Organometallics **2007,** *26,* 1123−1125

Isolation of Stable Organodysprosium(II) Complexes by Chemical Reduction of Dysprosium(III) Precursors

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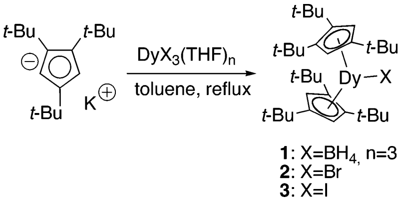
Received January 9, 2007

Summary: Reduction of bis(tri-tert-butylcyclopentadienyl)dysprosium(III) complexes by potassium/graphite in the presence of a crown ether afforded structurally characterized organodysprosium(II) ate complexes, a new class of divalent organolanthanide compounds. The organodysprosium(II) borohydride ate complex was oxidized by hexachloroethane into a structurally characterized organodysprosium(III) dichloride ate complex and was also shown to reductively couple diphenylacetylene.

The overwhelming majority of divalent organolanthanides possess Sm^{II}, Eu^{II}, or Yb^{II} as the metal;[1] outside this series, only a few Tm^{II} complexes[2−6] and a single La^{II} complex[7] have been structurally characterized recently. There are two main reasons for the paucity of these latter types of complexes. First, suitable “non-classical” precursors such as MI_2 (M = La−Nd, Gd−Tm, Lu), in which M is in the oxidation state +II, only exist with Tm, Dy, or Nd[8,9] and are less easily available than SmI_2, EuI_2, or YbI_2. Second, M^{2+} ions are very strong reducing agents and at the same time are very oxophilic; thus, polar reaction media such as THF can be a problem because of possible oxidation of M^{2+} by the solvent.[10,11] Therefore, stable THF-solvated “non-classical” divalent organometallic complexes, made by metathesis of MI_2 with anionic ligand precursors, have only been obtained so far with M = Tm,[2,3,5,6] the less reducing of the “non-classical” set.

However, it is also possible to obtain unsolvated divalent complexes of La^{II} and Tm^{II} by reduction of organometallic trivalent precursors: Lappert[7] used potassium metal and [18]-crown-6 to transform $[La(Cp^{tt})_3]$ into the anionic $[K([18]crown\text{-}6)(\eta^2\text{-}C_6H_6)_2][\{La(Cp^{tt}{}_2)\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)]$ ($Cp^{tt} = \eta^5\text{-}C_5H_3tBu_2\text{-}1,3$), and we recently used KC_8 in nonpolar solvents to reduce $[(Cp^{ttt})_2TmI]$ to the homoleptic $[Tm(Cp^{ttt})_2]$ ($Cp^{ttt} = \eta^5\text{-}C_5H_2\text{-}tBu_3\text{-}1,2,4$).[6] We felt that this route would be well-suited for the synthesis of hitherto unknown organodysprosium(II) complexes, since Dy^{2+} is the second least reducing ion of the “non-classical” series[12,13] after Tm^{2+}.

Scheme 1



As potential precursors, $[(Cp^{ttt})_2Dy(BH_4)]$ (**1**), $[(Cp^{ttt})_2DyBr]$ (**2**), and $[(Cp^{ttt})_2DyI]$ (**3**) were synthesized in fair yield by reaction of $[KCp^{ttt}]$ with $[Dy(BH_4)_3(THF)_3]$, $DyBr_3$, and DyI_3, respectively, in refluxing toluene.[14] (Scheme 1).

1 (Figure 1), **2**, and **3** were characterized by elemental analysis and X-ray crystallography. We also attempted to use NMR as an alternative method of characterization, and we found that, despite the high paramagnetism of Dy^{III}, acceptable proton spectra of complexes **1**−**3** could be obtained. The spectra span ca. 400 ppm and display three very broad peaks ($w_{1/2} \geq 2$ kHz) that we attribute to the three *tert*-butyl groups on the ring. The inequivalence of these groups implies restricted rotation around the metal−ring centroïd axis, a phenomenon that has been already observed in the related $[(Cp^{ttt})_2Ce(C_6F_5)]$.[15]

