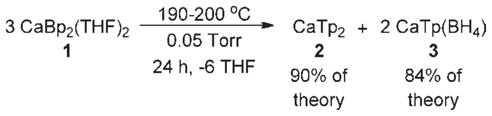
Supporting Information

ABSTRACT: Thermolysis of $CaBp_2(THF)_2$ (THF = tetrahydrofuran) at 190−200 °C and 0.05 Torr leads to a redistribution reaction to afford $CaTp_2$ (90%) and $CaTp(BH_4)$ (84%). Treatment of $CaTp(BH_4)$ with THF affords $CaTp(BH_4)(THF)_2$ and $[CaTp(BH_4)(THF)]_4$, both of which were structurally characterized. Methanolysis or ethanolysis/hydrolysis of the BH_4^--containing complexes affords $[TpCa(HOMe)_2(\mu_4\text{-}B(OMe)_4)Ca(HOMe)_2Tp][B(OMe)_4]$ and $[\{TpCa\}_3\{\mu_6\text{-}B(OB(OEt)_3)_3]\cdot EtOH$.

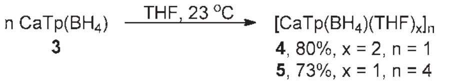
Hydrotris(pyrazolyl)borate (Tp) and dihydrobis(pyrazolyl)borate (Bp) ligands and substituted derivatives thereof are very common ligands.[1] A great advantage of Tp and Bp ligands is that they are usually inert toward reactions that occur at the metal center and thus serve as ancillary ligands that stabilize the complexes. However, there are examples of reactions that lead to the degradation of Tp and Bp ligands, resulting commonly in pyrazole complexes[2] or substitution of a B−H or B−N bond by a halogen or alkoxide group.[3] In a broader perspective, main-group and lanthanide (Ln) complexes containing borohydride (BH_4^-) and related B−H-bond-containing ligands are of recent interest as hydrogen storage materials,[4,5] polymerization precatalysts,[6] and thin-film-growth precursors.[7,8] Herein, we report the surprising conversion of $CaBp_2(THF)_2$[9] (**1**; THF = tetrahydrofuran) to $CaTp_2$ (**2**) and $CaTp(BH_4)$ (**3**) upon heating. These transformations are proposed to occur via reversible B−N and B−H cleavages within the coordination sphere of the Ca ion and are relevant to reactions that occur in hydrogen storage materials, polymerization catalysts, and thin film growth.

The heating of **1** at 190−200 °C and 0.05 Torr for 18 h, as described in the Supporting Information, led to the isolation of **2** (90%) as colorless crystals that sublimed to the cool zone of the apparatus and **3** (84%) as a nonvolatile white solid. On the basis of the isolated yields, the stoichiometry shown in Scheme 1 is proposed. Complex **1** melts at 116 °C,[9] and the thermolysis process initially formed a colorless liquid at 190−200 °C that slowly transformed to a white solid as sublimation of **2** proceeded. Complex **2** was identified by a comparison of its melting point and ^1H, $^{13}C\{^1H\}$, and ^{11}B NMR spectra with those of **2** prepared by a literature procedure[10] and by a comparison of the melting point and ^1H NMR spectrum with the reported values.[10] The composition of **3** was established by spectral and analytical data and by its reactions described below.[11] The IR spectrum of **3** showed a B−H stretch at 2442 cm^{-1}, which is similar to the value in **2** (2435 cm^{-1}), and B−H stretches at 2404 and 2283 cm^{-1}, which are similar to those observed in $Ca(BH_4)_2(THF)_2$ (2394 and 2265 cm^{-1}). The ^1H NMR spectrum of **3** in methanol-d_4 revealed resonances consistent with Tp [δ 7.65 (d), 7.61 (d), 6.12 (t)] and BH_4^- (−0.13 ppm, q, $J_{H-^{11}B}$ = 81.6 Hz) ligands, and the ^{11}B NMR spectrum in methanol-d_4 showed resonances at −0.62 (d, $J_{^{11}B-H}$ = 81.9 Hz) and −40.87 (pentet, $J_{^{11}B-H}$ = 80.4 Hz) ppm. The splitting patterns and positions of the resonances in the ^{11}B NMR data for **1** (−9.18, t, J_{11B-H} = 90.5 Hz) and **2** (−1.99 ppm, d, J_{11B-H} = 89.9 Hz) are consistent with a those of a Tp ligand in **3** and not with a Bp ligand. The ^{11}B NMR spectrum of $Ca(BH_4)_2(THF)_2$ in methanol-d_4 showed a pentet at −41.6 ppm ($J_{^{11}B-H}$ = 81.0 Hz) at 23 °C, suggesting a BH_4^- ligand in **3**.

