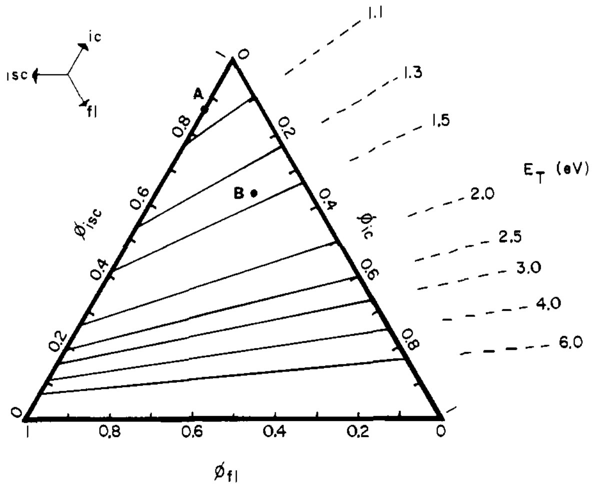


Figure 2. Triplet energy contours for *meso*-tetra-*p*-tolylporphyrin as a function of quantum yields. Shown are contour lines E_T = constant, for E_s = 1.90 eV, $\phi_{isc}E_T$ = 0.93 eV. Sample points: *A* (ϕ_{fl} = 0.13, ϕ_{isc} = 0.87, ϕ_{ic} = 0, E_T = 1.07eV), B (ϕ_{fl} = 0.13, ϕ_{isc} = 0.64, ϕ_{ic} = 0.23, E_T = 1.45 eV).

the unquenched triplet case. Oxygen was used for the quenched case; triplets are then quenched by oxygen diffusing into the polymer.[11,12] All samples were thermally thick over the frequency range employed. The above theoretical expression was fitted to the measured θ at several frequencies, with use of a least-squares criterion to determine the two fitting parameters R and τ. All measurements were taken at room temperature.

Two compounds, 1-chloroanthracene (Aldrich, purified by sublimation) and zinc tetraphenylporphyrin (chlorin-free, supplied by D. Gust) served as standards to establish the validity of this procedure. Phase data and fitted theoretical curves are shown in Figure 1a. For zinc tetraphenylporphyrin, with singlet-state parameters ϕ_{fl} = 0.033 and E_s = 2.08 eV,[13] the fitted curve parameters give $\phi_{isc}E_T$ = 1.59 ± 0.02 eV.[14] The current literature value is[13] (0.97)(1.60 eV) = 1.55 eV, in reasonable agreement. Similarly, using ϕ_{fl} = 0.08 and E_s = 3.31 eV for 1-chloroanthracene,[15,16] we obtain $\phi_{isc}E_T$ = 1.68 ± 0.04 eV, as compared to the literature value of[16] (0.92)(1.83 eV) = 1.69 eV.

In free base *meso*-tetra-*p*-tolylporphyrin (chlorin-free, supplied by D. Gust), two measurements were made at different excitation wavelengths (Figure 1b). With photophysical parameters ϕ_{fl} = 0.13 and E_s = 1.90 eV,[13] these two measurements give values for $\phi_{isc}E_T$ of 0.92 ± 0.01 and 0.96 ± 0.03 eV. Current literature values of ϕ_{isc} range from 0.74[17] to 0.87;[18] we have measured $\phi_{isc} \approx 0.9$ in styrene by flash spectroscopy.[19] A triplet energy of 1.45 eV for tetraphenylporphyrin has been quoted in the literature.[20-22] However, this value is questionable because no heavy-atom effect or excitation spectrum was observed.[21,22] Although these literature values are based on free base tetraphenylporphyrin, negligible perturbations are expected due to the para substituent.[13] Thus the literature product $\phi_{isc}E_T$ ranges from 1.07 to 1.26 eV, inconsistent with our results.

We do not believe this discrepancy is due to differences in molecular environment. For both standards the products $\phi_{isc}E_T$ we determine from polymer matrix data are the same as literature values from solutions. Moreover, for tetratolylporphyrin two different polymer matrices give the same value of $\phi_{isc}E_T$, within experimental error. Thus the only effect here of the matrix is to lengthen the triplet lifetime, to values typical of glasses at 77 K formed by rapid cooling of solutions.[23]

Our results may be summarized graphically in a contour diagram of the triplet energy surface as a function of the quantum yields (Figure 2). The photophysical parameters of tetratolylporphyrin must lie at a point on this surface, but the current literature values of ϕ_{isc}, ϕ_{fl}, and E_T do not satisfy this requirement. For instance, if internal conversion is small, then since $\phi_{fl} < 0.2$,[13] the photophysical parameters lie near point A of Figure 2, where the triplet energy is of the order of 1.1 eV, rather than 1.45 eV. Alternatively, with $E_T \simeq 1.45$ eV and $\phi_{fl} < 0.2$, internal conversion cannot be a minor decay path: $\phi_{ic} \gtrsim 0.2$ in the vicinity of point B. Note that at the upper apex of the triangle of the contour diagram, E_T is only weakly dependent on ϕ_{fl} and ϕ_{ic} at a constant ϕ_{isc} (horizontal line).

