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Synthesis and Reduction of Bimetallic Methyl-Bridged Rare-Earth Metal Complexes, \([(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ln}(\mu-\text{CH}_3)]_2\) (Ln = Y, Tb, Dy)

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Supporting Information

ABSTRACT: The complexes \([\text{Cp}^{'},\text{Ln}(\mu-\text{CH}_3)]_2\), \((\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3, \text{Ln} = \text{Y}, \text{Tb}, \text{Dy})\) were reduced to determine if these methyl-bridged complexes would form mixed valent 4f5d1 Ln(II)/4f6d0 Ln(III) compounds or bimetallic 4f5d1 Ln(II) compounds containing 5d−4f metal−metal bonds upon reduction. Reaction of the known bridged-chloride complexes, \([\text{Cp}^{'},\text{Ln}(\mu-\text{Cl})]_2\), \(1-\text{Ln} (\text{Ln} = \text{Y}, \text{Tb}, \text{Dy})\), with MeLi forms the bridged-methyl complexes \([\text{Cp}^{'},\text{Ln}(\mu-\text{CH}_3)]_2\), \(2-\text{Ln}\), which were characterized crystallographically. Reduction of 2-Yn in the presence of 2.2.2-cryptand produced 3-Y, 3-Tb, and 3-Dy, which exhibited intense dark colors and broad absorbance peaks around 400 nm with molar extinction coefficients of 1700, 2300, and 1800 M−1 cm−1, respectively, which are characteristics of Ln(II) ions. The dark maroon 3-Y product had an axial electron paramagnetic resonance spectrum at 77 K (\(g_1 = 1.99, A_1 = 17.9 \text{ G}, g_2 = 2.00, A_2 = 17.7 \text{ G}\)) and a two-line isotropic spectrum at 273 K (\(g = 1.99, A = 18.4 \text{ G}\)), which indicates an Y(II) ion is present. Although these results are indicative of Ln(II) ions present in the solution, crystallographic evidence was not obtained to establish the structure of these complexes.

INTRODUCTION

The +2 oxidation state has recently been identified in crystallographically characterizable mononuclear molecular complexes of yttrium and all of the lanthanides (except radioactive Pm). This was accomplished using the coordination environment of three trimethylsilyl-substituted cyclopentadienyl ligands, as shown in eq 1.1−6 Previously, the +2 oxidation state in molecular species had been limited to Eu, Yb, and Nd, which had 4f oxidation state in molecular species had been limited to Eu, Yb, and Nd, which had 4f configuration for Ln(III) compounds or bimetallic 4f Ln(II) compounds containing 5d−4f metal−metal bonds. Since the complexes of new 4f5d1 Ln(II) ions involve mononuclear complexes with sterically crowded ligand environments, they are not ideal for placing two lanthanides in close proximity to bond.

To address this problem, reductions of \([\text{Cp}^{'},\text{Y}(\mu-\text{Cl})]_2\), and \([\text{Cp}^{'},\text{Y}(\mu-\text{H})(\text{THF})]_2\), were explored.8 DFT calculations suggested that reduction of these bimetallic complexes could form complexes containing Y−Y bonds.10 Although spectroscopic studies, including electron paramagnetic resonance (EPR) spectroscopy and UV−vis spectroscopy, of the reductions of these complexes suggested the formation of an Y(II) ion,8,10,13 crystallographic evidence was elusive. In the case of complexes containing electron-deficient bridged hydride ligands, \([\text{Cp}^{'},\text{Y}(\mu-\text{H})(\text{THF})]_2\), only trinuclear tetrahydride complexes, \([\text{Cp}^{'},\text{Ln}(\mu-\text{H})_3](\mu-\text{H})\) (Ln = Y, Tb, Dy), were isolated from the reduction reactions.16 The reduction of \([\text{Cp}^{'},\text{Y}(\mu-\text{Cl})]_2\) provided an EPR spectrum at 77 K consistent with an Y(II) ion. However, this complex was extremely thermally unstable, which prohibited the collection of a room-temperature EPR spectrum, and a crystal structure could not be obtained.

To avoid the possibility of forming such trinuclear hydride-centered products, the reduction of complexes containing electron-deficient methyl-bridged ligands, \([\text{Cp}^{'},\text{Ln}(\mu-\text{CH}_3)]_2\), has been explored and is reported here. Reduction of the known complex, \([\text{Cp}^{'},\text{Y}(\mu-\text{CH}_3)]_2\), is described as well as

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Scheme 1. Syntheses of \([\text{Cp}^\prime\text{Ln}(\mu-\text{Cl})_2]_2\), 1-Ln, and \([\text{Cp}^\prime\text{Ln}(\mu-\text{CH}_3)_2]_2\), 2-Ln \{Cp’ = \{C_5\text{H}_4(Si\text{Me}_3)\}\}

\[
\text{L}n = \text{Y, Tb, Dy}
\]

analogous reactions of the Tb and Dy analogues, which were synthesized for this study and crystallographically characterized for definitive identification.

