Organometallics **2008,** *27,* 15–17

Communications

Single and Double Alkyl Abstraction from a Bis(anilido)xanthene Thorium(IV) Dibenzyl Complex: Isolation of an Organothorium Cation and a Thorium Dication

Carlos A. Cruz, David J. H. Emslie,* Laura E. Harrington, and James F. Britten

Department of Chemistry, McMaster University, 1280 Main Street West, Hamilton, ON, L8S 4M1, Canada

Received November 15, 2007

*Summary: Reaction of [(XA$_2$)ThCl$_2$(dme)] [XA$_2$ = 4,5-bis(2,6-diisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene] with 2 equiv of PhCH$_2$MgCl resulted in the formation of solvent-free [(XA$_2$)Th(CH$_2$Ph)$_2$] (**1**). Subsequent reaction of **1** with either 1 or 2 equiv of B(C$_6$F$_5$)$_3$ allowed isolation of the first non-cyclopentadienyl actinide alkyl cation, [(XA$_2$)Th(CH$_2$Ph)][PhCH$_2$B(C$_6$F$_5$)$_3$] (**2**), and a rare example of an actinide dication, [(XA$_2$)Th][PhCH$_2$B(C$_6$F$_5$)$_3$]$_2$ (**3**). The X-ray crystal structure of the dication reveals π-coordination of both PhCH$_2$B(C$_6$F$_5$)$_3$ anions, and solution NMR spectroscopy shows that a similar mode of contact ion pairing is operative in the monocation.*

Organometallic complexes of the early transition metals and lanthanides have received considerable recent attention, in no small part due to their proficiency as catalysts for transformations such as olefin polymerization, hydrogenation, and hydroamination.[1] Over the course of these studies, complexes supported by non-carbocyclic ancillary ligands have played an increasingly prominent role, providing a wide variety of metal-binding environments that contrast those provided by cyclopentadienyl anions, and allowing facile tuning of both steric and electronic properties.[2] By contrast, the vast majority of organoactinide(IV) chemistry has involved neutral complexes bearing carbocyclic (e.g. $C_5R_5^-$ or $C_8R_8^{2-}$) ancillaries.[3]

A major current focus of our research is investigation of the potential for rigid non-carbocyclic ligands to stabilize neutral and cationic organothorium(IV) and uranium(IV) complexes.[4,5] Such complexes are anticipated to be particularly reactive as a result of tetravalency (in contrast with predominantly trivalent group 3 and lanthanide metals) combined with the electropositive nature and large ionic radii of early actinides. The potential for covalency and f-orbital participation in early actinide metal–ligand bonding can also lead to reactivity that deviates substantially from that of related transition metal and lanthanide complexes.[6]

Herein we report the synthesis of a dibenzyl thorium complex, [(XA$_2$)Th(CH$_2$Ph)$_2$] (**1**; XA$_2$ = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene),[4,7] followed by reaction of **1** with either 1 or 2 equiv of B(C$_6$F$_5$)$_3$ to give the first non-cyclopentadienyl actinide alkyl cation and the first example of double alkyl abstraction to form an actinide dication.

Reaction of [(XA$_2$)ThCl$_2$(dme)][4] with 2 equiv of benzyl magnesium chloride at −78 °C resulted in the formation of base-free [(XA$_2$)Th(CH$_2$Ph)$_2$] (**1**)[7] as a hexane-soluble light yellow solid in 56% yield. At 50 °C, the ^{1}H NMR of **1** is suggestive of C_{2v} symmetry. However, at below −40 °C, a spectrum consistent with a C_s-symmetric complex lacking top−bottom symmetry and containing two distinct benzyl groups is observed.[8] The $^1J_{C,H}$ coupling constants of 120 and 139 Hz for *CH*$_2$Ph indicate that one benzyl group is η^1-coordinated, while the other adopts an η^2- or η^3-coordination mode.[9]

X-ray quality crystals of **1** were grown from hexanes at −30 °C. The unit cell contains two distinct molecules of **1** [Th−CH$_2$ = 2.503(3)–2.545(3) Å], and in both cases, one benzyl group is located in the ligand plane while the other occupies an apical site. For both molecules, the in-plane benzyl group adopts a bonding mode intermediate between η^2- and η^3-coordination [Th−CH$_2$−C$_{ipso}$ = 85.6(2)° and 87.5(2)°; Th−C$_{ipso}$ = 2.826(3)

---

* Corresponding author. E-mail: emslied@mcmaster.ca. Fax: (905)-522-2509. Tel: (905)-525-9140.

(1) (a) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1. (b) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161. (c) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673.

(2) (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851. (c) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233*, 131. (d) Gromada, J.; Carpentier, J.-F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397. (e) Arndt, S.; Okuda, J. *Adv. Synth. Catal.* **2005**, *347*, 339. (f) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404.