This calorimetric measurement should prove to be a powerful method for determining photophysical properties unobtainable by purely optical techniques. For molecules whose lowest triplet energy level can be determined by phosphorescence, it is an alternative method of measuring the intersystem crossing quantum yield.

Acknowledgment. This work was supported by NSF Grant CHE-8021718.

---

(12) Czarnecki, S.; Kryszewski, M. *J. Polym. Sci.* Polym. Chem. Ed. **1963**, *A1*, 3067-3077.

(13) Quimby, D.; Longo, F. *J. Am. Chem. Soc.* **1975**, *97*, 5111-5117.

(14) The errors quoted for parameters determined by curve fitting represent the 95% confidence interval for a t distribution with the appropriate number of degrees of freedom.

(15) Padhye, M.; McGlynn, S.; Kasha, M. *J. Chem. Phys.* **1956**, *24*, 588-594.

(16) Bowen, E. *Trans. Faraday Soc.* **1954**, *50*, 97-102.

(17) Petsold, O.; Byteva, I.; Gurinovich, G. *Opt. Spectrosc.* **1973**, *34*, 343-344.

(18) Solov'ev, K.; Tsvirko, M.; Gradyushko, A.; Kozhick, D. *Opt. Spectrosc.* **1972**, *33*, 480-483.

(19) Measurement made by T. Moore, D. Gust, and M. A. J. Rodgers at the Center for Fast Kinetic Research, University of Texas, Austin, TX, using the comparative method.

(20) Harriman, A.; Porter, G.; Searle, N. *Faraday Trans. 2* **1979**, *75*, 1515-1521.

(21) Gouterman, M.; Khalil, G. *J. Mol. Spectrosc.* **1974**, *53*, 88-100.

(22) Dolphin, D., Ed. "The Porphyrins"; Academic Press: New York, 1978; Vol. 3, Pt A, p 1-165.

(23) Gradyushko, A.; Tsvirko, M. *Opt. Spectrosc.* **1971**, *31*, 291-295.

Intra- and Intermolecular Organoactinide C-H Activation Pathways. Formation, Properties, and Reactions of Thoracyclobutanes

Joseph W. Bruno and Tobin J. Marks*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Victor W. Day*

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588, and Crystalytics Company
Lincoln, Nebraska 68501

Received August 2, 1982

The scope and mechanisms of intramolecular C-H activation processes that result in saturated hydrocarbon cyclometalation are justifiably topics of considerable current interest,[1-7] as are the

---

(1) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 211-228.

(2) (a) Whitesides, G. M. *Pure Appl. Chem.* **1981**, *53*, 287-292. (b) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13-20. (c) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 124-133. (d) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *Ibid.* **1981**, *103*, 948-949. (e) Foley, P.; DiCosimo, R.; Whitesides, G. M. *Ibid.* **1980**, *102*, 6713-6725.

(3) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448-2450.

(4) (a) Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 472-477. (b) Andersen, R. A.; Jones, R. A.; Wilkinson, G. *Ibid.* **1978**, 446-453.

(5) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149-194 and references therein.

(6) (a) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991-1995. (b) Cramer, R. E.; Maynard, R. B.; Gilje, J. W. *Ibid.* **1980**, *19*, 2564-2569.

0002-7863/82/1504-7357$01.25/0

Table I. ^{1}H and ^{13}C NMR Data for $Th[(CH_3)_5C_5]_2[(CH_2)_2C(CH_3)_2]$ (3) and $Th[(CH_3)_5C_5]_2[(CH_2)_2Si(CH_3)_2]$ (4)[a,b]

	η^5-$(CH_3)_5C_5$			metallacyclobutane				
compd	$^{1}H_{Me}$	$^{13}C_{Me}$	^{13}C	$^{1}H_{\alpha}$	$^{1}H_{Me}$	$^{13}C_{\alpha}$	$^{13}C_{Me}$	$^{13}C_{\beta}$
3	1.98	11.7 (q, 126.5)	123.3	0.93	1.29	94.0 (t, 122.8)	39.4 (q, 123.0)	15.8
4	1.98	11.7 (q, 125.8)	123.2	0.43	0.22	69.0 (t, 119.6)	2.4 (q, 119.6)	

[a] All chemical shifts relative to internal Me_4Si. Relative intensities are appropriate for assignments. [b] Quantities in parentheses are multiplicities (t = triplet, q = quartet) followed by observed coupling constants (J_{C-H}, Hz).

