

## A New Class of Actinide “Sandwich” Complexes: Synthesis and Molecular Structure of a Thorium Bis( $\eta^8$ -pentalene) Complex

F. Geoffrey N. Cloke\* and Peter B. Hitchcock

The Chemistry Laboratory, School of Chemistry  
Physics and Environmental Science  
University of Sussex, Brighton BN1 9QJ, U.K.

Received May 5, 1997

Of the two dianionic, aromatic 8-membered ring systems, the cyclooctatetraene ligand has historically played the most important role in early transition metal and f-element organometallic chemistry, particularly for the actinides.<sup>1</sup> The second, the pentalene dianion, has received comparatively very little attention, in part due to synthetic difficulties. Binuclear transition metal systems which contain the planar pentalene dianion have been reported, *e.g.*,  $[\text{M}_2(\eta^5, \eta^5\text{-C}_8\text{H}_6)_2]$  ( $\text{M} = \text{Co}, \text{Ni}$ ),<sup>2</sup>  $[(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\eta^5, \eta^5\text{-C}_8\text{H}_6)\text{Ni}(\eta^3\text{-C}_3\text{H}_5)]$ ,<sup>3</sup> and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\eta^5, \eta^5\text{-C}_8\text{H}_6)\text{M}(\eta^5\text{-C}_5\text{Me}_5)]$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ),<sup>4</sup> in which the two metal fragments bind to the adjacent 5-membered rings of the pentalene ligand in a *trans* disposition. Binding of two transition metal fragments on the same face of the pentalene ligand has also been described, *e.g.*,  $[\{\text{Ru}(\text{MMe}_3)(\text{CO})_2\}_2(\eta^5, \eta^5\text{-C}_8\text{H}_6)]$  ( $\text{M} = \text{Si}, \text{Ge}$ ),  $[\text{Ru}_3(\text{CO})_8(\eta^5, \eta^5\text{-C}_8\text{H}_6)]$ , and  $[\text{Ru}_3(\text{CO})_8(\eta^5, \eta^5\text{-C}_8\text{H}_4\{\text{SiMe}_3\text{-}1,4\}_2)]$ ,<sup>5</sup> but results in folding of the pentalene about the bridgehead C–C bond by *ca.* 10°. Binding to a single metal center in an  $\eta^8$  mode would require a much more extreme distortion; in the d-block elements, size and 16/18-electron rule considerations indicate that this is most likely to be achieved with an early metal. Indeed, very recently we have described the synthesis of  $[\text{Ta}(\eta^8\text{-C}_8\text{H}_4\{\text{SiMe}_3\text{-}1,4\}_2)\text{Cl}_3]$ , formed by protonolysis of  $[\text{Ta}(\eta^8\text{-C}_8\text{H}_6\{\text{SiMe}_3\text{-}1,4\}_2)\text{Me}_3]$  with  $[\text{R}_3\text{NH}]\text{Cl}$ , which represents the first example of such ligation for a pentalene ligand.<sup>6</sup> The large radii and irrelevance of electron counting rules in the f-block suggest the possibility of  $\eta^8$  coordination of a suitably sterically demanding pentalene ligand for these elements. In this paper, we report a unique thorium sandwich complex containing two  $\eta^8$ -bis(trialkylsilyl)-substituted pentalene rings, but prepared *via* a rational synthetic route involving the treatment of thorium tetrachloride with the dipotassium salt of the 1,5-bis(triisopropylsilyl)pentalene dianion. The preparation of the latter (see Supporting Information) will be described in full in a subsequent publication.<sup>7</sup>

The reaction between  $[\text{ThCl}_4]$  and 2 equiv of  $\text{K}_2[\text{C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,5)_2]$  in THF at room temperature affords, after work-up, deep orange crystals of  $[\text{Th}\{\text{C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,5)_2\}_2]$  (**1**) as a mixture of staggered (**1a**) and eclipsed (**1b**) (with respect to the pentalene carbon framework) isomers in 70% isolated yield (see Scheme 1).<sup>8</sup> Compound **1** is very soluble in hydrocarbon solvents and may be cleanly sublimed at 260 °C/5 × 10<sup>-6</sup> mbar. An intense absorption in the visible spectrum of **1** at 435 nm is ascribed to a ligand-to-metal charge-transfer (LMCT) transition.

