Low-Valent Thorium Complexes

Amide from Dinitrogen by In Situ Cleavage and Partial Hydrogenation Promoted by a Transient Zero-Valent Thorium Synthon**

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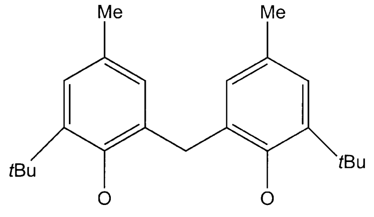
Current research efforts in the field of dinitrogen activation/fixation generally target N_2 cleavage and the incorporation of either nitrides or reduced N_2 moieties into organic substrates.[1] In the sequence of transformations discovered so far (cleavage,[2] incorporation of nitrides into substrates,[3] coordinated N_2 partial hydrogenation,[4] and nitride protonation[5]), the reactions are typically performed in a series of steps. The main challenge towards developing catalytic processes involving N_2 is posed by finding multiple transformations, as in the case of the nitrogenase enzyme, that combines electrons from an ancillary reducing system with protons from the solvent (water) to form ammonia in a catalytic fashion and under mild reaction conditions.[6] A major breakthrough in this direction is the recent discovery of a catalytic cycle for reduction to ammonia obtained by using an ammonium salt as a protonating agent, chromocene as a reductant, and a Mo complex as a N_2 coordinating agent.[7]

In this paper, we wish to present a novel, metal-promoted reduction of N_2 that was obtained during attempts to prepare a low-valent Th species. The reaction resulted in both dinitrogen cleavage and hydrogen abstraction to directly form an -NH_2 functionality.

Recently, actinides also entered the arena of N_2 activation with an example of reversible fixation[8a] and two-electron reduction.[8b] Furthermore, a trivalent uranium complex of a calix[4]tetrapyrrole ligand system, while in the presence of a strong reductant, afforded N_2 cleavage among a variety of other transformations.[9] The use of the same ligand and reducing agent afforded with Th an unprecedented divalent synthon.[10] In both cases, the ability of the ligand to work as both a σ and π donor is most likely the factor that provides sufficient stability to these highly reactive species. With the aim of increasing the reactivity even further, we have now attempted the synthesis of a low-valent Th complex/synthon supported by a robust σ-donor-based ligand system. In particular, we regarded the rare trivalent state of this metal[11] as particularly promising given that the possible $6d^1$ electronic configuration[12] may well provide an exceedingly reactive radical-type species. Herein we describe our findings.

The reaction of $[ThCl_4(dme)_2]$ with the dipotassium salt of the diphenol **1** afforded the corresponding mononuclear complex **2** (Scheme 1). The crystal structure of the complex does not display any particularly significant features. The octahedral coordination environment of the metal is defined by the four O donor atoms of the two diphenolate dianions, one dangling DME molecule, and one chlorine atom, which in turn bridges a potassium atom (Figure 1). The connection of the K cation to the Th-containing moiety is realized not only via the bridging chlorine atom but also through π coordination to one of the two aromatic rings of each of the diphenolate anions. Spectroscopic and analytical data in agreement with the formulation were also obtained. The only noticeable NMR feature is the resonance of the CH_2 group connecting the two phenyl rings, which displayed two sharp and well-separated doublets at $\delta = 5.02$ and 3.52 ppm ($J = 13.3$ Hz) coupled to the same C atom at 35.05 ppm.



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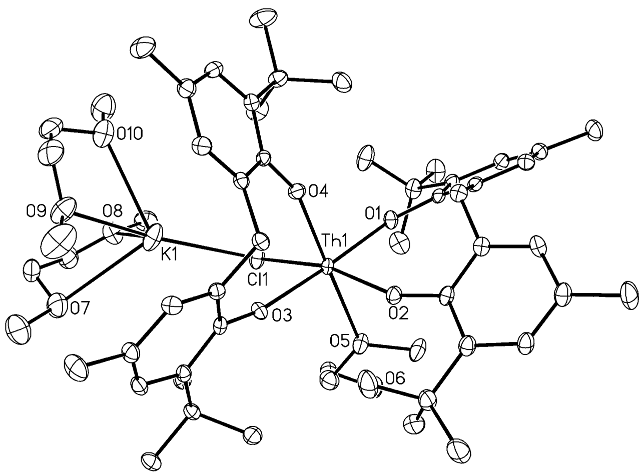

Figure 1. Thermal ellipsoid plot of **2**; bond lengths [Å] and angles [°]: Th-O1 2.209(3), Th-O2 2.208(3), Th-O3 2.240(3), Th-O4 2.197(3), Th-O5 2.613(3), Th-Cl 2.7941(11), Cl-K 3.1274(17); O1-Th-O2 87.56(10), O1-Th-O3 175.49(10), O1-Th-O4 90.33(10), O1-Th-O5 85.44(10), O1-Th-Cl 93.90(7), O2-Th-O3 91.61(10), O2-Th-O4 101.21(11), O2-Th-O5 84.48(10), O2-Th-Cl 164.20(8), O3-Th-O4 85.48(10), O3-Th-O5 98.91(10), O3-Th-Cl 88.10(7), O4-Th-O5 172.78(10), O4-Th-Cl 94.51(8), O5-Th-Cl 79.97(7).