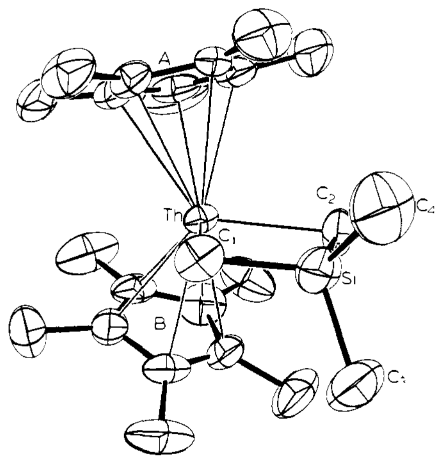
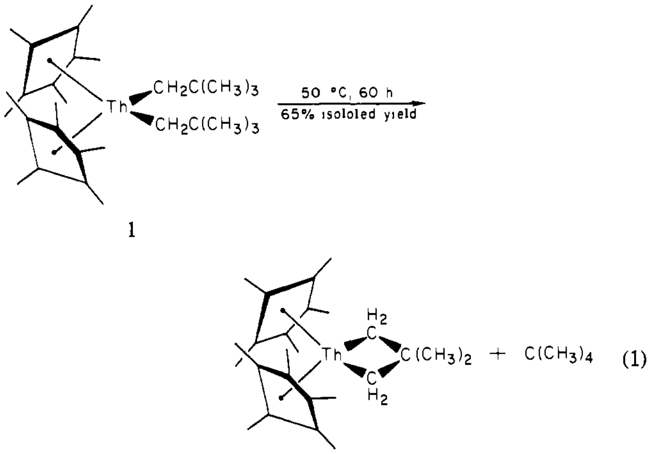


Figure 1. Perspective ORTEP drawing of the non-hydrogen atoms in $Th[\eta^5$-$(CH_3)_5C_5]_2[(CH_2)_2Si(CH_3)_2]$, **4**. All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Important bond lengths (Å) and angles (deg) for chemically distinct groups of atoms, averaged where appropriate according to idealized C_s-m symmetry, include Th–C_1 = 2.463 (13), Th–C_2 = 2.485 (14), Si–C_1 = 1.914 (15), Si–C_2 = 1.931 (14), Si–C_3 = 1.912 (21), Si–C_4 = 1.867 (19), Th–C(cyclopentadienyl) = 2.807 (14, 18, 50, 10), C–C(cyclopentadienyl) = 1.40 (2, 2, 6, 10), Th–C_g = 2.54(–, –, –, 2), C_1–Th–C_2 = 75.2 (4), Th–C_1(C_2)–Si = 90.6 (5, 5, 5, 2), C_1–Si–C_2 = 103.4 (6), C_g–Th–C_g = 138.5 (–), C_g–Th–C_1(C_2) = 106.3 (–, 4, 7, 4).

structures and reactions of the resulting or analogous metallacycloalkanes.[2,5,8–11] Tulip[3] has pointed out that such C–H activation pathways appear to fall into two general classes: (i) those involving initial, formal C–H oxidative addition to the metal center; (ii) those where a departing ligand is intimately involved in the activation process. The coordinative unsaturation, large metal ion size, oxidation state stability, and marked tendency to heterolytically activate two-center two-electron bonds suggested that thorium bis(hydrocarbyls) of the type $Th[\eta^5$-$(CH_3)_5C_5]_2R_2$[12,13] might provide new examples of class ii reactions as well as unusual types of metallacycles. We report here synthetic, mechanistic, and structural information, on the formation, via γ-C–H abstraction, and properties of a new, highly reactive class of actinacyclobutanes.[14]