(3) (a) Burns, C. J.; Clark, D. L.; Sattelberger, A. P. Actinides: Organometallic Chemistry. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Lukehart, C. M., Eds.; John Wiley & Sons: Chichester, England, 2005; Vol. 1, p 33. (b) Barnea, E.; Eisen, M. S. *Coord. Chem. Rev.* **2006**, *250*, 855.

(4) Cruz, C. A.; Emslie, D. J. H.; Harrington, L. E.; Britten, J. F.; Robertson, C. M. *Organometallics* **2007**, *26*, 692.

(5) (a) Jantunen, K. C.; Batchelor, R. J.; Leznoff, D. B. *Organometallics* **2004**, *23*, 2186. (b) Jantunen, K. C.; Haftbaradaran, F.; Katz, M. J.; Batchelor, R. J.; Schatte, G.; Leznoff, D. B. *Dalton Trans.* **2005**, 3083.

(6) Keogh, D. W. Actinides: Inorganic & Coordination Chemistry. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Crabtree, R. H., Eds.; John Wiley & Sons: Chichester, England, 2005; Vol. 1, p 2.

(7) For the synthesis of *N*-mesityl- and *N*-cyclohexyl-substituted 4,5-bis(amido)xanthene ligands, and the preparation of titanium(IV) bis(amido) and dibenzyl complexes, see: Porter, R. M.; Danopoulos, A. A. *Polyhedron* **2006**, *25*, 859.

(8) Selected ^{1}H and ^{13}C NMR chemical shifts (ppm): Complex **1** (C$_7$D$_8$, −50 °C): Th*CH*$_2$ (1.34, 1.26), *ipso*-CH$_2$*C*$_6$H$_5$ (149.3, 144.2), Th*C*H$_2$ (93.4, 90.9). Complex **2** (C$_6$D$_6$, 20 °C): BCH$_2$C$_6$*H*$_5$ (6.52 [*o*], 5.98 [*m*], 6.56 [*p*]), B*CH*$_2$ (3.25), Th*CH*$_2$ (2.40), *ipso*-BCH$_2$*C*$_6$H$_5$ (162.9), *ipso*-ThCH$_2$*C*$_6$H$_5$ (144.5), Th*C*H$_2$ (93.1), B*C*H$_2$ (35.9).

(9) (a) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649. (b) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424. (c) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473.

10.1021/om7011503 CCC: $40.75 © 2008 American Chemical Society
Publication on Web 12/20/2007

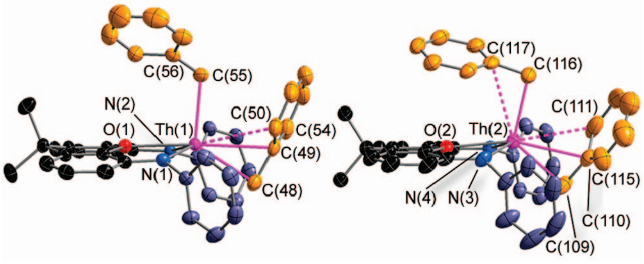


Figure 1. Molecular structure of $[(XA_2)Th(CH_2Ph)_2]$ (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms and isopropyl and *tert*-butyl groups are omitted for clarity.

and 2.851(3) Å; $Th(1)-C_{ortho} = 3.191(3)$ and 3.510(3) Å; $Th(2)-C_{ortho} = 3.126(4)$ and 3.647(4) Å].[10] By contrast, the apical benzyl group is η^1-coordinated in one molecule [$Th(1)-CH_2-C_{ipso} = 115.1(2)°$; $Th(1)-C_{ipso} = 3.402(3)$ Å], but approaches η^2-coordination in the other [$Th(2)-CH_2-C_{ipso} = 96.1(2)°$; $Th(2)-C_{ipso} = 3.058(3)$ Å].[9]

Slow addition of dibenzyl complex **1** to 1 equiv of $B(C_6F_5)_3$ in hexanes resulted in the immediate precipitation of $[(XA_2)Th(CH_2Ph)][PhCH_2B(C_6F_5)_3]$ (**2**) as a bright yellow solid in 95% yield. Despite numerous attempts, X-ray quality crystals of **2** were not obtained. However, the nature of **2** was established by NMR spectroscopy, elemental analysis, and reactivity (*vide infra*). The only other well characterized molecular actinide alkyl cations are $[(C_5Me_5)_2Th(CH_2SiMe_3)][C_0(B_9C_2H_{11})_2]$ and $[(C_5Me_5)_2ThMe(THF)_n]X$ ($n = 0$, 1 or 2; X = various weakly-coordinating anions) reported by Marks et al.,[11] and $[(C_5Me_5)_2UMe(THF)][BPh_4]$ reported by Evans et al.[12]