The molecular structure of **1** has been determined by X-ray diffraction and is shown in Figure 1.<sup>9</sup>

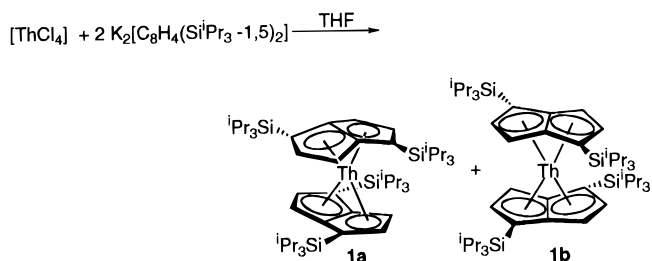
(1) *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1996; Vol. 4.  
(2) Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1972**, *94*, 3281. Katz, T. J.; Acton, N.; McGinnis, J. *J. Am. Chem. Soc.* **1972**, *94*, 6205.

(3) Miyake, A.; Kanai, A. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 801.  
(4) Bunel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Barra, C.; Gonzalez, M.; Munoz, N.; Visconti, G.; Aizman, A.; Manriquez, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 6597.

(5) Knox, S. A. R.; Stone, F. G. A. *Acc. Chem. Res.* **1974**, *7*, 321.  
(6) Abbasali, Q. A.; Cloke, F. G. N.; Hitchcock, P. B. *J. Chem. Soc., Chem. Commun.* Accepted for publication.

(7) Cloke, F. G. N. Manuscript in progress.

### Scheme 1



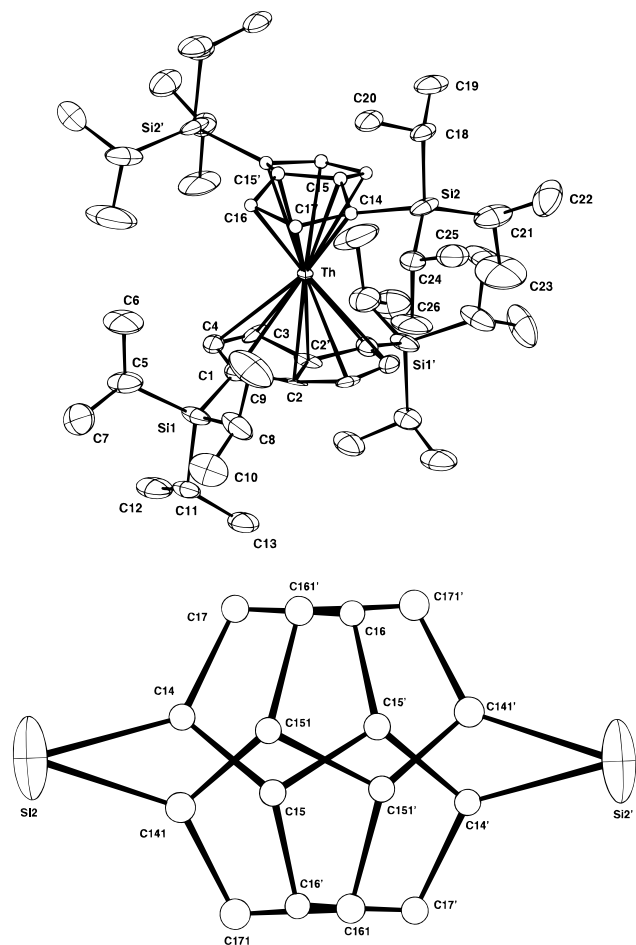
The molecule lies on a crystallographic 2-fold rotation axis which passes through the midpoints of the two pentalene ligands. The pentalene group attached to Si(2) is disordered; the disorder was modeled by a 0.52:0.48 occupancy of two orientations related by an approximate mirror plane through Th, Si(2), and Si(2)' (see Figure 1b). Thus, the single crystal of **1** contains an almost equal mixture of two isomers, which differ in the relative faces of the pentalene rings presented to the thorium and in the twist angles (as defined by the angles between the two bridgehead C–C vectors) of the two pentalene rings. The latter are 83° and 38° and correspond to the virtually staggered and the semieclipsed (with respect to the pentalene framework) forms **1a** and **1b**, respectively. This effect is ascribed to domination of the crystal packing forces by the bulky triisopropylsilyl groups, whose disposition is virtually identical in both isomers (see Scheme 1 and Figure 2). Since the two faces of the  $\{\text{C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,5)_2\}^{2-}$  ligand are enantiotopic, **1a** is the meso (idealized as  $S_4$ ) form of the virtually staggered conformation, while **1b** is the chiral ( $D_2$ ) form of the semieclipsed conformation. Compound **1c**, which is formed from **1b** by relative rotation of the ligands, and compound **1d**, which is formed in a similar manner from **1a**, are unlikely on steric grounds (see Figure 2).