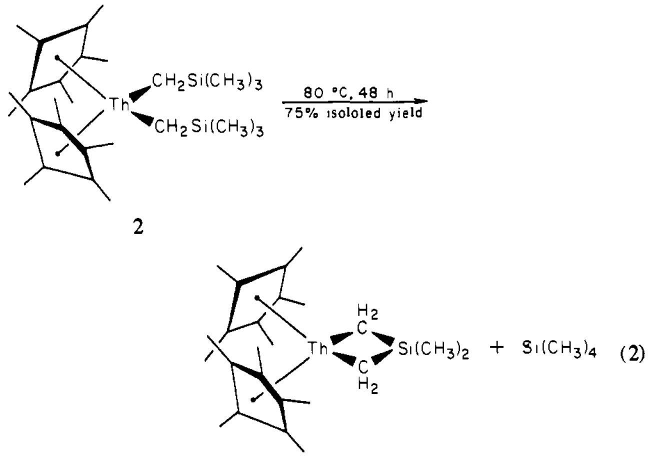
Thermolysis of the compounds[12b] $Th[(CH_3)_5C_5]_2[CH_2C(CH_3)_3]_2$ (**1**) and $Th[(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]_2$ (**2**) in saturated hydrocarbon (but not aromatic for **1**; vide infra) solvents proceeds cleanly and quantitatively (by ^{1}H NMR) to yield metallacyclobutanes **3** and **4** (eq 1 and 2). The new complexes were characterized by elemental analysis, cryoscopic molecular weight



1

3

(1)



2

4

(2)

---

(7) (a) Chang, B.-H.; Tung, H.-S.; Brubaker, C. H., Jr. *Inorg. Chim. Acta* **1981**, *51*, 143–148. (b) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 238–239. (c) Adam, G. J. A.; Davies, S. G.; Ford, K. A.; Ephritikhine, M.; Green, M. L. H. *J. Mol. Catal.* **1980**, *8*, 15–24 and references therein. (d) Bennett, C. R.; Bradley, D. C. *J. Chem. Soc., Chem. Commun.* **1979**, 29–30. (e) Duff, J. A.; Shaw, B. L.; Turtle, B. L. *J. Organomet. Chem.* **1974**, *66*, C18–C19.

(8) (a) Calderon, N.; Lawrence, J. P.; Ofstead, E. A.; *Adv. Organomet. Chem.* **1979**, *17*, 449–492. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**,, *24*, 1–50. (c) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283–317. (d) Rocklage, S. M.; Fellmann, J. D.; Rupprecht, G. A.; Messerle, L. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 1440–1447.

(9) (a) Ott, K. C.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2942–2944. (b) Lee, J. B.; Gajda, G. L.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *Ibid.* **1981**, *103*, 7358–7361. (c) Howard, T. F.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1980**, *102*, 6876–6878.

(10) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147–2157.

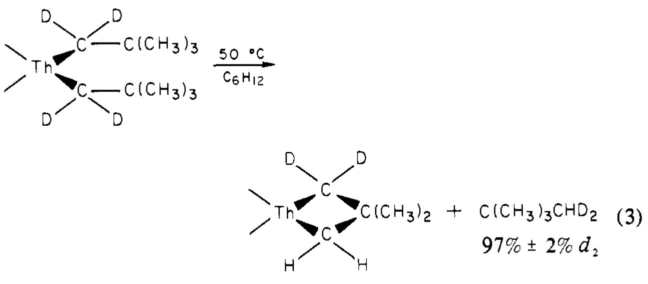
(11) (a) Eisenstein, O.; Hoffmann, R.; Rossi, A. R. *J. Am. Chem. Soc.* **1981**, *103*, 5582–5584. (b) Rappé, A. K.; Goddard, W. A. *Ibid.* **1982**, *104*, 448–456.

(12) (a) Katahira, D. A.; Moloy, K. G.; Marks, T. J. "Advances in Catalytic Chemistry"; Hanson, F. V., Ed.; Plenum Press: New York; Vol. II, in press. (b) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667. (c) Maatta, E. A.; Marks, T. J. *Ibid.* **1981**, *103*, 3576–3578. (d) Fagan, P. J.; Manriquez, J. M.; Marks, T. J. In Marks, T. J., Fischer, R. D., Eds. "Organometallics of the f-Elements"; Reidel: Dordrecht, Holland, 1979; Chapter 4. (e) Manriquez, J. M.; Marks, T. J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 3939–3941.