Solution NMR data for **2** between 50 and −90 °C are commensurate with a C_s-symmetric complex lacking top−bottom symmetry.[8] These data, as well as the high solubility of **2**, indicate tight ion pairing, presumably through π-coordination of the anion. Evidence for this coordination mode is provided by a $\Delta\delta_{m-p}$ value of 3.93 ppm in the ^{19}F NMR spectrum, the upfield position of the *m*-BCH_2Ph protons (5.98 ppm), and the downfield shift of the *ipso*-BCH_2Ph carbon (162.9 ppm) relative to that of the "free" anion (148.2 ppm). Through-space coupling between the *o*- and *m*-BCH_2Ph protons and one of the $CHMe_2$ groups was also observed by 2D-ROESY NMR spectroscopy. The benzyl group on thorium is η^1-coordinated, based on a $^1J_{C,H}$ value of 119 Hz for $ThCH_2Ph$.[9]

Slow diffusion of a hexane solution of $B(C_6F_5)_3$ into a toluene solution of **2** at −30 °C resulted in precipitation of a bright orange crystalline solid. Solution NMR spectroscopic studies on this product were not possible due to insolubility in solvents with which it did not react. However, the complex was identified as dicationic $[(XA_2)Th][PhCH_2B(C_6F_5)_3]_2$ (**3**; Figure 1) by X-ray crystallography and elemental analysis.[13]

The solid-state structure of **3** is shown in Figure 2. The XA_2 backbone is approximately planar and the benzyl borate anions

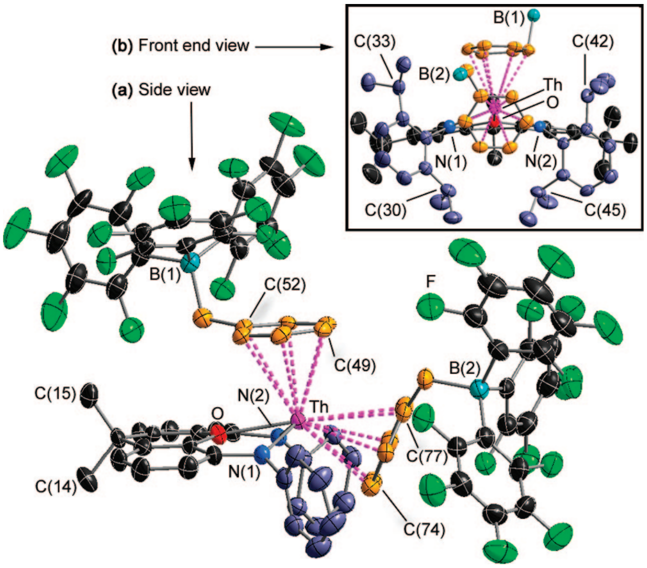
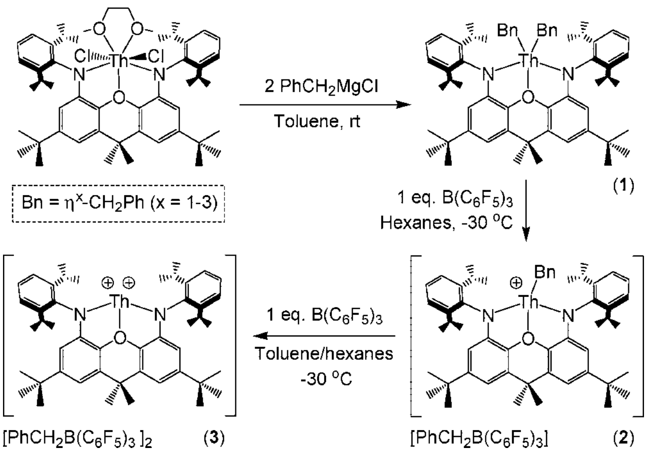


Figure 2. Molecular structure of $[(XA_2)Th][PhCH_2B(C_6F_5)_3]_2 \cdot 3toluene \cdot 2hexane$ with thermal ellipsoids at the 50% probability level: (a) side view, (b) front end view. Hydrogen atoms and solvent are omitted for clarity. Isopropyl and *tert*-butyl groups are also omitted in (a). Pentafluorophenyl groups are omitted in (b).

Scheme 1. Synthesis of Complexes 1−3



are π-coordinated to thorium both in the ligand plane and in the apical site, with Th−C(X) bond distances increasing in the order $C(X) = C_{para} < C_{meta} < C_{ortho} < C_{ipso}$ [from 2.900(7) to 3.280(7) Å and 2.937(6) to 3.257(7) Å for the borate anions in the ligand plane and the apical site, respectively]. To minimize unfavorable steric interactions between benzylborate anions and ligand isopropyl groups, the thorium atom resides 0.908(6) Å above the plane defined by the NON-donor atoms, and the 2,6-diisopropylphenyl groups are rotated to give C(30)···C(45) and C(33)···C(42) distances of 4.139(12) and 8.531(11) Å, respectively.