Attempts to reduce **2** to the trivalent state were carried out by treating it with one equivalent of [K(naphthalenide)] in DME (Scheme 1). The reaction afforded a dark-red solution upon mixing. While the reaction carried out under Ar gave

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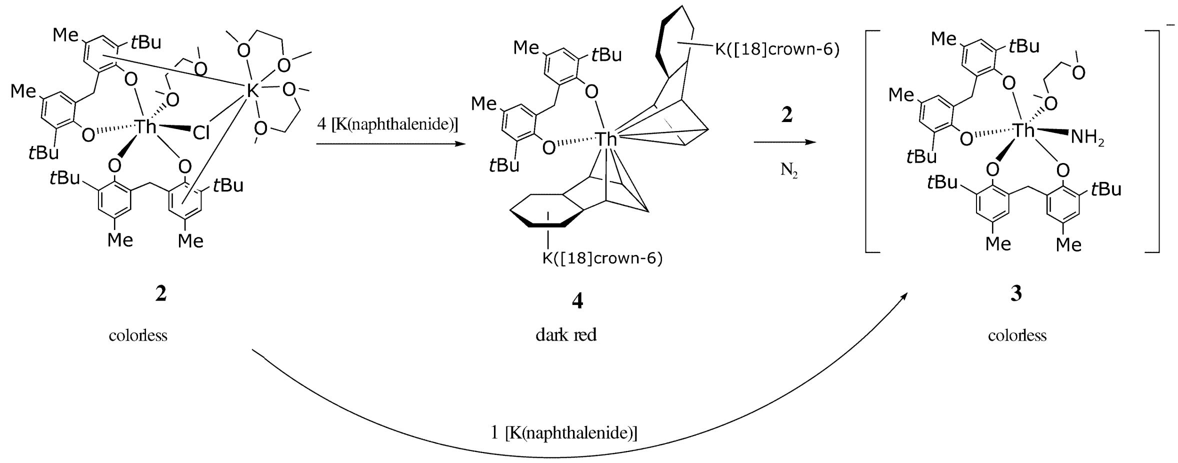
[**] This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC).

DOI: 10.1002/ange.200352205



Scheme 1.

only intractable, dark-colored materials, reaction mixtures kept under nitrogen slowly discolored after about two days. Standard work up of the resulting colorless solution afforded the amide complex **3**, which was isolated as colorless crystals in reasonable yield (47%). The very low percentage of nitrogen in the molecule made analytical values inconclusive although they were in excellent agreement with the proposed formulation obtained from the single-crystal X-ray structure. The arrangement around the thorium atom is very similar to that in **2** (Figure 2) showing the presence of the two diaryloxide ligands with comparable bond lengths and angles. The dangling DME molecule is also present in a *cis* position with respect to the NH_2 group. However, no direct connection is present with the K counterion, which is solvated by four molecules of DME and well separated from its anionic counterpart.

The identification of the amide atom as nitrogen was initially suggested by optimization of the refinement of the thermal parameters. However, the most conclusive evidence about the identity of the nitrogen atom and its origin from gaseous nitrogen was provided by NMR spectroscopy. An identical reaction carried out under $^{15}N_2$ afforded the ^{15}N-labeled **3** in crystalline form. Its ^{15}N NMR spectrum clearly showed the presence of a sharp triplet centered at 155.01 ppm ($J = 57.2$ Hz) coupled to a doublet at $\delta = 2.00$ ppm in the ^{1}H NMR spectrum (broad singlet in the ^{14}N sample). Furthermore, the proton resonance at $\delta = 2.00$ ppm did not show coupling with any carbon atom. This indicates without doubt the presence of an -NH_2 function generated from dinitrogen. All other spectral features were as expected and similar to those of **2**.