Scheme 1. Synthesis of 2 and 3 from 1



Scheme 2. Synthesis of 4 and 5 from 3



The stirring of **3** in THF at ambient temperature led to its rapid dissolution to form a colorless solution. Layering of this solution with hexane and allowing it to stand at 23 °C for 18 h afforded $CaTp(BH_4)(THF)_2$ (**4**; 80%) as colorless crystals upon workup (Scheme 2). Recrystallization of **4** from toluene/hexane afforded colorless crystals of $[CaTp(BH_4)(THF)]_4$ (**5**; 73%) upon workup. Complexes **4** and **5** were identified from their spectral and analytical data and by X-ray crystallography.[11] The ^1H, $^{13}C\{^1H\}$, and ^{11}B NMR data of **4** and **5** in methanol-d_4 were identical with those of **3** in the same solvent.

Dissolution of **4** in methanol led to gas evolution over ca. 0.5 h, and crystallization of the resulting product from warm methanol afforded $[TpCa(HOMe)_2(\mu_4\text{-}B(OMe)_4)Ca(HOMe)_2Tp][B(OMe)_4]$ (**6**; 80%) as colorless crystals (Scheme 3). Related dissolution of **4** in 95% aqueous ethanol, followed by layering of the reaction solution with hexane and allowing it to stand at 23 °C for 48 h, afforded $[\{TpCa\}_3\{\mu_6\text{-}B(OB(OEt)_3)_3]\cdot EtOH$ (**7**; 77%) as colorless crystals (Scheme 3). The Tp ligands in **3**−**7** are inert to protonolysis at ambient temperature. A kinetics study of the

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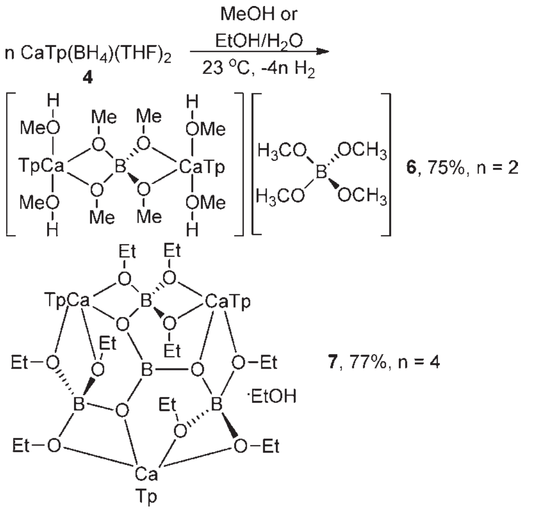
Scheme 3. Synthesis of 6 and 7 from 4



hydrolysis and methanolysis of $NaBH_4$ was recently reported.[12] Because **7** contains four BH_4^--derived B atoms per molecule, the stoichiometry must entail 4 equiv of **4**; 1 equiv of a CaTp-containing fragment may be lost as an insoluble species. Complexes **6** and **7** were characterized by spectral and analytical techniques and by X-ray crystallography.[11] Dissolving **4** in isopropyl alcohol or water led to variable yields of **2** and powders that were insoluble in all solvents. This behavior may correspond to a slow Schlenk-type equilibrium to afford **2** and $Ca(BH_4)_2(THF)_2$, and the precipitates may correspond to alcoholysis and/or hydrolysis products derived from the latter.