RESULTS AND DISCUSSION

Reaction of the known bridged-chloride complexes, \([\text{Cp}^\prime\text{Ln}(\mu-\text{Cl})_2]_2\), 1-Ln, with 2 equiv of methyl lithium generates the bridged-methyl complexes \([\text{Cp}^\prime\text{Ln}(\mu-\text{CH}_3)_2]_2\), 2-Ln, needed for this study, Scheme 1 (\(Ln = \text{Y, Tb, Dy}\)). The previously reported Y complex was identified by \(^{1}H\) NMR spectroscopy, and the paramagnetic Tb and Dy complexes were identified by X-ray crystallography, Figure 1. 2-Tb and 2-Dy are isomorphous with 2-Y. Crystallographic details can be found in the Supporting Information.

![Figure 1. ORTEP depiction of \([\text{Cp}^\prime\text{Dy}(\mu-\text{CH}_3)_2]_2\) 2-Dy, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.](image)

The crystallographic data show that the methyl-bridged complexes, 2-Ln, have shorter \(\text{L}n-\text{L}n\) distances than either the chloride precursors, 1-Ln, or the tetrahydrofuran (THF)-solvated hydrides, \([\text{Cp}^\prime\text{Ln}(\mu-\text{H})(\text{THF})_2]_2\), Table 1. For example, the \(\text{Tb}-\text{TB}\) distances in the two molecules in the unit cell of 2-Tb were determined to be 3.5415(5) and 3.5745(4) \(\text{Å}\) compared to 4.0792(9) and 3.7042(3) \(\text{Å}\) for 1-Tb and \([\text{Cp}^\prime\text{Tb}(\mu-\text{H})(\text{THF})_2]_2\) respectively. The \(\text{Ln}-\text{X}-\text{Ln}\) angles in 2-Ln were also determined to be the smallest when compared to the chloride and hydride analogues. These were 89.73(8) and 90.17(8)° in 2-Tb compared to 97.29(2) and 120.7(2)° in 1-Tb and \([\text{Cp}^\prime\text{Tb}(\mu-\text{H})(\text{THF})_2]_2\) respectively. These smaller distances could facilitate an interaction between the two rare-earth ions upon reduction by bringing the metal centers closer to each other.

Table 1. Comparison of the \(\text{Ln}^\text{II}^\text{−}^\text{−}^\text{−} \text{L}n\) Distances and \(\text{Ln}−\text{X}−\text{Ln}\) Angles in 1-Ln, 2-Ln, and \([\text{Cp}^\prime\text{Ln}(\mu-\text{H})(\text{THF})_2]_2\)

| complex          | \(\text{Ln}−\text{Ln}\) distance (\(\text{Å}\)) | \(\text{Ln}−\text{X}−\text{Ln}\) angle (deg) |
|------------------|-----------------------------------------------|---------------------------------------------|
| \([\text{Cp}^\prime\text{Y}(\mu-\text{H})(\text{THF})_2]_2\) 2-Y       | 3.5361(9)                                      | 89.18(13)                                   |
| \([\text{Cp}^\prime\text{Y}(\mu-\text{Cl})_2]_2\) 1-Y          | 4.0792(9)                                      | 98.4(1)                                     |
| \([\text{Cp}^\prime\text{Tb}(\mu-\text{H})(\text{THF})_2]_2\) 2-Tb  | 3.5415(5)                                      | 90.17(8)                                    |
| \([\text{Cp}^\prime\text{Tb}(\mu-\text{Cl})_2]_2\) 1-Tb          | 3.5745(4)                                      | 89.73(8)                                    |
| \([\text{Cp}^\prime\text{Dy}(\mu-\text{H})(\text{THF})_2]_2\) 2-Dy  | 3.7042(3)                                      | 119.4(14)                                   |
| \([\text{Cp}^\prime\text{Dy}(\mu-\text{Cl})_2]_2\) 1-Dy          | 3.8086(5)                                      | 97.89(1)                                    |

\(\text{Ln} = \text{Y, Tb, Dy}\)

