8

$$\text{3} \xrightarrow[\text{70 °C, 10 h}]{C_6H_6 \ (k_H)} \text{Th}\begin{smallmatrix}C_6H_5\\C_6H_5\end{smallmatrix} + C(CH_3)_4 \qquad (5)$$

9

$$\xrightarrow[\text{70 °C, 10 h}]{C_6D_6 \ (k_D)} \text{Th}\begin{smallmatrix}C_6D_5\\C_6D_5\end{smallmatrix} + C(CH_3)_2(CH_2D)_2 \qquad (6)$$

$$97 \pm 5\% \ d_2$$

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
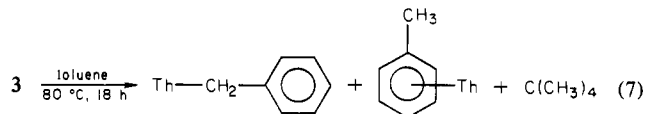
assessed by ^{1}H NMR and GC–MS) with olefins *does not* result in significant metathesis[8,9,26] but rather (e.g., propylene) in the formation of complex mixtures of ring-opened products.[27] The difficult accessibility of alkylidene species such as **8** (possibly due to an unfavorable formal thorium 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.

Supplementary Material Available: Tables of fractional atomic coordinates and of anisotropic thermal parameters for non-hydrogen atoms of Th[η⁵-(CH₃)₅C₅]₂[(CH₂)₂Si(CH₃)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[((CH₃)₅C₅]₂R₂ 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 ThCH₂C(CH₃)₃ functionalities and quenching with D₂O produces C(CH₃)₃(CH₂D) (98 ± 2% d_1). Further studies to elucidate the nature of these products are in progress.

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Formation of the Bridging Acylium Complex (C₅H₅)₂Fe₂(CO)₂(μ-CO)(μ-CHCO)⁺PF₆⁻ by Addition of CO to a Bridging Methylidyne–Iron Complex

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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-Cp₂Fe₂(CO)₂(μ-CO)(μ-CH)]⁺PF₆⁻ (1),[3] Cp = η-C₅H₅), yields the acylium complex [cis-Cp₂Fe₂(CO)₂(μ-CO)(μ-CHCO)]⁺PF₆⁻ (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 CH₃C≡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-Cp₂Fe₂(CO)₂(μ-CO)[μ-CHN(CH₃)₃]}⁺PF₆⁻ (3, 80%),[4] and K⁺OC(CH₃)₃⁻, which produces a 5:1 mixture of the two possible isomers of Cp₂Fe₂(CO)₂(μ-CO)[μ-CHOC(CH₃)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., [Cp₂Fe₂(CO)₂(μ-CO)(μ-CCH₃)]⁺BF₄⁻) are inert to CO.[6] When a slurry of **1** in CH₂Cl₂ 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% ¹³CO gave the μ-CH¹³CO complex **2**-¹³C. No evidence for scrambling of the ¹³C label with the metal-bound carbonyl ligands of **2**-¹³C was detected by IR or NMR spectroscopy. In the ^{1}H NMR spectrum of **2**-¹³C, the resonance due to μ-CH¹³CO 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**-¹³C.

The molecular structure of **2** was determined by X-ray crystallography[8] and consists of discrete [Cp₂Fe₂(CO)₂(μ-CO)(μ-

†NSF Postdoctoral Fellow, 1981–1982.

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(4) See supplementary material.

(5) The related iron complex Cp₂Fe₂(CO)₂(μ-CO)(μ-CHOCH₃) has recently been prepared, and triphenylphosphine has been demonstrated to react with complex **1** generated in situ from Cp₂Fe₂(CO)₂(μ-CO)(μ-CHOCH₃) and HBF₄ 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 ((CD₃)₂CO) δ 6.94 (1 H, s, μ-CH), 5.67 (10 H, s, Cp); ¹³C NMR [(CD₃)₂CO, 0 °C] δ 249.6 (μ-CO), 209.2 (CO), 162.6 (μ-CHCO), 91.1 (Cp, $J_{^{13}C-H}$ = 183 Hz), 27.5 (μ-CHCO, $J_{^{13}C-H}$ = 174 Hz in CD₃NO₂); IR (KBr pellet) 2092, 2002, 1819 cm⁻¹. Anal. Calcd for C₁₅H₁₁O₄PF₆Fe₂: 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.
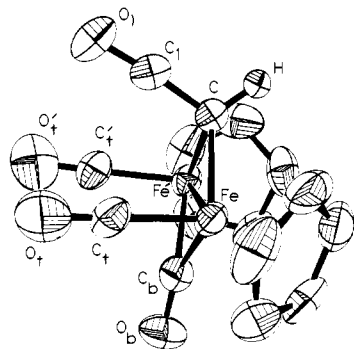
Communications to the Editor