Perspective views of **4**−**7** are shown in Figure 1. Each complex contains κ^3-Tp ligands with Ca−N distances of 2.465(1)−2.481(1) Å for **4**, 2.432(3)−2.465(3) Å for **5**, 2.445(4)−2.521(4) Å for **6**, and 2.458(2) and 2.465(2) Å for **7**. These values are similar to those observed in $CaTp^{Et2}_2$ [2.453(2)−2.465(2) Å; Tp^{Et2} = hydrotris(3,5-diethylpyrazolyl)borate].[8d] The coordination sphere in **4** also contains two THF and one κ^3-BH_4^- ligands, and this complex is monomeric. The Ca−O distances are 2.372(1) and 2.395(1) Å, and the Ca−H distances range between 2.41(1) and 2.42(2) Å. Mountford recently described the synthesis of $CaTp^{tBu,Me}(BH_4)(THF)$ [$Tp^{tBu,Me}$ = hydrotris(3-*tert*-butyl-5-methylpyrazolyl)borate], although the X-ray crystal structure was not reported.[6b] Complex **5** exists as a tetrameric molecule with μ_4:κ^2,κ^2-BH_4^- ligands that bridge between the Ca ions and one THF ligand per Ca ion. The Ca−O distances are 2.369(2) and 2.376(3) Å, and the Ca−H distances are between 2.43(4) and 2.59(4) Å. Complex **6** is a dimeric, ionic complex with a cationic fragment that contains a central μ_4:κ^2,κ^2-$B(OMe)_4^-$ ligand, to which two $CaTp(HOMe)_2$ units are coordinated. The Ca−O distances in the cation range from 2.352(3) to 2.423(3) Å, and the values for the $B(OMe)_4$ and methanol ligands are similar within experimental error. There is a $B(OMe)_4^-$ anion, which balances the cation charge and is not coordinated to the Ca ions. The structure of **7** consists of a central $[B(OB(OEt)_3)_3]^{3-}$ ion with three $[CaTp]^+$ units bonded to this anion. Each Ca ion is bonded in a κ^2 fashion to the O atoms of a $B(OEt)_2$ fragment and in a κ^2 fashion to the O atoms of a BO(OEt) fragment. The central B atom of the $[B(OB(OEt)_3)_3]^{3-}$ ion has trigonal-planar geometry, with a symmetry-imposed O−B−O angle of 120° and a B−O distance of 1.353(2) Å. Each of the three remaining B

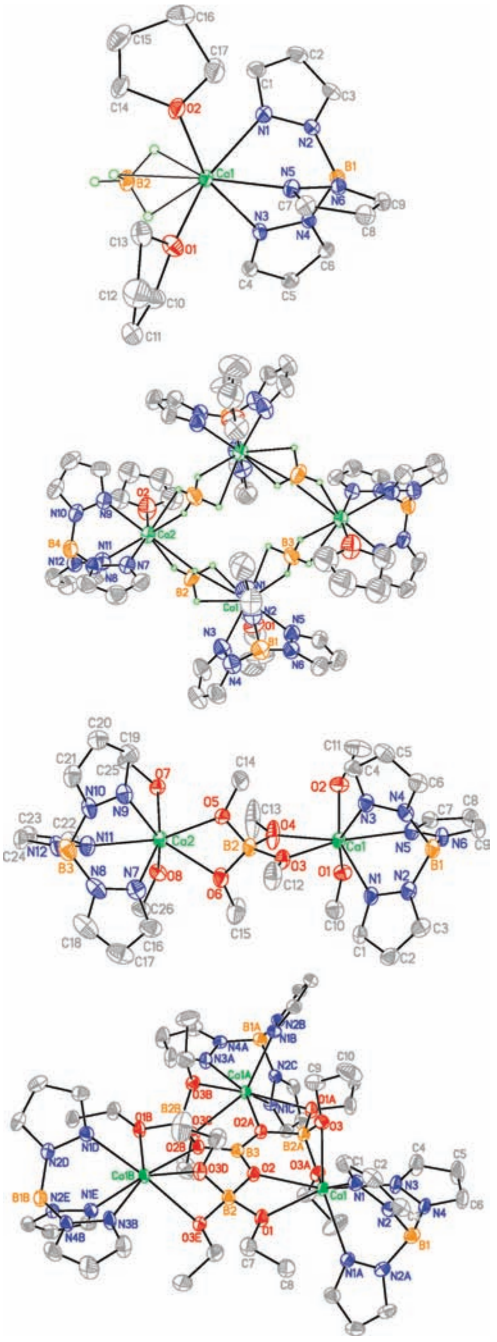


Figure 1. Perspective views of **4**−**7** with selected bond lengths (Å) and angles (deg): (top) **4**, Ca−O1 2.395(1), Ca−O2 2.372(1), Ca−N1 2.465(1), Ca−N3 2.465(1), Ca−N5 2.481(1), Ca−HB2 2.42(2), 2.41(2), 2.42(2); (second) **5**, Ca1−O1 2.369(2), Ca2−O2 2.376(3), Ca1−N1 2.432(3), Ca1−N3 2.465(3), Ca−N5 2.464(3), Ca2−N7 2.462(3), Ca2−N9 2.444(3), Ca2−N11 2.464(3), Ca1−HB 2.43(4), 2.50(5), 2.51(4), 2.52(5), 2.59(4); (third) cationic fragment of **6**, Ca1−O1 2.361(3), Ca1−O2 2.379(3), Ca1−O3 2.404(3), Ca1−O4 2.352(3), Ca2−O5 2.372(3), Ca2−O6 2.423(3), Ca2−O7 2.397(3), Ca2−O8 2.386(3), Ca1−N1 2.466(4), Ca1−N3 2.504(4), Ca1−N5 2.535(4), Ca2−N7 2.445(4), Ca2−N9 2.491(4), Ca2−N11 2.521(4), O3−B2−O4 98.9(3), O3−B2−O5 114.9(4), O3−B2−O6 115.5(4), O4−B2−O5 114.3(4), O4−B2−O6 114.8(4), O5−B2−O6 99.3(3); (bottom) **7**, Ca−O1 2.536(2), Ca−O2 2.372(2), Ca−O3 2.431(2), Ca−N1 2.465(2), Ca−N3 2.458(2), B2−O1 1.450(3), B2−O2 1.485(3), B2−O3 1.468(2), B3−O2 1.353(2).