The formation of the -NH_2 function is very surprising and implies the participation of several equivalents of reductant, since N_2 cleavage alone requires six electrons. In addition, the acquisition of the two H atoms by the N atom in a non-protic solvent such as DME most likely implies radical-type hydrogen abstraction. In an attempt to clarify this unprecedented and complex transformation, we have focused on the transient red intermediate formed in the initial stage of the reaction. The intense dark color possibly indicates the formation of a low-valent species or synthon, while the slow discoloration in the presence of nitrogen gas indicates that this species is capable of further reaction with N_2. Immediate work-up of the dark-red reaction mixture, or even of identical reactions with two and four equivalents of [K(naphtalenide)], which did not discolor after several days, afforded the same

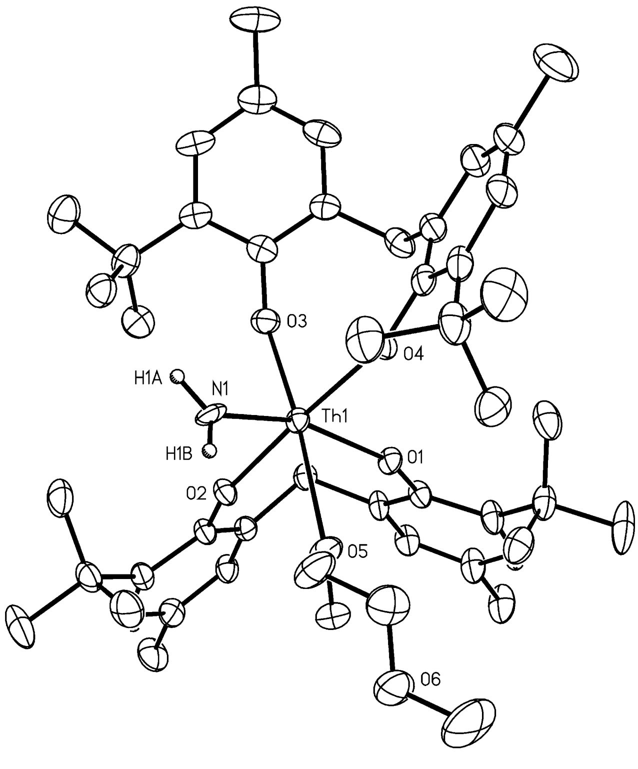


Figure 2. Thermal ellipsoid plot of the anionic moiety of **3**; bond lengths are [Å] and angles [°]: Th-N1 2.2431(6), Th-O1 2.265(4), Th-O2 2.254(4), Th-O3 2.217(5), Th-O4 2.279(4), Th-O5 2.620(5); O1-Th-O2 85.96(14), O1-Th-O3 99.96(16), O1-Th-O4 88.92(15), O1-Th-O5 81.24(15), O1-Th-N1 160.52(18), O2-Th-O3 91.83(16), O2-Th-O4 174.57(14), O2-Th-O5 82.64(16), O2-Th-N1 92.98(16), O3-Th-O4 87.29(17), O3-Th-O5 174.27(16), O3-Th-N1 99.52(17), O4-Th-O5 98.36(17), O4-Th-N1 92.45(17), O5-Th-N1 79.33(17).

very air-sensitive crystalline compound **4** in low yield. As expected, the reaction with four equivalents of reductant gave the best yield (30 %). Despite treatment with [18]crown-6 to improve solubility and crystallinity, compound **4** could not be isolated in an analytically pure form as it was always contaminated by red crystals of [(naphthalene){K([18]-crown-6)}$_2$] and colorless crystals of a new Th complex (not yet identified), thus preventing a complete characterization. The formulation was yielded only by an X-ray analysis (Figure 3). The structure consists of one thorium atom in a pseudotetrahedral environment with the coordination sphere defined by two oxygen atoms of one diaryloxide ligand and the two centroids of two rings of two separate naphthalene molecules. Similar to the case of the calix-tetrapyrrole–naphthalene divalent synthon recently reported,[10] the π-bonding mode of the metal center to one of the two naphthalene rings causes a major ring distortion towards a diene-type arrangement. The other ring of each naphthalene group coordinates one potassium atom, which is in turn coordinated to the six oxygen atoms of one molecule of crown ether.