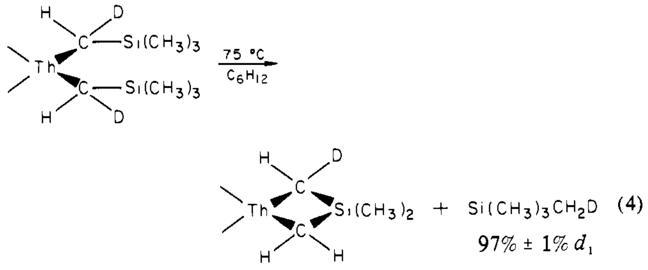
(13) (a) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989–997. (b) Fagan, P. J.; Maatta, E. A.; Manriquez, J. M.; Moloy, K. G.; Seyam, A. M.; Marks, T. J. In Edelstein, M. M., Ed. "Actinides in Perspective"; Pergamon Press: Oxford, 1982; pp 433–452. (c) Marks, T. J.; Ernst, R. D. In Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. "Comprehensive Organometallic Chemistry"; Pergamon Press, in press.

(14) (a) Actinacycles containing N, Si,[6a] and P[6b] heteroatoms have been recently reported. (b) This work was presented in part at "Inorganic Chemistry: Toward the 21st Century"; Bloomington, IN, May 16–19, 1982.

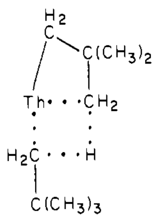
measurements, ^1H and ^{13}C NMR (Table I), mass spectrometry,[15] and for **4**, by single-crystal X-ray diffraction (vide infra). That thermolysis in C_6D_{12} does not produce detectably deuterated Me_4Si or neopentane argues against homolytic bond-scission processes, while the deuterium-labeling results[16-18] shown in eq 3 and 4 rule out significant α-hydrogen abstraction,[19] assuming reasonable[2,20a-c] kinetic isotope effects.[20d,e] As monitored quantitatively by ^1H NMR, reactions 1 and 2 obey clean first-order kinetics over ca. 4 half-lives. At 70 °C, **1** is more reactive than **2** by a factor of ca. 20. The Arrhenius parameters[21] [(**1**) E_a = 21.3 ± 0.6 kcal/mol, log A = 9 ± 1 ($\Delta H^\ddagger$ = 20.6 ± 0.6 kcal/mol, $\Delta S^\ddagger$ = −17 ± 2 eu); (**2**) E_a = 25.9 ± 0.9 kcal/mol, log A = 11 ± 1 ($\Delta H^\ddagger$ = 25.2 ± 0.9 kcal/mol, $\Delta S^\ddagger$ = −9 ± 1 eu)] also reflect these trends. The rather low log A values (negative $\Delta S^\ddagger$) suggest highly ordered transition states such as **7**, and markedly contrast the log $A \approx$ 20 values reported for the thermolysis of $Pt[P(C_2H_5)_3]_2[CH_2C(CH_3)_3]_2$ and related compounds.[2c,d] These latter data were interpreted in terms of rate-limiting alkane reductive elimination from Pt(IV) alkylhydrides.



5



6



7

Single crystals of **4** are monoclinic at 20 ± 1 °C, space group $P2_1/n$ [an alternate setting of $P2_1/c$-C_{2h}^5 (No. 14)] with a = 10.777 (4) Å, b = 16.328 (6) Å, c = 14.469 (4) Å, β = 100.92 (2)°, and Z = 4 (ρ_{calcd} = 1.564 g cm^{-3}; μ_a(Mo Kα) = 6.23 mm^{-1}). Three-dimensional X-ray diffraction data were collected for 5752 independent reflections having $2\theta_{Mo K\bar{\alpha}} < 55°$ on a Nicolet P$\bar{1}$ autodiffractometer using graphite-monochromated Mo Kα radiation and full (1.00° wide) ω scans. The structure was solved by using the heavy-atom technique. The resulting structural parameters have been refined to convergence [R (unweighted, based on F) = 0.048 for 3624 independent absorption-corrected reflections having $I > 3\sigma(I)$ and $2\theta_{Mo K\bar{\alpha}} < 55°$] by using empirically weighted full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All calculations were performed on a Data General Eclipse S-200 computer using locally modified versions of the Nicolet EXTL interactive software system. As can be seen in Figure 1,[22] the crystal is composed of discrete, mononuclear $Th[(CH_3)_5C_5]_2[(CH_2)_2Si(CH_3)_2]$ molecules with the familiar, pseudotetrahedral, "bent sandwich" actinide coordination geometry.[12,13,23] Although the molecule is not required to possess any rigorous crystallographic symmetry, it approximates C_s-m symmetry with Th, Si, C_3, C_4, and the two five-carbon ring centers of gravity (C_{gA} and C_{gB}, respectively) determining the pseudo mirror plane (these six atoms or points are coplanar to within 0.02 Å). The five-carbon rings of the two $(CH_3)_5C_5^-$ ligands are each coplanar to within 0.01 Å and adopt a staggered configuration.