atoms in the $[B(OB(OEt)_3)_3]^{3-}$ ion is bonded to one oxide ion of the central BO_3 unit and to three ethoxy groups. These B—O distances are 1.485(3), 1.450(3), and 1.468(2) Å for B2—O2, B2—O1, and B2—O3, respectively. The Ca—O distances are 2.372(2) Å for coordination to the B—O—B linkage and 2.431(1) and 2.536(2) Å for coordination to the ethoxy groups containing O1 and O3, respectively. No complexes containing Ca—O—B linkages are listed in version 5.32 of the Cambridge Crystallographic Database.

KBp and other Bp-based salts can be accessed in high yields by thermolysis routes from KBH_4 and pyrazoles,[1] which implies that redistribution reactions similar to those documented herein with **1** either do not occur during these syntheses or are very slow. Trofimenko noted in an early paper that sublimation of MBp_2 (M = divalent metal ion) was sometimes accompanied by decomposition to many products, which included pyrazabole, metal pyrazolates, and MTp_2,[1b] but details of the exact metals and product yields were not given and further insights into these processes have never been reported. The mechanism by which the present process occurs is not understood but may involve intermediates such as calcium hydrides[13] and calcium pyrazolates[14] generated by reversible B—H and B—N bond-cleavage reactions. Harder and co-workers have reported the isolable hydride complex $[CaL(H)(THF)]_2$, where L is $[((2,6\text{-}iPr_2C_6H_3)NCMe)_2CH]^-$.[13] The treatment of $[CaL(H)(THF)]_2$ with 9-BBN afforded the borohydride complex $CaL(THF)(H_2BC_8H_{14})$.[13b] Additionally, hydride transfer from B to Rh was documented upon the treatment of $RhBp^{Me2}(CO)(py)$ [Bp^{Me2} = dihydrobis(3,5-dimethylpyrazolyl)borate] with methyl iodide.[13c] Thermal decomposition of $LiBH_4$ ultimately yields LiH, solid B, and H_2 and may proceed via intermediate borohydride clusters.[4] Many calcium complexes containing pyrazolate ligands have been reported, and terminal κ^2 coordination is favored in monomeric species.[14] Trofimenko has proposed a 1,2-B—N bond shift to account for the formation of $Co(HB(3\text{-}iPrpz)_2(5\text{-}iPrpz))_2$ upon the treatment of $Co(NO_3)_2$ with 2 equiv of $K(HB(3\text{-}iPrpz)_3$,[15a] and there are examples where the treatment of KTp or KBp with transition-metal halides led directly to metal pyrazolate complexes.[15,16]

The results of this work suggest that other complexes containing Bp and related ligands may undergo similar hydride and pyrazolyl redistribution reactions. In olefin polymerization catalysis with Ln precatalysts containing BH_4^- ligands,[6] it is possible that hydride transfer equilibria from B to Ln are present, which allow polymerization initiation through olefin insertion into the Ln—H bond. We have recently reported the atomic layer deposition growth of MB_2O_4 (M = Ca, Sr, Ba) films from **2**, $SrTp_2$, and $Ba(Tp^{Et2})_2$ and water and noted that the B atoms in the precursors are very efficiently incorporated into the films to afford precise 2:1 B-to-metal ratios in the films.[8] By contrast, Girolami et al. described the chemical vapor deposition growth of B-free Y_2O_3 films using $Y(H_3BNMe_2BH_3)_3$ and water at 300 °C.[7b] The facile B incorporation from Tp-based precursors and the very low B level in films derived from the (dimethylamino)boranate precursor may reflect the lack of an accessible hydride transfer path from B to metal in the Tp-based precursors and low energy hydride transfers in $Y(H_3BNMe_2BH_3)_3$ to afford B-free YH_3-derived film growth intermediates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthetic procedures and analytical and spectroscopic data for **4**—**7** and X-ray crystallographic data for **4**—**7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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