In contrast to $[(Cp^{ttt})_2TmI]$, attempted reduction of **1**−**3** with KC_8 in toluene or cyclohexane was unsuccessful. However, when KC_8 was used in the presence of 1 equiv of [18]crown-6 at room temperature, the solutions immediately turned dark red and we observed a dramatic change in the proton NMR spectra. The peaks attributed to the *tert*-butyl groups had shifted ca. 100−250 ppm to low field, while a new peak appeared between −32 and −63 ppm. We were able to isolate dark red crystals from toluene or cyclohexane solutions, and X-ray crystallographic analyses showed that the structures of the products obtained by reduction of **1** and **2** were those of ate complexes: $[(Cp^{ttt})_2Dy(\mu\text{-}X)K([18]crown\text{-}6)]$ (**4**, X = BH_4; **5**, X = Br). Charge balance indicates that **4** and **5** are indeed Dy^{II} complexes.

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(14) Synthesis of **1**: in the glovebox, a mixture of $[Dy(BH_4)_3(THF)_3]$ (0.30 g, 0.71 mmol) and KCp^{ttt} (0.42 g, 1.56 mmol) was placed in a Schlenk tube fitted with a J. Young valve. Dry toluene (20 mL) was vacuum-distilled onto this mixture at −78 °C, and the suspension was warmed to room temperature. The reaction mixture was heated to reflux with stirring for 48 h. After that time the yellow solution was cooled to room temperature and centrifuged. The solvent was evaporated, and the crude product was recrystallized from pentane at −30 °C and was obtained as a colorless powder in 57% yield (0.26 g, 0.40 mmol). ^1H NMR (300 MHz, C_6D_{12}): δ (ppm) −6 (br s, $w_{1/2} \approx 2$ kHz, tBu), −173 (br s, $w_{1/2} \approx 2$ kHz, tBu), −275 (br s, $w_{1/2} \approx 1$ kHz, tBu). Anal. Calcd for $C_{34}H_{62}BDy$ (644.17): C, 63.39; H, 9.70. Found: C, 63.38; H, 9.91. Crystals suitable for X-ray diffractometry were obtained from pentane at −30 °C.

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10.1021/om0700213 CCC: $37.00

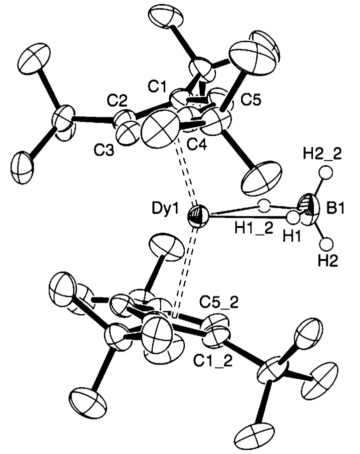


Figure 1. ORTEP plot (50% ellipsoids) of one molecule of [$(\mathrm{Cp^{ttt}})_2$-Dy(BH_4)] (**1**). Hydrogen atoms (except those on the borohydride) have been omitted for clarity.

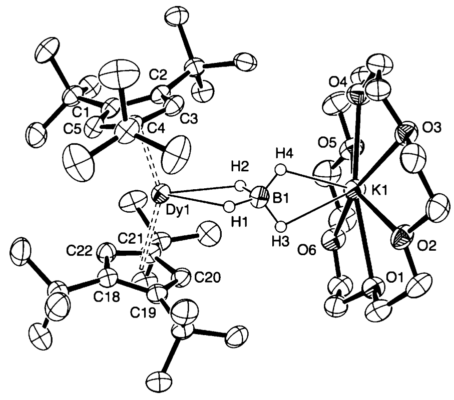
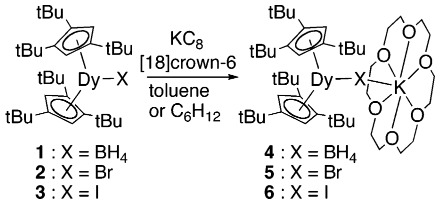


Figure 2. ORTEP plot (50% ellipsoids) of one molecule of [$(\mathrm{Cp^{ttt}})_2$-Dy(μ-BH_4)K([18]crown-6)] (**4**). Hydrogen atoms (except those on the borohydride) have been omitted for clarity.