Double alkyl, aryl, or hydride abstraction has been observed only in a handful of cases,[14−17] and the resulting dications are typically stabilized by additional Lewis base (O-, N-, or P-donor) coordination. To the best of our knowledge, the only other "Lewis base-free" dications formed

---

[10] Bond alternation, as found in the ring of the η^3-coordinated benzyl group in $[Cp^*Zr(\eta^3-CH_2Ph)(\eta^7-CH_2Ph)]^+$, was not observed: Pellecchia, C.; Immirzi, A.; Pappalardo, D.; Peluso, A. *Organometallics* **1994**, *13*, 3773.

[11] (a) Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127. (b) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840. (c) Yang, X.; King, W. A.; Sabat, M.; Marks, T. J. *Organometallics* **1993**, *12*, 4254. (d) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755. (e) Chen, Y.-X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451. (f) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842.

[12] (a) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 3407. (b) The uranium alkynyl cation, $[(Et_2N)_2U(C_2tBu)(HC_2tBu)][BPh_4]$, has also been reported: Dash, A. K.; Wang, J. X.; Berthet, J.-C.; Ephritikhine, M.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *604*, 83.

[13] Other structurally characterized organoactinide dications are $[(COT)U(hmpa)_3][BPh_4]_2$ and $[Cp^*{}_2U(NCMe)_5]X_2$ (X = I, OTF or BPh_4): (a) ref 14b. (b) Maynadié, J.; Berthet, J.-C.; Thuéry, P.; Ephritikhine, M. *J. Am. Chem. Soc.* **2006**, *128*, 1082. (c) Maynadié, J.; Berthet, J.-C.; Thuéry, P.; Ephritikhine, M. *Organometallics* **2006**, *25*, 5603.

by this method are $[(t\text{Bu}_3\text{PN})_2\text{Ti}]\text{X}_2$,[15] $[(\text{nacnac})\text{Sc}]\text{X}_2$,[16] and $[(\text{C}_5\text{H}_4\text{CMe}_2\text{Ph})_2\text{Zr}]\text{X}_2$,[17] where X is the $\text{MeB(C}_6\text{F}_5)_3$ anion, and $[\text{LSc(CH}_2\text{SiMe}_3)][\text{B(C}_6\text{F}_5)_4]_2$ generated *in situ* and characterized by NMR spectroscopy (L = 1,1,1-tris[(*S*)-4-isopropyloxazolinyl]ethane)[18] or suggested on the basis of extremely high 1-hexene polymerization activity (L = 1,4,7-trithiacyclononane).[19]

Dibenzyl complex **1** and monocation **2** were tested as catalysts for ethylene polymerization under 1 atm of C_2H_4 at 25 and 60 °C. However, polymer formation was not observed, even after 24 h, presumably due to the ability of thorium to engage in strong π-arene coordination, despite flanking of the metal with bulky *N*-(2,6-diisopropylphenyl) groups. Future work will focus on the reactivity of **2** with various unsaturated substrates, including alkenes under more forcing conditions. Bis(anilido) xanthene thorium alkyl cations with a reduced tendency toward arene coordination will also be pursued.

Acknowledgment. D.J.H.E. thanks NSERC of Canada for a Discovery Grant and Canada Foundation for Innovation (CFI) and Ontario Innovation Trust (OIT) for New Opportunities Grants. D.J.H.E. also thanks McMaster University for support in the form of a start-up fund, and C.A.C. thanks the Government of Ontario for an Ontario Graduate Scholarship (OGS).

Supporting Information Available: Experimental and X-ray crystallographic data in PDF format and CIF files are available free of charge via the Internet at http://pubs.acs.org.

OM7011503

---

(14) (a) See for example: Bosch, B. E.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1997**, *16*, 5449. (b) Cendrowski-Guillaume, S. M.; Lance, M.; Nierlich, M.; Ephritikhine, M. *Organometallics* **2000**, *19*, 3257. (c) Arndt, S.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5075. (d) Elvidge, B. R.; Arndt, S.; Zeimentz, P. M.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2005**, *44*, 6777. (e) Bambirra, S.; Meetsma, A.; Hessen, B. *Organometallics* **2006**, *25*, 3454. (f) reference 2e.

(15) Guérin, F.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1298.

(16) Hayes, P. G.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 2132. nacnac = $\text{CH\{C}t\text{BuN(C}_6\text{H}_3i\text{Pr}_2\text{-2,6)\}}_2$.

(17) Green, M. L. H.; Sassmannshausen, J. *Chem. Commun.* **1999**, 115.

(18) Ward, B. D.; Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1668.

(19) Tredget, C. S.; Bonnet, F.; Cowley, A. R.; Mountford, P. *Chem. Commun.* **2005**, 3301.