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Cis Double Addition of CO_2 to a Coordinated Arene of a Thorium Complex

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Summary: Treatment of a Th−arene complex with CO_2 afforded the first case of cis double insertion into an M−arene π bond.

The chemistry of reduced early actinides complexes poses considerable challenges, due to the fact that these species are exceedingly rare, possibly as a result of an extreme reactivity.[1,2] Furthermore, these species display an intriguing feature as far as the oxidation state is concerned. Even in the very few existing examples of complexes where a *formal* low-valent state could be attributed to the metal on the basis of the molecular connectivity,[3,4] the *spectroscopic* oxidation is higher due to the presence of extensive metal-to-ligand charge-transfer interactions. Nonetheless, the chemical behavior of these compounds indeed remains that of strongly reducing agents, as could be expected from low-valent compounds.

A particularly ingenious strategy to get around the difficulties associated with the synthesis of such reactive species relies on the preparation of low-valent synthetic equivalents (synthons).[5,6] The basis of this methodology is 2-fold. The first consists of using higher valent species which, in the presence of reductants, afford transformations that would be expected from genuine low-valent species.[6] The second relies on the preparation of *formally* low-valent complexes in which the metal engages in extensive back-bonding interactions with neutral ligands (e.g. arenes).[3b,7] In this case, dissociation of the ligand usually accompanies the reactivity with the substrate.

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[1] See for example: (a) Avens, L. R.; Barnhardt, D. M.; Burns, C. J.; McKee, S. D. *Inorg. Chem.* **1996**, *35*, 537. (b) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *Chem. Commun.* **2002**, *23*, 2764. (c) Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 15734. (d) Roussel, P.; Scott, P. *J. Am. Chem. Soc.* **1998**, *120*, 1070. (e) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6877. (f) Mindiola, D. J.; Tsai, Y. C.; Hara, R.; Chen, Q.; Meyer, K.; Cummins, C. C. *Chem. Commun.* **2001**, *1*, 125. (g) Cloke, F. G. N.; Hitchcock, P. B. *J. Am. Chem. Soc.* **2002**, *124*, 9352. (h) Evans, W. J.; Kozimor, S. A., Ziller, J. W. *J. Am. Chem. Soc.* **2003**, *125*, 14264. (i) Korobkov, I.;, Gambarotta, S.; Yap, G. P. A. *Organometallics* **2001**, *20*, 2552. (j) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 3433.

[2] For a recent review see: Korobkov, I.; Gambarotta, S. *Prog. Inorg. Chem.*, in press.

[3] (a) Guggenberger, L. J.; Jacobson, R. A. *Inorg. Chem.* **1968**, *7*, 2257. (b) Diaconescu, P.; Arnold, P. L.; Baker, T.; Mindiola, D.; Cummins, C. C. *J. Am. Chem. Soc.* **2000,** *12*, 6108. (c) Diaconescu, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2002**, *124*, 7660. (d) Arliguie, T.; Lance, M.; Nierlich, M.; Vigner, J.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1994**, 847.

[4] (a) Parry, J. S.; Cloke, G. F. N.; Cole, S. J.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1999**, *121*, 6867 and references cited therein. (b) Kannellakopulos, B.; Dornberger, E.; Baumgaertner, F. *In. Nucl. Chem. Lett.* **1974**, *10*, 155. (c) Blake, P. C.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1148. (d) Spirlet, M. R.; Rebizant, J.; Goffart, J. *Acta Crystallogr., Sect. B* **1982**, *38*, 2400.

[5] The term "synthon" was forged by Corey and used to define "a structural unit within a molecule related to possible synthetic operation". In coordination and organometallic chemistry, it can be also attributed to molecules that behave as synthetic equivalents of species that are not likely to exist.

[6] (a) Warner, B. P.; Scott, B. L.; Burns, C. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 959. (b) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S. S.; Vollmer, H.; Day, V. W. *Organometallics* **1982**, *1*, 170.