Scheme 2



The X-ray data for the product isolated by reduction of **3** were less satisfactory because of disorder problems which could not be adequately modeled; however, the overall geometry of the molecule could be obtained and was similar to that of **4** and **5**. Thus, we could assign it the structure of **6**: [$(\mathrm{Cp^{ttt}})_2$Dy(μ-I)K-([18]crown-6)] (Scheme 2 and Figure 2).[16]

In addition, **4**−**6** have similar but not identical proton spectra; the new peak appearing between −32 and −63 ppm was attributed to the protons belonging to the crown ether.

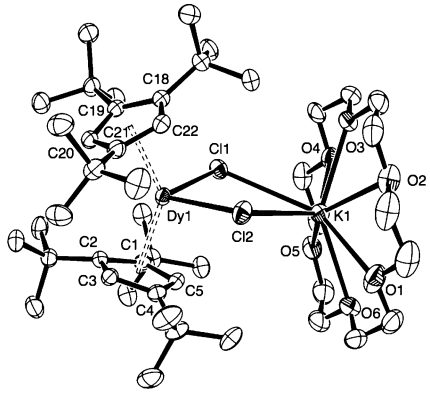
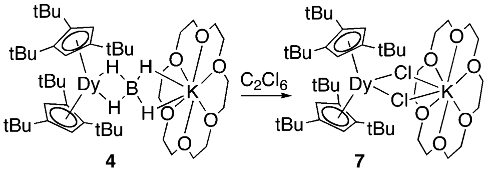


Figure 3. ORTEP plot (50% ellipsoids) of one molecule of [$(\mathrm{Cp^{ttt}})_2$-Dy(μ-Cl)$_2$K([18]crown-6)] (**7**). Hydrogen atoms have been omitted for clarity.

Scheme 3



The only previous example of a lanthanate complex featuring a crown ether complexed potassium halide is that of a $\mathrm{Ho^{III}}$ compound that has three Cp groups bonded to the metal, [$\mathrm{Cp_3}$-Ho(μ-Cl)K([18]crown-6)],[17] while in [$(\mathrm{Cp^{ttt}})_2$Dy(μ-I)K([18]-crown-6)] (**4**−**6**) only two $\mathrm{Cp^{ttt}}$ groups are coordinated to $\mathrm{Dy^{II}}$.

Although it is not possible to distinguish between $\mathrm{Dy^{II}}$ (f^{10}: expected $\mu_{\mathrm{eff}} = 10.607\ \mu_{\mathrm{B}}$) and $\mathrm{Dy^{III}}$ (f^9: expected $\mu_{\mathrm{eff}} = 10.646\ \mu_{\mathrm{B}}$) on the basis of magnetic moments,[18] we believe that the dramatic shift observed by NMR from **1**−**3** to **4**−**6** is indicative of a change of oxidation state; however, we next attempted to obtain more evidence of the divalent nature of dysprosium in complexes **4**−**6** by their reaction with oxidants. This proved to be surprisingly challenging; for instance, reaction of **4** with thallium phospholide, [Tl(C_4H_4P)], precipitated thallium metal but gave back **3** instead of the expected phospholyl-substituted $\mathrm{Dy^{III}}$ complex. Eventually, reaction of **4** with C_2Cl_6 resulted in an immediate color change to yellow and we were able to isolate crystals of an oxidation product, which was characterized by X-ray diffraction as the $\mathrm{Dy^{III}}$ ate complex [$(\mathrm{Cp^{ttt}})_2$Dy(μ-Cl)$_2$K-([18]crown-6)] (**7**) (Scheme 3 and Figure 3).[19]

Potassium coordination similar to that in **7** had previously been found in palladium and platinum chemistry,[20] e.g. in [(η^2-cis-pent-2-ene)Pt(μ-Cl)$_2$K([18]crown-6)],[20a] and also in a uranyl complex, [UO_2(μ-Br)$_4K_2$([18]crown-6)$_2$].[21]