The four-atom Th–C–Si–C metallacycle is folded by 5.8° along the $C_1 \cdots C_2$ vector; this small distortion appears to result from a close intramolecular contact between C_4 and a ring methyl group. In comparison, the titanacyclobutanes[9a] examined to date are largely planar, while both planar[10] and folded[2b,3,5] group 8 metallacyclobutanes are known. Ring folding is not evident in the room-temperature NMR spectra of **3** and **4**, suggesting either planarity or rapid inversion in solution. The Th–C bond lengths in **4** are equal to within experimental error and do not differ significantly from those in **2** (2.484 (12), 2.474 (12) Å).[23c] There is no evidence for the importance of a carbene-olefin structure (**8**) either in ^{13}C NMR spectra of **5** (δ $^{13}CH_2$ vs. $^{13}CD_2$[9a,24]) or in the chemistry (vide infra).

Metallacycle **3** reacts cleanly with benzene under mild conditions to yield the known[12b] diphenyl compound (**9**, eq 5)) and

---

(15) (a) Compound 3. Anal. Calcd for $C_{25}H_{40}Th$: C, 52.54; H, 7.04; M_r, 501. Found: C, 51.96; H, 6.86. Mass spectrum (20 eV, m/e) 501 (22), 136 (7), 121 (9), 57 (100). (b) Compound 4. Anal. Calcd for $C_{24}H_{40}SiTh$: C, 48.96; H, 6.85; M_r, 589. Found: C, 48.69; H, 6.96; M_r, 572 (cryoscopic in cyclohexane). Mass spectrum (20 eV, m/e) 588 (15), 501 (100), 73 (20).

(16) $LiCD_2C(CH_3)_3$: (a) Nystrum, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 1197–1199. (b) Riley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *Ibid.* **1964**, *86*, 964–966. (c) Reference 2e.

(17) $LiCDHSi(CH_3)_3$: Burford, C.; Cooke, F.; Ehlinger, E.; Magnus, P. *J. Am. Chem. Soc.* **1977**, *99*, 4536–4537.

(18) (a) Isotopic analyses were carried out by GC–MS employing precautions and assumptions discussed elsewhere.[2e,18b,c] (b) Bruno, J. W.; Kalina, D. G.; Mintz, E. A.; Marks, T. J. *J. Am. Chem., Soc.* **1982**, *104*, 1860–1869. (c) Katz, T. J.; Rothchild, R. *J. Am. Chem. Soc.* **1976**, *98*, 2519–2526.

(19) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104. (b) Schrock, R. R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellman, J. *J. Mol. Catal.* **1980**, *8*, 73–83. (c) Fellman, J. D.; Schrock, R. R.; Traficante, D. D. *Organometallics* **1982**, *1*, 481–484. (d) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.

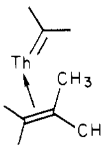
(20) (a) Parshall, G. W. *Chem. Soc. Spec. Periodical Report, Catalysis,* **1977**, *1*, 335–368. (b) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97–143. (c) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147–188. (d) Although involvement of ring C–H functionalities cannot yet be rigorously excluded, past experience[12,20e] indicates that such processes generally require far more drastic thermal conditions for thorium. (e) Fagan, P. J.; Jones, N. L.; Marks, T. J., unpublished results.

(21) Arrhenius plots were based on kinetic data taken over a 30 °C temperature range and were fit by standard linear regression techniques.

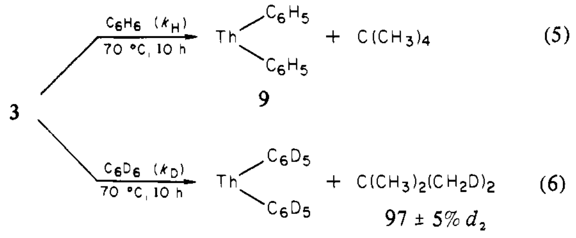
(22) (a) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value. (b) C_g refers to the center of gravity for the five-membered ring of a $(CH_3)_5C_5^-$ ligand.

(23) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Vollmer, S. H.; Day, C. S.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 2206–2220. (b) Marks, T. J.; Manriquez, J. M.; Fagan, P. J.; Day, V. W.; Day, C. S.; Vollmer, S. H. *ACS Symp. Ser.* **1980**, *131*, 1–29. (c) Bruno, J. W.; Day, V. W.; Marks, T. J., submitted for publication.