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Figure 1. ORTEP drawing of the $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO)]^+$ in **2**. The following selected bond lengths are given in angstroms, and bond angles are given in degrees: Fe–Fe, 2.548 (1); Fe–C_t, 1.776 (4); Fe–C_b, 1.948 (4); (CHCO)Fe–C, 1.994 (4); Fe–C_g, 1.730 (–); C_t–O_t, 1.135 (7); C_t–O_t, 1.134 (7); C_b–O_b, 1.164 (7); C–C_1, 1.338 (8); C–C_1–O_1, 174.9 (6); H–C–C_1, 111 (2); Fe–C–C_1, 110.6 (3); Fe–C–H, 121 (2); Fe–C_t–O_t, 177.7 (4); Fe–C_b–O_b, 139.1 (1); Fe–C_b–Fe′, 81.7 (2); Fe′–Fe–Fe′, 79.4 (2); C_b–Fe–C, 99.2 (2); C_t–Fe–C_b, 89.2 (2); C_t–Fe–C, 97.9 (2); Fe′–Fe–C_g, 137.6 (–); C_g–Fe–C_t, 122.1 (–); C_g–Fe–C_b, 118.3 (–); and C_g–Fe–C, 123.0 (–). C_g is the center of gravity of the Cp group.

Scheme I
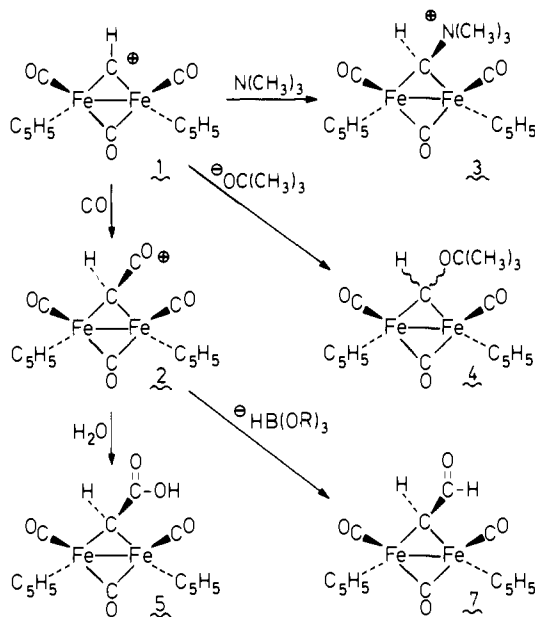
$CHCO)]^+$ cations (Figure 1) and PF_6^- anions. The cation possesses rigorous crystallographic C_s-m symmetry with the μ-CHCO and μ-CO ligands lying in the mirror plane at $x = 0$ in the lattice. The C–C–O angle of the μ-CHCO ligand is 174.9 (6)° and the acylium carbonyl is directed anti to the cis-Cp ligands of **2**. Formation of this stereoisomer is the result of nucleophilic attack of CO on the μ-CH ligand of **1** from the side opposite the relatively large Cp rings.