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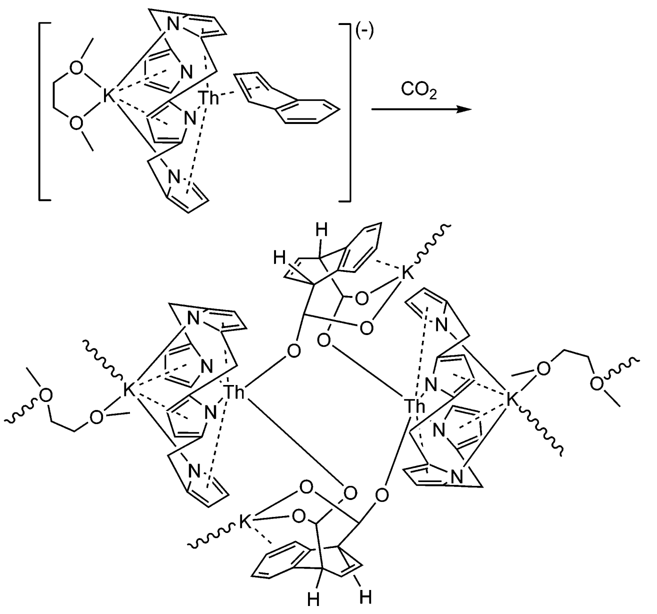
Scheme 1



By reducing the tetravalent [(Et$_8$-calyx-[4]-tetrapyrrole)Th(μ-Cl)]$_2$[K(DME)]$_2$ with K(naphthalene), it was possible to obtain a unique example of the Th arene complex {[(Et$_8$-calyx-[4]-tetrapyrrole)ThK(DME)](μ,μ'-η^4:η^6-C$_{10}$H$_8$)(μ-K)}$_n$ (Scheme 1).[8] Similar to the case of some lanthanide arene complexes,[9] the coordinated naphthalene showed a very noticeable structural deformation, clearly indicative of extensive back-bonding and consequent loss of aromaticity. The complex acts as a two-electron reductant and performs unusual reactions by releasing the intact arene, as would be expected for a divalent species.[8,10] We now describe the reaction of the same complex with CO$_2$, which is well known to perform interesting insertion reactions in lanthanide chemistry.[11a] In line with the reactivity previously reported,[8] a predominance of reduced-species behavior would be expected to produce arene dissociation and consequent oxidative addition of CO$_2$, in turn affording coordination, disproportionation, or deoxygenation. Vice versa, a genuinely tetravalent complex, as is in fact suggested by the deformation of the coordinated naphthalene ring, should promote insertion of CO$_2$ into an M$-$C$_{\text{arene}}$ bond, in analogy with the behavior of dienes while coordinated to early transition metals.[11b] On the other hand, insertion reactions into the M$-$arene bonds, affording addition and irreversible loss of aromaticity, are very rare and have been reported only for divalent lanthanide complexes (Sm, Eu, Yb) of the naphthalene dianion.[9,12]

The exposure of a deep red toluene solution of {[(Et$_8$-calyx-[4]-tetrapyrrole)ThK(DME)](μ,μ'-η^4:η^6-C$_{10}$H$_8$)(μ-K)}$_n$ to CO$_2$ at room temperature and 1 atm afforded a gradual discoloration of the reaction mixture within 15 min (Scheme 1).[13] The colorless solution gave colorless crystals of the new compound [(Et$_8$-calyx-[4]-tetrapyrrole)ThK(DME)]$_2$[*m-cis*-1,4-(CO$_2$)$_2$C$_{10}$H$_6$K(DME)$_{1.5}$]$_2$ (**1**), resulting from the cis insertion of two molecules of CO$_2$ at 1- and 4-positions of the coordinated naphthalene ring.