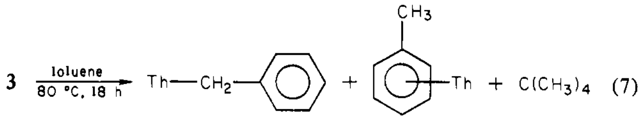
(24) (a) The ^{13}C shift of the undeuterated α-carbon atom in **5** is less than 0.1 ppm downfield of the α-carbon in **3**. Although we are as yet unable to unambiguously locate the broadened multiplet of the deuterated α-carbon atom of **5**, it is reasonable to assume that it exhibits a normal, intrinsic deuterium-induced upfield displacement. Assuming $\Delta \approx$ 100 ppm in **8**,[9a] the present calculated value of $\delta/\Delta \leq 10^{-3}$ indicates the absence of rapidly equilibrating species having structure **8**. (b) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070–8071. (c) Saunders, M.; Kates, M. R. *Ibid.* **1977**, *99*, 8071–8072. (d) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *Ibid.* **1977**, *99*, 8072–8073.



8



with C_6D_6 to yield the diphenyl-d_{10} complex and neopentane-d_2 (eq 6)).[18] There are no detectable intermediates, and kinetic measurements by ^{1}H NMR reveal that the reaction is first order in both **3** and benzene, that $k_H/k_D = 1.5$ (1), and that **3** is the intermediate in the reaction[12b] of **1** with benzene to yield **9**. In contrast, neither **2** nor **4** react with benzene over the course of 12 h at 80 °C. Toluene reacts with **3** to yield neopentane and both benzylic- and ring-metalated products, the latter predominating (75 ± 10%; eq 7).[25] Interestingly, the reaction of **3** (as



assessed by ^{1}H NMR and GC–MS) with olefins *does not* result in significant metathesis[8,9,26] but rather (e.g., propylene) in the formation of complex mixtures of ring-opened products.[27] The difficult accessibility of alkylidene species such as **8** (possibly due to an unfavorable formal thorium oxidation state or to poor thorium–alkylidene orbital overlap) is also underscored by the lack of reactivity of **3** with phosphines; alkylidenephosphine complexes[28] are not formed.

These results suggest not only that the organoactinides will display a rich cyclometalation chemistry but that the reaction patterns of the resulting metallacycles will be in many respects unusual. The degree to which this is so is under continuing investigation.

Acknowledgment. We thank the National Science Foundation (CHE8009060) for generous support of this research.

Registry No. 1, 79301-21-6; **2**, 69040-88-6; **3**, 83692-52-8; **4**, 83692-53-9; **5**, 83692-54-0; **6**, 83692-55-1; **9**, 79301-39-6; $Th[(CH_3)_5C_5]_2(C_6D_6)_2$, 79301-28-3; C_6H_6, 71-43-2; C_6D_6, 1076-43-3; bis(η^5-permethylcyclopentadienyl)bis(trimethylsilyldideuteriomethyl)thorium, 83692-56-2; bis(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)bis(1-deuteriotrimethylsilylmethyl)thorium, 83692-57-3; toluene, 108-88-3.

Supplementary Material Available: Tables of fractional atomic coordinates and of anisotropic thermal parameters for non-hydrogen atoms of $Th[\eta^5\text{-}(CH_3)_5C_5]_2[(CH_2)_2Si(CH_3)_2]$ (**4**) (2 pages). Ordering information is given on any current masthead page.

---

(25) The product distribution could be approximately assayed by analysis of the 270-MHz ^{1}H NMR spectrum.

(26) This is not the case for $Th[(CH_3)_5C_5]_2R_2$ complexes adsorbed on high-area metal oxide supports: He, M.-Y.; Burwell, R. B., Jr.; Marks, T. J., submitted for publication.

(27) NMR spectra indicate the presence of $ThCH_2C(CH_3)_3$ functionalities and quenching with D_2O produces $C(CH_3)_3(CH_2D)$ (98 ± 2% d_1). Further studies to elucidate the nature of these products are in progress.

(28) For group 4B analogues, see: (a) Schwartz, J.; Gell, K. I. *J. Organomet. Chem.* **1980**, *184*, C1–C2. (b) Grubbs, R. H.; Straus, D. A.; Stille, J.; Ho, S.; Hentges, S. 183rd National Meeting of the American Chemical Society Las Vegas, NV March 28–April 2, 1982; American Chemical Society: Washington, DC; INOR O13.