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(8) Single crystals of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO)]^+PF_6^-$ (**2**) obtained by diffusion of an ether layer into an acetone solution of **2** at 0 °C are orthorhombic, space group $Cmca\text{-}D_{2h}^{18}$ (No. 64) with $a = 17.696$ (3) Å, $b = 13.043$ (3) Å, $c = 15.273$ (3) Å, and $Z = 8$ {$(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)(\mu\text{-}CHCO)(CO)_2]PF_6$} formula units ($d_{calcd} = 1.93$ g/cm³; μ_a(Mo Kα) = 1.87 mm⁻¹). Three-dimensional diffraction data [a total of 3113 independent reflections having $2\theta_{MoK\alpha} < 63.70°$ (the equivalent of 1.5 limiting Cu Kα spheres)] were collected on a computer-controlled Nicolet P1 autodiffractometer using graphite-monochromated Mo Kα radiation and full 1° wide ω-scans. The structural parameters have been refined to convergence [R (unweighted, based on F) = 0.044 for 1594 independent absorption-corrected reflections having $2\theta_{MoK\alpha} < 63.7°$ and $I > 3\sigma(I)$] in cycles of weighted cascade-blocked least-squares refinement that employed weights based on counting statistics, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all hydrogen atoms. See paragraph at end regarding supplementary material.

While the μ-CHCO ligand of cation **2** can be formulated as an acylium species A, some contribution from a bridging ketene
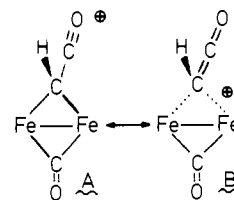
formulation B with two-electron three-center bonding is required to explain the observed bond lengths and IR spectra. The C–O bond length of 1.135 (7) Å for the μ-CHCO ligand is 0.03 Å longer than the C–O bond of $CH_3C\equiv O^+SbF_6^-$ (1.108 (15) Å)[9] and 0.03 Å shorter than the C–O bonds of $CH_2=C=O$ (1.16 (1) Å)[10] and $(CH_3)HC=C=O$ (1.171 (2) Å).[11] Similarly, the C–C bond of the μ-CHCO ligand (1.338 (8) Å) is 0.05 Å shorter than the C–C bond of $CH_3C\equiv O^+SbF_6^-$ (1.385 (16) Å)[9] and 0.03 Å longer than the C–C bonds of $CH_2=C=O$ (1.31 (1) Å)[10] and $(CH_3)HC=C=O$ (1.306 (2) Å).[11] The infrared stretching frequency of the μ-CHCO ligand of **2** (2092 cm⁻¹) is 208 cm⁻¹ lower in energy than the CO stretch of $CH_3C\equiv O^+$ (2300 cm⁻¹)[9] and is comparable to that observed for ketene (2153 cm⁻¹) and metal-substituted ketenes (1990–2018 cm⁻¹).[2c] Comparison of the IR stretching frequencies of the μ-CO ligands of the complexes $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2)$, **2**, and **1**, which are seen at 1773, 1822, and 1856 cm⁻¹, respectively, suggests that the positive charge on **2** is partially delocalized onto the iron framework.

The closest analogies to the acylium complex **2** are the complexes $Cp(CO)_2Mn[\mu\text{-}C(CO)C_6H_5]Re(CO)_4$[12] and $Cp(CO)_2Mn[\mu\text{-}C(CO)C_6H_4\text{-}p\text{-}CH_3]Mn(CO)_4$.[13] In the latter complex, the μ-C(CO)R ligand has a C–C bond length of 1.326 (6) Å and a C–O bond length of 1.167 (5) Å. Bridging ketene formulations were stressed by the authors in describing the structures of these complexes.[12,13]

The bridging acylium complex **2** is readily attacked by nucleophiles at the acylium carbon. Reaction of **2** with water in CH_2Cl_2 gives the carboxylic acid $cis\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCO_2H)$ (**5**, 40%);[4] ammonia gives the amide $cis\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCONH_2)$ (**6**, 30%);[4] $K^+HB[OCH(CH_3)_2]_3^-$ gives the aldehyde $cis\text{-}Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHCHO)$ (**7**, 50%).[4]

The ease with which the bridging methylidyne complex **1** reacts with CO to form the new carbon–carbon bond of the acylium complex **2** suggests that such processes should be considered as possibilities in heterogeneous catalysis where surface-bound methylidyne species have been proposed.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters for atoms in crystalline **2** and ¹H NMR, ¹³C NMR, infrared, and analytical data on complexes **3–7** (5 pages). Ordering information is given on any current masthead page.

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