The connectivity was provided by an X-ray crystal structure (Figure 1). The complex is a symmetry-generated dimer with two identical (Et$_8$-calyx-[4]-tetrapyrrole)Th units bridged by two *cis*-1,4-dihydronaphthalene-1,4-dicarboxylato dianions (Th(1)$-$O(3) = 2.249(9) Å, Th(1)$-$O(6A) = 2.353(11) Å). Of the four potassium atoms connected to the dinuclear unit, two are each attached to one calyx-[4]-tetrapyrrole ligand by adopting both the σ (K(1)$-$N(2) = 3.076(13) Å, K(1)$-$N(4) = 3.113(15) Å) and π bonding modes (K(1)$-$N(1) = 3.095(14) Å, K(1)$-$C(1) = 3.329(16) Å, K(1)$-$C(3) = 3.392(18) Å, K(1)$-$C(4) = 3.208(18) Å). The other two potassium atoms are each connected to the two oxygen atoms of the two carboxylic functions of the same dicarboxylato dianion (K(2)$-$O(4) = 2.656(12) Å, K(2)$-$O(5) = 2.644(13) Å) and to a section of the aromatic ring of the dihydronaphthalene residue (K(2)$-$C(45) = 3.377(15) Å, K(2)$-$C(46) = 3.375(16) Å). Each calyx-[4]-tetrapyrrole unit adopts the usual bonding mode[10] with thorium, in which the two pyrrolide groups in the trans positions of the macrocyclic ring are π bonded (Th(1)$-$N(2) = 2.739(13) Å) and the remaining two are σ bonded (Th(1)$-$N(1) = 2.537(12) Å, Th(1)$-$N(3) = 2.551(11) Å). The two dicarboxylato dianions bridge the two thorium atoms using one of the two oxygen atoms of each carboxylato group. The second oxygen atom of each carboxylato group is instead bonded to the same potassium atom. Of the two rings of the dihydronaphthalene residue, one has the aromatic ring intact, while the second, which bears the two carboxylato functions, shows a substantially short C$-$C bond for the two carbon atoms between the carboxylato groups (C(48)$-$C(49) = 1.32(2) Å), indicative of a substantial localization of double-bond character. Each potassium attached to the carboxylato groups also coordinates one DME molecule and one oxygen atom of a dangling DME molecule, which in turn is bonded to a similar potassium atom of another dinuclear unit. The two potassium atoms connected to the tetrapyrrolide anions are each

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[13] A solution of Th(C$_{36}$H$_{48}$N$_4$)(C$_{10}$H$_8$)K$_2$(DME)$_3$ (0.40 g, 0.321 mmol) in DME (5 mL) was prepared inside a drybox and placed in a Schlenk tube. The reaction mixture was frozen, and N$_2$ was removed and replaced by CO$_2$. Immediately upon melting, the color of the reaction mixture started to fade and completely disappeared after 15 min to afford a pale yellow solution. The solution was concentrated to 2.5 mL and layered with 10 mL of *n*-heptane. After 2 days, colorless prisms of **1** separated (0.178 g, 0.138 mmol, 43%). Anal. Calcd. (found) for [Th(C$_{36}$H$_{48}$N$_4$)(C$_{12}$H$_8$O$_4$)K(DME)]K(DME)$_{1.5}$: C, 54.06 (53.98); H, 6.34 (6.29); N, 4.35 (4.27). ^{1}H NMR (500 MHz, d_8-THF, 27 °C; δ): 7.20–6.40 (series of m, C$-$H napht, 4H), 6.49 and 6.09 (br s, C$-$H olef, 2H), 5.63 (m, C$-$H pyrr, 8H), 4.45 (s, C$-$H exo, 2H), 3.42 (s, CH$_2$ DME, 10H), 3.25 (s, CH$_3$ DME, 15H), 1.90 (overlapping q, CH$_2$, 16H), 0.50 (two series of overlapping t, CH$_3$, 24H). ^{13}C NMR (125.72 MHz, CDCl$_3$; δ): CH pyrrole, 101.31 and 100.86; CH$_2$ ethyl groups, 30.43 and 29.45; CH$_3$ ethyl groups, 9.15 and 9.27; CH 1,4-tetrahydronaphthalene ring, 51.69 (ipso), 115.51 (olefinic), 115.23 (aromatic), and 127.24 (aromatic); CH$_3$ DME, 59.10; CH$_2$ DME, 72.87; quaternary C, 156.92, 153.54, 136.97, 105.58, 47.60.

[14] Crystal data for **1**: C$_{58}$H$_{81}$K$_2$N$_4$O$_9$Th, $M_r = 1287.50$, monoclinic, $P2c$, $a = 17.034(5)$ Å, $b = 16.684(5)$ Å, $c = 20.545(6)$ Å, $b = 94.161(5)°$, $V = 5823(3)$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.469$ Mg m^{-3}, absorption coefficient 2.761 mm^{-1}, $F(000) = 2624$, 41 513 reflections collected, 7075 independent reflections, GOF = 1.112, R1 = 0.0791, wR2 = 0.1824.