The UV−vis spectra of 3-Y, 3-Tb, and 3-Dy, Figure 3, show broad absorbance peaks at 420, 405, and 410 nm with molar extinction coefficients of approximately 1700, 2300, and 1800 M\(^{-1}\) cm\(^{-1}\), respectively, based on the moles of metal present in the sample. The \(\epsilon\) values are lower estimates that are based on the amount of 2-Ln used to form the sample assuming complete reduction to 3-Ln. In comparison, \([\text{K(crown)}]^−\cdot\text{Cp}^\prime\text{Y}^+\) and \([\text{K(crypt)}]\text{[Cp}^\prime\text{Y}]^+\) have absorptions at 530 nm \((\epsilon = 2500 \text{ M}^{-1}\text{ cm}^{-1})\) and 520 nm \((\epsilon = 4500 \text{ M}^{-1}\text{ cm}^{-1})\), respectively. The data on 3-Ln can also be compared with those from the reductions of \([\text{Cp}^\prime\text{Y}(\mu-\text{H})(\text{THF})_2]_2\) 794 nm \((\epsilon = 1000 \text{ M}^{-1}\text{ cm}^{-1})\), \([\text{Cp}^\prime\text{Tb}(\mu-\text{H})(\text{THF})_2]_2\) 837 nm \((\epsilon = 840 \text{ M}^{-1}\text{ cm}^{-1})\), and \([\text{Cp}^\prime\text{Dy}(\mu-\text{H})(\text{THF})_2]_2\) 715 nm \((\epsilon = 640 \text{ M}^{-1}\text{ cm}^{-1})\), Figure 4.
The dark-colored solutions of 3-Ln maintained their color in solution at −30 °C for several days, but they did not yield crystalline products suitable for definitive characterization by X-ray diffraction. Attempts to make analogues with 18-crown-6 instead of crypt were similarly unsuccessful.

**CONCLUSIONS**

Although the bridged-methyl complexes \([\text{Cp'}_2\text{Ln}(\mu-\text{H})(\text{THF})]_2\) can be reduced to form dark solutions with EPR and UV–vis spectroscopic features consistent with Ln(II), isolation of crystallographically characterizable Ln(II) complexes has not been possible. These results indicate that the bis(Cp') coordination environment is not optimum for crystallizing bimetallic complexes with a rare-earth metal in the +2 oxidation state.

**EXPERIMENTAL DETAILS**

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Elemental analyses were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. UV–vis spectra were collected at 298 K using a Jasco V-670 absorption spectrometer. EPR spectra were collected using X-band frequency (9.3–9.8 GHz) on a Bruker EMX spectrometer equipped with an ER041XG microwave bridge, and the magnetic field was calibrated with DPPH (\(g = 2.0036\)). Infrared (IR) transmittance measurements were taken as compressed solids on a Cary 630 spectrophotometer with a diamond ATR attachment. 2.2.2-Cryptand (Sigma-Aldrich) was placed under vacuum (10⁻³ Torr) overnight before use. The solvent was removed under vacuum from a solution of methyl lithium in Et₂O (Sigma-Aldrich) to isolate it as a white powder. Anhydrous LnCl₃ (Ln = Y, Tb, Dy),22 KC₈,23 and KC₅H₄(SiMe₃) (KCp')₂₄ were prepared according to the literature. \([\text{Cp'}_2\text{Ln}(\mu-\text{H})]_2\) (Ln = Y, Tb, Dy),18 1-Ln, and \([\text{Cp'}_2\text{Y}(\mu-\text{CH₃})]_2\) were prepared by a modification of the literature procedure.

\(\text{[Cp'}_2\text{Y}(\mu-\text{CH₃})]_2\), 2-Dy. A solution (−30 °C) of 1-Dy (150 mg, 0.158 mmol) in Et₂O (5 mL) was slowly added to a −30 °C slurry of MeLi (12 mg, 0.546 mmol) in Et₂O (5 mL). The total volume of the solution was increased to 20 mL with cold Et₂O. The slightly cloudy colorless solution was allowed to warm to room temperature and stirred overnight. The volatiles were removed from the solution in vacuo. The product was extracted into hexane (10 mL) and then centrifuged to remove white solids, presumably LiCl. The white solids were washed with hexane (5 mL) twice. The volatiles were removed from the hexane solution to isolate a white powder. The white powder was extracted into hexane (10 mL) again, and any insoluble materials were discarded. The volatiles were removed from the hexane solution to isolate 2-Dy as a white powder (123 mg, 0.136 mmol, 86%). X-ray quality crystals were grown from a concentrated hexane solution at −30 °C. IR: 3079(w), 2950(w), 2885(w), 1440(w), 1360(w), 1343(w), 1242(s), 1176(m), 1038(s), 905(m), 890(w), 829(s), 772(s), 751(s), 688(m). Anal. calcd for C₃₄H₅₈Dy₂Si₄: expected = C, 41.97; H, 6.47. Found: C, 41.97;
were combined in THF (2 mL) and passed through a KC8 column to form a dark red-brown solution, 2-Y.

Reduction of 2-Y. In an argon-filled glovebox, a colorless solution of

Reduction of 2-Dy. In a procedure analogous to the

Reduction of 2-Tb. In a procedure analogous to the

X-ray Crystallographic Data. Crystallographic information for complexes 2-Tb (1871704) and 2-Dy (1871703) are in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

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Notes

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