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(16) Synthesis of **4**: in the glovebox, a mixture of [$(\mathrm{Cp^{ttt}})_2$Dy(BH_4)] (100 mg, 156 μmol) and [18]crown-6 (42 mg, 156 μmol) was placed in a centrifugation tube and dissolved in cyclohexane (8 mL). After addition of KC_8 (42 mg, 312 μmol) the reaction mixture was shaken, immediately giving a dark red solution from which the product precipitated over 24 h at room temperature. The supernatant was removed, and the precipitate was taken up in toluene (15 mL). After centrifugation, the solution was evaporated, yielding pure **4** as a dark red powder (95 mg, 100 μmol, 64% yield). ^{1}H NMR (300 MHz, toluene-d_8): δ (ppm) 343 (br s, $w_{1/2} = 3$ kHz, tBu), 133 (br s, $w_{1/2} = 3$ kHz, tBu), −49 (br s, $w_{1/2} = 2$ kHz, [18]crown-6), −178 (br s, $w_{1/2} = 3$ kHz, tBu). Crystals suitable for X-ray diffractometry were obtained from toluene at −30 °C.

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(19) Reaction of **6** with hexachloroethane: addition of hexachloroethane (14 mg, 79 μmol) to a solution of **6** (75 mg, 79 μmol) in toluene (8 mL) led to an immediate color change from dark red to yellow. The solvent was reduced, and pentane was slowly added onto the solution. After 24 h white crystals of **7** were obtained in 28% yield (22 mg, 22 μmol). ^{1}H NMR (300 MHz, toluene-d_8): δ (ppm) −10 (br s, $w_{1/2} = 0.3$ kHz, [18]crown-6), −67 (br s, $w_{1/2} = 0.6$ kHz, tBu). Crystals suitable for X-ray diffractometry were obtained from THF/pentane at room temperature.

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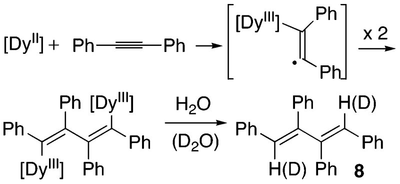
Scheme 4



Finally, since Evans has shown that diphenylacetylene could be reduced by decamethylsamarocene[22] and DyI_2,[18] we undertook the reaction of **4** with diphenylacetylene. The solution instantaneously turned green. However, since we were unable to obtain crystals from the reaction mixture, we decided to hydrolyze it and to analyze the organic fraction. We thus could isolate crystalline (*E*,*E*)-1,2,3,4-tetraphenylbuta-1,3-diene (**8**), which was characterized by proton NMR, mass spectroscopy, and an X-ray crystal structure. When the hydrolysis was performed with D_2O, (*E*,*E*)-1,2,3,4-tetraphenylbuta-1,3-diene-1,4-d_2 was obtained. In this reaction, tetraphenylbutadiene likely arises from one-electron reduction of diphenylacetylene by a Dy^{II} species followed by coupling of the resulting radical and subsequent hydrolysis of the $[Dy^{III}]-C$ bonds (Scheme 4). In relation to this, (a) reduction of diphenylacetylene with lithium[23a] or $TiCl_3/Zn$[23b] also produces tetraphenylbutadiene after hydrolysis and (b) Bochkarev and Schumann have recently shown that TmI_2-induced reductive coupling of pyridine resulted in the formation of a 4,4′-dihydro-4′,4-bipyridinyl Tm^{III} bimetallic complex.[24] On the other hand, reduction of diphenylacetylene by DyI_2 exclusively afforded *cis*-stilbene.[18]

In summary, we have isolated a series of stable organodysprosium(II) complexes, a new class of “non-classical” low-valent organolanthanides, and have shown evidence of their reducing properties. Our next goal will be to study in more detail the reactivity of these complexes, particularly with small molecules: reduced Ln^{III}/K systems have recently shown to activate nitrogen.[25]

Acknowledgment. Financial support of this work was provided by the CNRS and Ecole Polytechnique.

Supporting Information Available: Text and figures giving full experimental details, paramagnetic NMR spectra, and ORTEP plots of all structurally characterized compounds and a CIF file giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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