The bond lengths and angles within the triisopropylsilyl substituents are unexceptional; the silicon atoms are bent (*ca.* 17°) out of the planes of the 5-membered rings away from the metal center, as is found in ring-substituted cyclopentadienyl complexes and results in improved ring–metal orbital overlap. The discussion will now focus on the nondisordered pentalene ring system (C1–C4 and C2'). The pentalene ring in **1** is folded about the bridgehead (C2–C2') bond, with a fold angle of 24°; this compares with a value of 33° for that found in  $[\text{Ta}(\eta^8\text{-C}_8\text{H}_4\{\text{SiMe}_3\text{-}1,4\}_2)\text{Cl}_3]$ ,<sup>6</sup> presumably a reflection of the relative size of Th *vs* Ta. In the metal–metal-bonded complex  $[\text{Ru}_3(\text{CO})_8(\eta^5, \eta^5\text{-C}_8\text{H}_3\{\text{SiMe}_3\text{-}1,3,5\})]$ , in which the pentalene ligand bridges one edge of the  $\text{Ru}_3$  triangle, the fold angle is 9°.<sup>10</sup> The thorium–ring carbon distances range from 2.543(10) for the bridgehead carbon C2 to 2.908(11) Å for the “wingtip” carbon C4; in  $[\text{Ta}(\eta^8\text{-C}_8\text{H}_4\{\text{SiMe}_3\text{-}1,4\}_2)\text{Cl}_3]$  the analogous distances are shorter, as expected, at 2.217(12) and 2.583(12) Å, respectively.<sup>6</sup> Further comparisons are difficult due to the lack of other, related compounds, but we note that

(8) To mixture of solid  $[\text{ThCl}_4]$  (0.373 g, 1 mmol) and solid  $\text{K}_2[\text{C}_8\text{H}_4(\text{Si}^i\text{Pr}_3\text{-}1,5)_2]$  (0.984 g, 2 mmol) was added THF (75 mL), and the resultant suspension stirred overnight at room temperature. The solvent was then removed *in vacuo*, and the residue was extracted with pentane (150 mL) and filtered through Celite on a frit. Concentration of the filtrate and slow cooling to –50 °C afforded deep orange crystals of **1**, which were washed with cold (–78 °C) pentane and dried under vacuum. Yield = 0.74 g, 70%. MS (EI):  $m/z$  1061 (100%) ( $[\text{M} + \text{H}]^+$ ). Anal. Found: C, 59.22; H, 9.04. Calcd for  $[\text{C}_{52}\text{H}_{92}\text{Si}_4\text{Th}]$ : C, 58.83; H, 8.73.