Formation of the Bridging Acylium Complex $(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO)^+PF_6^-$ by Addition of CO to a Bridging Methylidyne-Iron Complex

Charles P. Casey* and Paul J. Fagan†

Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Victor W. Day

Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588, and Crystalytics Company
Lincoln, Nebraska 68501

Received August 27, 1982

The interaction of carbon monoxide with small carbon fragments bound to metal atoms is believed to be important in CO reduction and related chemistry.[1,2] Here we report that reaction of carbon monoxide with the bridging methylidyne complex, $[cis\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)]^+PF_6^-$ (**1**),[3] $Cp = \eta\text{-}C_5H_5$), yields the acylium complex $[cis\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO)]^+PF_6^-$ (**2**). The structure, spectra, and chemical properties of **2** suggest that the bonding of the μ-CHCO ligand in **2** should be regarded as analogous to that in acylium cations such as $CH_3C{\equiv}O^+$, with a contributing formulation as a two-electron three-center bound bridging ketene (see Scheme I).

The methylidyne carbon of **1** is electrophilic[3] and is attacked by nucleophiles such as trimethylamine, which produces the adduct $\{cis\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CHN(CH_3)_3]\}^+PF_6^-$ (**3**, 80%),[4] and $K^+OC(CH_3)_3^-$, which produces a 5:1 mixture of the two possible isomers of $Cp_2Fe_2(CO)_2(\mu\text{-}CO)[\mu\text{-}CHOC(CH_3)_3]$ (**4**, 43%)[4] in which the Cp ligands are cis to one another.[5]

Remarkably, **1** is electrophilic enough to form a 1:1 adduct with CO, whereas the related bridging alkylidyne complexes (e.g., $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CCH_3)]^+BF_4^-$) are inert to CO.[6] When a slurry of **1** in CH_2Cl_2 was stirred under a CO atmosphere (500 torr) for 2 h at room temperature, the dark red-purple crystalline solid **2** formed and was isolated in 90% yield.[7] Similarly reaction of **1** with 90% ^{13}CO gave the μ-CH^{13}CO complex **2**-^{13}C. No evidence for scrambling of the ^{13}C label with the metal-bound carbonyl ligands of **2**-^{13}C was detected by IR or NMR spectroscopy. In the ^{1}H NMR spectrum of **2**-^{13}C, the resonance due to μ-C*H*^{13}CO at δ 6.94 appears as a doublet with $J_{^{13}CH} = 4.4$ Hz. The infrared band for the μ-CHCO carbonyl of **2** appears at 2092 cm^{-1} and is shifted to 2057 cm^{-1} for **2**-^{13}C.

The molecular structure of **2** was determined by X-ray crystallography[8] and consists of discrete $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}$

---

† NSF Postdoctoral Fellow, 1981–1982.

(1) (a) Herrmann, W. A. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 117–130. (b) Shriver, D. F. *ACS Symp. Ser.* **1981**, *152*, 1–18. (c) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (d) Ponec, V. *Catal. Rev.—Sci. Eng.* **1978**, *18*, 151–171. (e) Biloen, P.; Helle, J. N.; Sachtler, W. M. H. *J. Catal.* **1979**, *58*, 95–107. (f) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61–103.

(2) For the interaction of carbon monoxide with mononuclear metal carbynes, see, for example: (a) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766–768. (b) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632–633. (c) Uedelhoven, W.; Eberl, K.; Kreissl, F. R. *Chem. Ber.* **1979**, *112*, 3376–3389 and references therein.

(3) (a) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134–1136. (b) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951.

(4) See supplementary material.

(5) The related iron complex $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOCH_3)$ has recently been prepared, and triphenylphosphine has been demonstrated to react with complex **1** generated in situ from $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHOCH_3)$ and HBF_4 to form the corresponding triphenylphosphine adduct: Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911–918.

(6) Fagan, P. J.; Casey, C. P., unpublished results.

(7) (a) **2**: ^{1}H NMR ($(CD_3)_2CO$) δ 6.94 (1 H, s, μ-CH), 5.67 (10 H, s, Cp); ^{13}C NMR [$(CD_3)_2CO$, 0 °C] δ 249.6 (μ-CO), 209.2 (CO), 162.6 (μ-CHCO), 91.1 (Cp, $J_{^{13}C\text{-}H} = 183$ Hz), 27.5 (μ-*C*HCO, $J_{^{13}C\text{-}H} = 174$ Hz in CD_3NO_2); IR (KBr pellet) 2092, 2002, 1819 cm^{-1}. Anal. Calcd for $C_{15}H_{11}O_4PF_6Fe_2$: C, 35.20; H, 2.17; P, 6.05. Found: C, 35.13; H, 2.34; P, 6.07. (b) Complex **2** can be recrystallized quickly from cold (0 °C) acetone/ether, but substantial decomposition occurs.

0002-7863/82/1504-7360$01.25/0