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Cleavage and capture of tetrahydrofuran by dysprosium(II) species: a novel tetranuclear Dy_2Li_2O unit

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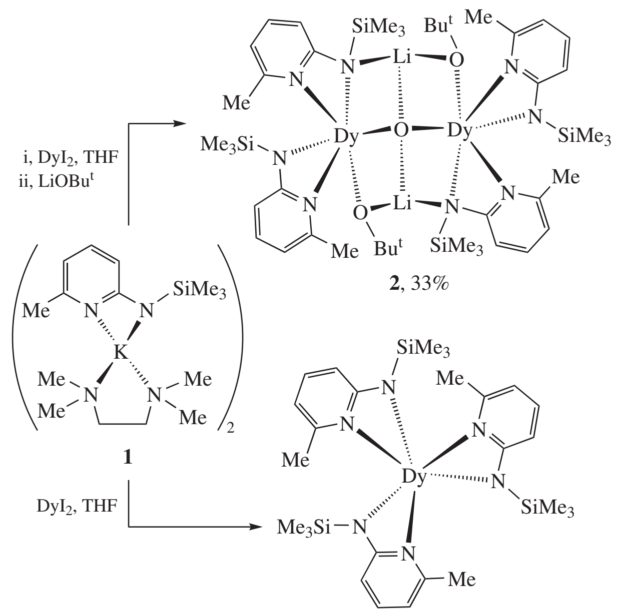
The reaction of DyI_2 with substituted 2-pyridyl amide $[N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]^-$ (L) and lithium alkoxide can give a new complex $[\{(L)_2Dy(\mu_2\text{-}OBu^t)Li\}_2(\mu_4\text{-}O)]$ with a Dy_2Li_2O group, which was characterized by X-ray crystallography.

Recently, lanthanide chemistry has been one of the most rapidly developing areas in organometallic/inorganic chemistry.[1] Divalent lanthanides in organometallic chemistry have been traditionally restricted by europium, ytterbium and samarium.[2] It is interesting that a divalent lanthanide metal center has a high reducing power. Therefore, the reduction of CO_2,[3] N_2[4] and various organic or inorganic substrates, as well as the cleavage of THF or Et_2O,[5] by lanthanide(II) complexes have been reported.[3–6] Dinitrogen with strong N≡N bonds was coordinated and even activated by lanthanide metal centers under mild conditions.[7] Generally speaking, divalent lanthanide complexes with high reactive metal centers such as Dy^{II}, Nd^{II} and Tm^{II} are very difficult to prepare.[8]

The desired reactivity and catalytic activity of lanthanide complexes might be achieved through careful ligand design.[9] Successful isolation of first neutral homoleptic lanthanide(III) triamides, $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Yb and Lu), was reported.[10] Lanthanide complexes derived from pyridyl amido ligands were studied.[11] Bochkarev and Fagin found that DyI_2 and NdI_2 could be obtained in glass vessels by the reaction of a lanthanide with iodine at ~1500 °C.[12] We synthesized several divalent lanthanide complexes $[(L)_2Ln(TMEDA)]$ {L = $[N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)]^-$, Ln = Eu or Yb}.[13,†] These results inspired us to extend the coordination chemistry of pyridyl amido ligand (L) to stabilize the dysprosium(II) center. Here, we report that divalent dysprosium can cleave the tetrahydrofuran (THF) molecule and in the presence of $[(L)K(TMEDA)]_2$ **1** and $LiOBu^t$ form lanthanide complex $[\{(L)_2Dy(\mu_2\text{-}OBu^t)Li\}_2(\mu_4\text{-}O)]$ **2**,[14,‡]



Scheme 1

which was characterized by elemental analysis, IR spectroscopy and X-ray crystallography. In the absence of the ligand $LiOBu^t$, the homoleptic complex $[Dy(L)_3]$ **3** was isolated from hexane solution (Scheme 1) and also characterized by X-ray crystallography.[13,†]

According to single-crystal X-ray crystallography (Figure 1),[§] the dysprosium ions in molecule of **2** are surrounded by two N,N′-chelating pyridyl amido ligands and two bridging oxygen atoms. Normally, the $Dy\text{–}N_{pyridyl}$ bond lengths [Dy(1)–N(1) 2.515(7) Å, Dy(2)–N(7) 2.474(7) Å] are apparently longer than

† The divalent lanthanide complexes $[(L)_2Ln(TMEDA)]$ (Ln = Eu and Yb) and homoleptic complex $[Dy(L)_3]$ were prepared at the Chinese University of Hong Kong.[13]

‡ All procedures were performed under vacuum using a standard Schlenk technique or a dry box (O_2, H_2O < 5 ppm). THF was distilled from sodium benzophenone ketyl prior to use. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl or CaH_2. All other commercial chemicals were used after appropriate purification. A yellow solution of $[(L)K(TMEDA)]_2$ (1.52 g, 2 mmol)[13] in anhydrous THF (20 ml) was treated with DyI_2 (0.84 g, 2 mmol)[12] for 4 h at room temperature. A deep dark red suspension changed slowly into a yellow solution, which indicated that Dy^{II} was oxidized to a corresponding Dy^{III} complex, and then add the ligand $LiOBu^t$ (0.16 g, 2 mmol). The solvent was removed under reduced pressure followed by the addition of hexane (40 ml). The hexane extract of the solid was filtered, reduced to ~5 ml, and left for several days at room temperature to give compound **2** as colorless crystals (yield 33%). IR (ν/cm^{-1}): 3386 (w), 3330 (w), 3062 (w), 2962 (s), 2869 (m), 1601 (m), 1586 (w), 1484 (m), 1460 (m), 1440 (s), 1383 (m), 1362 (m), 1327 (m), 1255 (s), 1220 (w), 1195 (m), 1179 (w), 1153 (m), 1108 (m), 1071 (w), 1044 (m), 968 (m), 909 (s), 880 (m), 802 (w), 775 (s), 753 (m), 691 (s), 545 (w), 523 (w). Found (%): C, 42.98; H, 6.68; N, 8.98. Calc. for $C_{44}H_{78}Dy_2Li_2N_8O_3$ (%): C, 43.37; H, 6.45; N, 9.19.