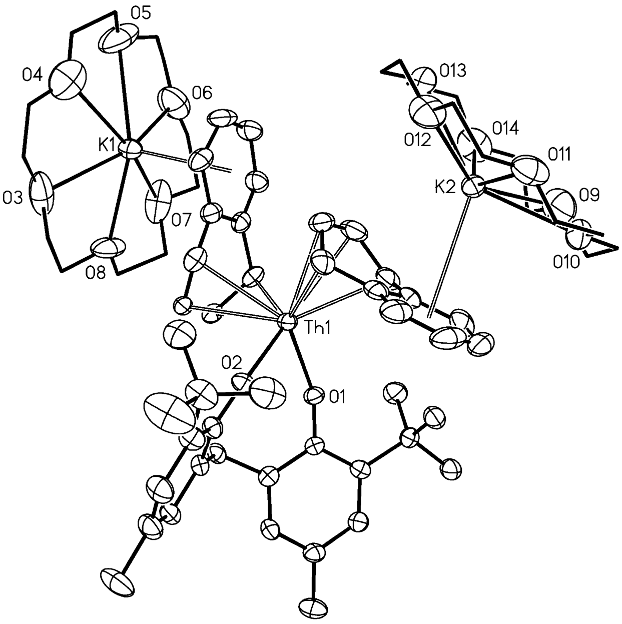


Figure 3. Thermal ellipsoid plot of the anionic moiety of **4**; bond lengths [Å] and angles [°]: Th-O1 2.284(5), Th-O2 2.258(5), Th-C24 2.737(8), Th-C25 2.745(7), Th-C26 2.732(7), Th-C27 2.710(8), Th-C34 2.671(8), Th-C35 2.760(9), Th-C36 2.784(8); O1-Th-O2 83.49(17).

The presence of only one diaryloxide ligand and two potassium atoms around the thorium center assigns a formal zero-valent state to the thorium atom. However, the severe distortion of the two naphthalene rings clearly indicates that the extent of back-bonding is substantial and that complex **4** most likely should be regarded as a tetravalent species or a zero-valent synthon. Its formation, through a reaction with a 1:1 stoichiometric ratio that requires four electrons, confirms that the reaction initially affords **4** through a very rapid process. While this accounts for the transient intense red color observed during the formation of **3**, the lack of reductant necessarily leaves behind a substantial amount of unreacted **2**. The fact that the formation of **3** is not observed in the reactions carried out with larger amounts of [K(naphthalenide)] possibly suggests that it is the reaction of **2** with **4** that triggers a process through which dinitrogen is coordinated, cleaved, and partly hydrogenated, to afford the colorless **3**.

Obviously, a complete rationalization of this remarkable reaction is premature at this stage. We are currently focusing on the working hypothesis that a trivalent Th synthon, either directly formed as a transient intermediate or via comproportionation between **2** and **4**, may react with dinitrogen. Subsequent reaction of the dinitrogen complex with **4** may afford both cleavage and hydrogenation from the solvent via H abstraction. Further work to test this hypothesis is being actively pursued at the moment.

Experimental Section

2: A solution of ligand **1** (0.65 g, 1.92 mmol) in DME (10 mL) was treated with KH (0.15 g, 3.84 mmol). A vigorous reaction took place accompanied by gas evolution. After stirring the mixture for an additional 60 min, a solution of [ThCl$_4$(dme)$_2$] (0.53 g, 0.96 mmol) in DME (5 mL) was added. The resulting pale-brown suspension was stirred for an additional 4 h then centrifuged to eliminate KCl, concentrated to a small volume, and heptane was added. The solution was allowed to stand at −30 °C overnight, upon which colorless crystals of **2** were formed (1.03 g, 0.82 mmol, 86 %). Elemental analysis calcd (%) for $C_{58}H_{90}O_{10}KClTh$: C 55.56, H 7.23; found: C 55.41, H 7.17. ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): $\delta = 7.35$ and 7.07 (d, CH phenyl ring, 4 H each), 5.02 and 3.52 (d, CH$_2$ (ligand), 2 H each), 3.73 (s, CH$_2$ (DME), 12 H), 3.58 (s, CH$_3$ (DME), 18 H), 2.49 (s, Me (ligand), 12 H), 1.76 ppm (br s, *t*Bu (ligand), 36 H); ^{13}C NMR (125.72 MHz, [D$_8$]THF, 25 °C): $\delta = 162.19$, 137.01, 134.90, 35.54 (quat C), 129.27 and 124.98 (CH aromatic), 72.71 (CH$_2$ (DME)), 58.97 (Me (DME)), 35.05 (CH$_2$ (ligand)), 31.20 (*t*Bu), 21.35 ppm (Me (ligand)).