(9) Crystal data for **1**: monoclinic, fw 1061.7, deep orange diamonds, space group  $C2/c$  (No. 15);  $a = 21.296(4)$ ,  $b = 13.357(2)$ , and  $c = 21.095(13)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 95.26(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $Z = 4$ . Final residual  $wR_2$  (all data) = 0.169 ( $R = 0.068$ , with goodness of fit = 1.215 on  $F^2$ ).

(10) Howard, J. A. K.; Woodward, P.; Stansfield, R. F. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1812.



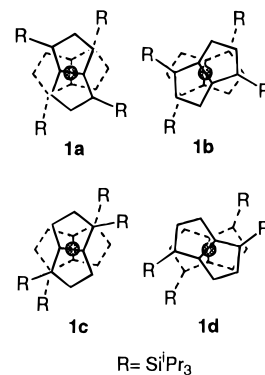
**Figure 1.** (a) ORTEP<sup>16</sup> view of **1** (thermal ellipsoids at 50%). Selected bond lengths (Å): Th–C1, 2.797(11); Th–C2, 2.543(10); Th–C3, 2.748(10); Th–C4, 2.908(11); C1–C4, 1.46(2); C2–C3, 1.49(2); C2–C2', 1.39(2); C3–C4, 1.36(2); Th–C14, 2.78(2); Th–C15, 2.55(2); Th–C16, 2.75(2); Th–C(17), 2.88(2); C14–C17, 1.43(2); C15–C16, 1.41(2); C15–C15', 1.47(3); C14–C15, 1.43(2). (b) Disorder in upper pentalene ring.

the Th–C distances in  $[\text{Th}(\eta^8\text{-C}_8\text{H}_8)_2]$ <sup>11</sup> lie in the range of 2.679(14)–2.714(12) Å and those for the  $\eta^5\text{-C}_5\text{H}_5$  rings in the tetracyclopentadienyl complex  $[\text{Th}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^5, \eta^1\text{-C}_5\text{H}_4)_2]$ <sub>2</sub> average at 2.83 Å.<sup>12</sup> The pentalene ring C–C bond lengths in **1** range from 1.36(2) Å (C3–C4) to 1.49(2) (C2–C3) Å with a bridgehead (C2–C2') bond length of 1.39 Å, virtually identical (within esds) to those found in  $[\text{Ta}(\eta^8\text{-C}_8\text{H}_4\{\text{SiMe}_3\text{-}1,4\}_2)\text{Cl}_3]$ .<sup>6</sup> In the *planar* pentalene ring system found in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\eta^5, \eta^5\text{-C}_8\text{H}_6)\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)]$ , the ring C–C distances lie between 1.464(5) Å (for the bridgehead) and 1.408(5) Å. For the *folded* (9°) ligand in  $[\text{Ru}_3(\text{CO})_8(\eta^5, \eta^5\text{-C}_8\text{H}_3\{\text{SiMe}_3\}_3\text{-}1,3,5)]$ , the ring C–C distances range from 1.430(24) to 1.469(33) Å for the bridgehead.<sup>10</sup>

Solution NMR spectra of **1** confirm the presence of two isomers, assumed to be **1a** and **1b** on the basis of steric

(11) Ardeef, A.; Raymond, K. R.; Hodgson, K. O.; Zalkin, A. *Inorg. Chem.* **1972**, *11*, 1083.

(12) Baker, E. C.; Raymond, K. R.; Marks, T. J.; Wachter, W. A. *J. Am. Chem. Soc.* **1974**, *96*, 7586.