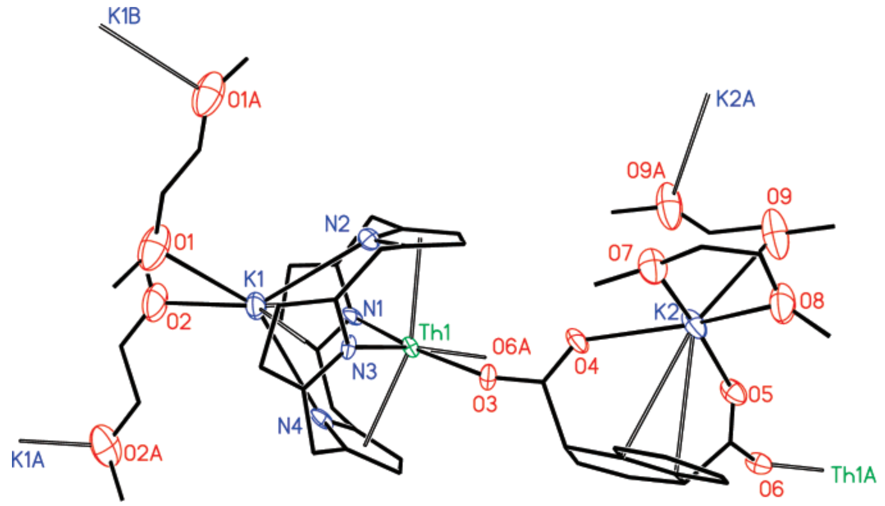

Figure 1. Thermal ellipsoid plot of **1** at the 30% probability level. Ethyl groups have been omitted for clarity.

coordinated to two oxygen atoms of two dangling DME groups, which are also bonded to another potassium atom of other dimeric units. The bridging interactions between potassium atoms via the coordinated DME molecules assemble an infinite three-dimensional array.

The 3-D polymeric structure observed in the solid-state crystal structure is unlikely to be preserved in solution. However, the complexity of the ^{1}H NMR spectrum, often observed in the f-block complexes of this ligand system,[1i] strongly suggests that the dimeric structure is retained in solution. The eight ethyl groups are present as two complex sets of overlapping triplets and quadruplets centered at 0.50 and 1.90 ppm, respectively. However, only two resonances were observed in the ^{13}C NMR spectrum for the methylene group, with two resonances for methyl carbon atoms. A multiplet at 5.63 ppm was observed for the pyrrolide C−H groups, which corresponds to two resonances at 103.31 and 100.86 ppm in the ^{13}C NMR spectrum. The *cis*-1,4-dihydronaphthalene-1,4-dicarboxylato anions gave resonances for the aromatic ring as a series of multiplets in the range 7.20 and 6.40 ppm. The olefinic C−H groups are found as a rather broad triplet at 6.49 and 6.09 ppm, while the exo H atom is present at 4.45 ppm.

There are two conclusions which can be drawn about the insertion of CO_2 described in this work. First, the insertion occurs at two of the four Th−C contacts formed by the metal with one of the two naphthalene rings. The fact that the stereochemistry of the addition is cis clearly indicates that the double insertion occurs at the same metal center and that the final bridging dinuclear arrangement may in fact be due to a subsequent rearrangement. Second, the fact that two molecules of CO_2 have been added to naphthalene implies a two-electron reduction of one of the two aromatic rings. The insertion at the positions 1 and 4 has a stringent analogy with the behavior of Zr(diene) derivatives[11] and with the lanthanide naphthalene complexes,[12] although the stereochemistry of the CO_2 double addition to the aromatic ring has not been clarified. Therefore, while the behavior of the coordinated arene might be expected, given its structural distortion and the probable presence of a tetravalent thorium atom, it is conceptually different from the previous reactivity of this complex, showing that the two-electron redox transformations were occurring at the metal center rather than at the coordinated arene.[8,10]

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Supporting Information Available: Complete crystallographic data (including CIF files) for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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