3: A solution of **2** (0.76 g, 0.61 mmol) in DME (5 mL) was reacted at room temperature with a solution of [K(naphthalenide)] in DME, which was prepared by dissolving K (0.024 g, 0.61 mmol) with naphthalene (0.078 g, 0.61 mmol) in DME (5 mL), to afford a dark-red mixture. Stirring was continued for 72 h upon which the color slowly faded forming a nearly colorless solution. The suspension was filtered and layered with heptane at room temperature for two days, upon which colorless crystals of **3** were formed (0.45 g, 0.29 mmol, 47 %). Elemental analysis calcd (%) for $C_{76}H_{120}NO_{14}KTh$: C 59.16, H 7.84, N 0.91; found: C 59.09, H 7.77, N 1.03. ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): $\delta = 8.09$ and 7.70 (m, naphthalene, 4 H each), 7.25 and 6.98 (d, CH phenyl ring, 4 H each), 4.99 and 3.35 (d, CH$_2$ (ligand), 2 H each), 3.69 (s, CH$_2$ (DME), 12 H), 3.54 (s, CH$_3$ (DME), 18 H), 2.41 (s, Me (ligand), 12 H), 2.00 (br s, NH$_2$, 2 H), 1.73 ppm (s, *t*Bu (ligand), 36 H). ^{13}C NMR (125.72 MHz, [D$_8$]THF, 25 °C): $\delta = 162.71$, 137.01, 134.54, 123.25, 35.55 (quat C), 129.28 and 125.00 (CH aromatic), 128.64 and 126.55 (naphthalene), 72.78 (CH$_2$ (DME)), 58.94 (Me (DME)), 34.51 (CH$_2$ (ligand)), 30.85 (*t*Bu), 21.39 ppm (Me (ligand)). ^{15}N NMR (50.66 MHz, [D$_8$]THF, 25 °C): $\delta = 155.01$ ppm (t, $J =$ 57.2 Hz).

4: A solution of **2** (1.02 g, 0.81 mmol) in DME (10 mL) was reacted at room temperature with a solution of K(naphthalenide) in DME, which was prepared by dissolving K (0.13 g, 3.3 mmol) with naphthalene (0.41 g, 3.5 mmol) in DME (7 mL) affording a dark-red mixture. The dark-red suspension was immediately centrifuged and the supernatant concentrated to about half of the volume and treated with a solution of [18]crown-6 (0.38 g, 1.5 mmol) in toluene. The solution was placed in a freezer for one day at −30 °C and afforded dark-red crystals of **4** contaminated by [(naphthalene){K([18]crown-

6)}$_2$] and another unidentidfied tetravalent thorium complex (approximately 30 %).

Crystal data for **2**: $C_{58}H_{90}O_{10}KClTh$, $M_r = 1253.89$, monoclinic, *P*21/*m*, $a = 15.015(2)$, $b = 20.836(3)$, $c = 19.740(3)$ Å, $\beta = 99.144(3)°$, $V = 6096.9(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.366\ \mathrm{Mg\,m^{-3}}$; absorption coefficient 2.610 mm^{-1}, $F(000) = 2576$, reflections collected 43472, independent reflections 14178, GOF = 1.006, $R = 0.0417$, $wR^2 = 0.0839$.

Crystal data for **3**: Two crystallographically independent but chemically equivalent molecules were found in the asymmetric unit. $C_{152}H_{240}N_2O_{28}K_2Th_2$, $M_r = 3085.74$, monoclinic, *P*21/*c*, $a = 25.9697(12)$, $b = 21.0627(9)$, $c = 30.5093(15)$ Å, $\beta = 99.895(2)°$, $V = 16440.1(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.247\ \mathrm{Mg\,m^{-3}}$; absorption coefficient 1.921 mm^{-1}, $F(000) = 6432$, reflections collected 47999, independent reflections 32316, GOF = 1.008, $R = 0.0572$, $wR^2 = 0.1520$.

Crystal data for **4**: The data for this compound is not unquestionable due to the very poor crystal quality observed. For example, in spite of the β angle being equal to 90°, the systematic absences clearly indicate a monoclinic symmetry rather than orthorhombic; a chemically meaningful solution was obtained for a treatment in the monoclinic system. $C_{74}H_{102}O_{14}K_2Th$, $M_r = 1525.80$, monoclinic, *P*21/*m*, $a = 17.391(9)$, $b = 21.163(11)$, $c = 19.701(11)$ Å, $\beta = 90.000(9)°$, $V = 7251(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.398\ \mathrm{Mg\,m^{-3}}$; absorption coefficient 2.233 mm^{-1}, $F(000) = 3144$, reflections collected 45100, independent reflections 12764, GOF = 1.031, $R = 0.0561$, $wR^2 = 0.1152$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC-213059 (**2**) -213060 (**3**), and -213061 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: June 23, 2003 [Z52205]

Keywords: nitrogen · O ligands · subvalent compounds · synthons · thorium

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