**Figure 2.** Isomers of  $[\text{Th}(\eta^8\text{-C}_8\text{H}_4\{\text{Si}^i\text{Pr}_3\text{-}1,5\}_2)]$ .

arguments.<sup>13,14</sup> Thus, the <sup>1</sup>H NMR spectrum shows two pairs of doublets for the ring protons and two pairs of doublets for the diastereotopic methyl groups of the isopropyl substituents on silicon; integration gave an isomer ratio of 60:40, but this is very close to that observed in the crystal (50:50) within the limits of accuracy of proton integrations.<sup>15</sup> Similarly, the <sup>13</sup>C-<sup>1</sup>H NMR spectrum exhibits two sets of four resonance for the ring carbons in **1**, two pairs of isopropyl group methyl carbons and two methine carbons; the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **1** displays the expected two resonances. Assignment of the two isomers by a variety of NMR experiments was not possible, due to the symmetry of the rings. Variable-temperature experiments up to 373 K gave no indication of isomer interconversion on the NMR time scale, and a spin saturation transfer experiment at 373 K gave no evidence of any exchange process between them. This is perhaps not surprising since interconversion of **1a** and **1b** would require complete dissociation of one of the ligands and subsequent reattachment from the opposite face.

Photoelectron spectroscopy and theoretical studies to examine the bonding and electronic structure in **1** are in progress.

**Acknowledgment.** We thank EPSRC for funding, Dr. A. G. Avent and Mr. J. M. Keates for advice and assistance with the NMR studies, and Dr. J. C. Green (Oxford) for helpful discussions.

**Supporting Information Available:** Experimental details for the preparation of **1** and X-ray data and figures for **1** (14 pages). See any current masthead page for ordering and Internet access instructions.

JA9714371

(13) NMR data for **1** (toluene-*d*<sub>8</sub>, 295 K, Bruker DMX300): <sup>1</sup>H δ 6.69 (d, 2H, ring CH, *J*<sub>HH</sub> 3.1 Hz), 6.67 (d, 2H, ring CH, *J*<sub>HH</sub> 3.0 Hz), 5.65 (d, 2H, ring CH, *J*<sub>HH</sub> 3.0 Hz), 5.51 (d, 2H, ring CH, *J*<sub>HH</sub> 3.1 Hz), 1.23 (m, 12H, <sup>i</sup>Pr-CH), 1.11 (d, 18H, <sup>i</sup>Pr-CH<sub>3</sub>, *J*<sub>HH</sub> 7.4 Hz), 1.10 (d, 18H, <sup>i</sup>Pr-CH<sub>3</sub>, *J*<sub>HH</sub> 7.4 Hz), 1.09 (d, 18H, <sup>i</sup>Pr-CH<sub>3</sub>, *J*<sub>HH</sub> 7.3 Hz), 1.06 (d, 18H, <sup>i</sup>Pr-CH<sub>3</sub>, *J*<sub>HH</sub> 7.3 Hz); <sup>13</sup>C{<sup>1</sup>H} δ 156.9 (ring-C), 155.9 (ring-C), 137.4 (ring-CH), 134.3 (ring-CH), 111.6 (ring-C<sup>i</sup>Pr<sub>3</sub>), 111.2 (ring-CH), 109.5 (ring-C<sup>i</sup>Pr<sub>3</sub>), 106.9 (ring-CH), 20.2 (<sup>i</sup>Pr-CH<sub>3</sub>), 20.1 (<sup>i</sup>Pr-CH<sub>3</sub>), 19.9 (<sup>i</sup>Pr-CH<sub>3</sub>), 19.7 (<sup>i</sup>Pr-CH<sub>3</sub>), 13.1 (<sup>i</sup>Pr-CH), 13.0 (<sup>i</sup>Pr-CH); <sup>29</sup>Si{<sup>1</sup>H} δ 2.37 (Si<sup>i</sup>Pr<sub>3</sub>), 1.83 (Si<sup>i</sup>Pr<sub>3</sub>).

(14) Although solid state <sup>13</sup>C and <sup>29</sup>Si CPMAS spectra were obtained for **1**, **1a** and **1b** could not be unambiguously distinguished due the inherent limitations on resolution and complication by magnetic inequivalence in the solid phase. Hence, they will not be reported here.

(15) Increasing the delay time from 1 to 20 s had no effect on the integration ratio.

(16) Johnson, C. K. ORTEP II, Report ORNL-5738; Oak Ridge National Laboratory: Oakridge, TN, 1976.