§ *Crystal data for* **2**: $C_{44}H_{78}Dy_2Li_2N_8O_3$, monoclinic, space group $P2_1$, a = 12.2973(5), b = 19.6144(7) and c = 13.2491(5) Å, β = 109.8640(10)°, V = 3005.6(2) Å^3, Z = 2, μ = 2.585 mm^{-1}, S = 1.021, R = 0.0438, wR = 0.0897. X-ray diffraction data were collected at room temperature on a SMART APEX diffractometer (graphite-monochromated MoKα radiation, Φ-ω-scan technique, λ = 0.71073 Å). The intensity data were integrated by means of the SAINT program. SADABS was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against F^2 using all reflections with the aid of the SHELXTL package. All non-hydrogen atoms were refined anisotropically.

CCDC 682392 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2011.

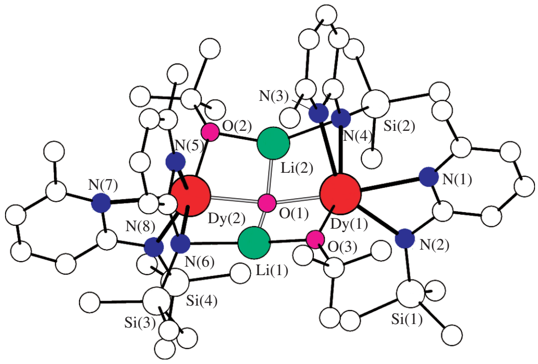
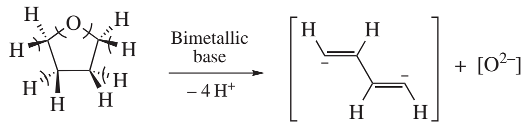


Figure 1 Structure of complex $[\{(L)_2Dy(\mu_2\text{-OBu}^t)Li\}_2(\mu_4\text{-O})]$ **2**. Selected distances (Å): Dy(1)–O(1) 2.174(5), Dy(2)–O(1) 2.165(5), Dy(1)–O(3) 2.187(5), Dy(2)–O(2) 2.176(6), Dy(1)–N(1) 2.515(7), Dy(1)–N(2) 2.351(6), Dy(1)–N(3) 2.456(8), Dy(1)–N(4) 2.505(7), Dy(2)–N(5) 2.490(7), Dy(2)–N(6) 2.523(6), Dy(2)–N(7) 2.474(7), Dy(2)–N(8) 2.337(7), Li(1)–O(1) 2.007(15), Li(2)–O(1) 1.977(15), Li(2)–O(2) 1.818(14), Li(1)–O(3) 1.852(15), Dy(1)–Li(1) 2.879(15), Dy(1)–Li(2) 2.947(14), Dy(2)–Li(2) 2.824(14), Dy(2)–Li(1) 2.953(13).

Dy–N_{amido} bond lengths [Dy(1)–N(2) 2.351(6)Å, Dy(2)–N(8) 2.337(7) Å], respectively. However, we noticed that the Dy–$N_{pyridyl}$ bond lengths [Dy(1)–N(3) 2.456(8) Å, Dy(2)–N(5) 2.490(7) Å] are shorter than Dy–N_{amido} bond lengths [Dy(1)–N(4) 2.505(7)Å, Dy(2)–N(6) 2.523(6) Å], respectively, due to N_{amido} [N(4) and N(6)] also bridged by lithium ions. Interestingly, the four metal ions of Dy^{3+} and Li^+ are bridged by μ_2-pyridyl amido, μ_2-alkoxide and μ_4-oxygen. This generates a novel lanthanide structure with four coplanar subunits. The center place Dy(1)–N(4)–Li(2)–O(2)–Dy(2)–N(6)–Li(1)–O(3) of complex **2** may be viewed as a big window locked by a center μ_4-oxygen O(1). To the best of our knowledge, complex **2** represents the rare observation of a lanthanide cluster, which is in the center of oxygen as a guest in lanthanide chemistry.

Complexes **2** and **3** are reproducible; thus, we concluded that the divalent dysprosium could react with a THF solvent and the central oxygen in complex **2** was from THF. From the standpoint of THF, the cleavage reaction can be represented formally as the breaking of two C–O ring bonds and four substituent C–H bonds (one from each C-ring atom), which leads to two distinct fragments (Scheme 2). To explore this problem, the divalent dysprosium complex has a strong reducing power leading to solvent cleavage confirmed by GC analysis of the reaction mother liquor. Our viewpoint suggests that the origin of the bridging oxygen atom is likely to be ascribed to a two-electron attack on a solvent molecule occurring slowly and irreversibly in a solution of the divalent dysprosium complex, accompanied by the formation of a dianionic diene fragment.[14]



Scheme 2

The synthesis of amido complex forming Dy^{II}-mediated reductive cleavage of THF has been successfully achieved, yielding an oxygen-bridged lanthanide cluster. A careful choice of ligands, metal to ligand ratio and solvent system allowed us to isolate lanthanide complexes. The unique structure of complex **2** showed that a novel lanthanide cluster with μ_4-oxygen is ascribed to the cleavage of the THF molecule. We believe that this method should be applicable to the synthesis of complexes with other lanthanide elements.

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