

tential energy curve for bending of an ethyl group ($\text{Th}-\text{C}^1-\text{C} = \alpha$) in $\text{Cp}_2\text{Th}(\text{C}_2\text{H}_5)_2$, with the $\text{Th}-\text{C}^2-\text{C}$ angle being fixed at 132.1° . Superimposed on it, for comparison, is the energy of an ethyl ligand so bent in a d-transition-metal congener, $\text{Cp}_2\text{Nb}(\text{H}_2\text{C}=\text{CH}_2)(\text{C}_2\text{H}_5)$ (**2**). For the Nb complex, the theoretically optimized angle of $\alpha = 121^\circ$ and the corresponding experimental value of $\alpha = 118.6^\circ$ (7°)⁶ may well represent a "normal" mode of alkyl coordination to a metal center. On the other hand, the Th complex exhibits a very soft energy curve with a shallow minimum at about $\alpha = 160^\circ$. Nonrigidity of the alkyl orientation at a Th center was suggested also by the NMR data for **1**.² Thus the optimum angle α may be varied by small electronic and/or steric perturbations, but nevertheless it is encouraging to find that the computed $\text{Th}-\text{C}^1-\text{C}$ angle fits satisfactorily to the geometry of **1**.

From an orbital analysis, to be presented in detail elsewhere, we noticed that the $\text{Cp}_2\text{Th}(\text{C}^2\text{H}_2\text{CH}_3)^+$ fragment carried two low-lying vacant levels right above the f-block orbitals, namely "d_σ" and "d_π".⁷ The contour plots of these orbitals are shown in Figure 2. When the $\text{C}^1\text{H}_2\text{CH}_3$ ligand adopts a normal coordination mode ($\alpha = 120\text{--}130^\circ$), it is bound to Th mostly through an interaction with d_σ. Distortion weakens this interaction, but only slightly, because the main lobe of d_σ exhibits a large spatial extension toward the incoming ligand so that even at large α 's the ethyl donor orbital can overlap well with d_σ. This is the most striking aspect of the $\text{Cp}_2\text{Th}(\text{C}^2\text{H}_2\text{CH}_3)^+$ fragment and is a crucial factor that allows the Th atom to maintain a strong bond with the highly distorted ethyl. At the same time, d_π starts to participate in the $\text{Th}-\text{C}^1$ bonding to a certain degree, which may also assist the ethyl to distort.⁸ The presence of an analogous low-lying vacant d_π in d⁰ $\text{Cp}_2\text{M}(\text{C}_2\text{H}_5)_2$ ($\text{M} = \text{Ti}, \text{Zr}, \text{or Hf}$) may cause a similar ethyl distortion, but the deformation, if any, would not be as large as the Th case due to a smaller size of d_σ.

The evolution of the overlap populations supports the above view. The $\text{Th}-\text{C}^1$ overlap population $P(\text{Th}-\text{C}^1)$ stays large over the wide range of α , and at $120^\circ \leq \alpha \leq 160^\circ$ it is even larger than the $P(\text{Th}-\text{C}^2)$. As the angle α opens up, a new interaction turns on between Th and the α -hydrogen atoms on C^1 (**3**). Although the calculated $P(\text{Th}-\text{H}_\alpha)$ is not particularly great, e.g., 0.042 at $\alpha = 160^\circ$, the agostic interaction helps the $\text{C}^1\text{H}_2\text{CH}_3$ group to deform, and perhaps it is another reason behind the $\text{Th}-\text{C}^1$ bond shrinkage in **1**. Thus the $\text{Th}-(\text{C}^1\text{H}_2\text{CH}_3)$ group overlap population (GOP), defined as a sum of all the $\text{Th}-\text{C}$ and $\text{Th}-\text{H}$ overlap populations associated with the ethyl ligand, is notably larger than the $\text{Th}-(\text{C}^2\text{H}_2\text{CH}_3)$ GOP, i.e., 0.554 and 0.437, respectively, at $\alpha = 160^\circ$.

(4) The extended Hückel parameters for Th are the followings. Orbital exponent: 7s and 7p, 1.834; 6d, 2.461 (0.7612) + 1.165 (0.4071); 5f, 4.477 (0.7682) + 1.837 (0.4267); 6p, 3.806. H_{ii} : 7s and 7p, -5.39 eV; 6d, -10.11 eV; 5f, -9.64 eV; 6p, -27.83 eV. The H_{ij} values for 6d and 5f were determined by charge-iterative calculations on $\text{Cp}_2\text{Th}(\text{butadiene})$, and the details will be presented elsewhere. The off-diagonal elements H_{ij} were calculated by a weighted Wolfsberg-Helmholtz formula with the standard K value of 1.75. See, for example: Tatsumi, K.; Nakamura, A.; Hoffmann, P.; Hoffmann, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4467-4476.

(5) The Nb parameters were taken from: Tatsumi, K.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 3328-3341.

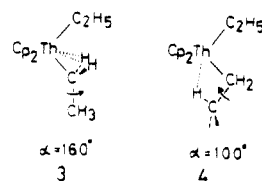
(6) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420-5427.

(7) These fragment orbitals are locally σ - and π -types with respect to an incoming ligand, $\text{C}^1\text{H}_2\text{CH}_3^-$ in this case. Tatsumi, K.; Nakamura, A.; Hoffmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440-4451.

(8) An effect similar to this d_π participation was emphasized in assessing the electronic origin of the deformation of carbene ligands in some Ta complexes and methyl tilting in Ti complexes. (a) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667-7676. (b) Eisenstein, O.; Jean, Y. *Ibid.*, **1985**, *107*, 1177-1186.

In the case of $\text{Cp}_2\text{Nb}(\text{H}_2\text{C}=\text{CH}_2)(\text{C}_2\text{H}_5)$, the computed Nb-C(ethyl) and the Nb-(C_2H_5) GOP both follow the trend of the energy curve in Figure 1. The Nb-ethyl bonding interaction is maximized at around $\alpha = 120^\circ$. This is traced to the optimum overlap again between the C_2H_5^- donor orbital and the vacant d_σ of $\text{Cp}_2\text{Nb}(\text{H}_2\text{C}=\text{CH}_2)^+$ shown in Figure 2. The Nb d_σ lobe is, however, much more compact in size than the Th d_σ lobe, and the ethyl ligand in the Nb complex does not have much freedom to choose various orientations. The good Nb-C interaction is achieved only in a narrow range of α around 120° . The vacant d_π orbital is absent in this case, for it is used up in the interaction with $\text{H}_2\text{C}=\text{CH}_2 \pi^*$.

We have emphasized the characteristic shape of $\text{Cp}_2\text{Th}(\text{C}_2\text{H}_5)^+ d_\sigma$, which allows the $\text{Th}-\text{C}^1-\text{C}$ angle to open up (**3**) without a loss of $\text{Th}-\text{C}^1$ bond strength. Pivoting the ethyl in the direction opposite to **3** is not a costly



deformation as well. For instance, the geometry **4** ($\alpha = 100^\circ$) is less stable than **3** by only 0.18 eV. A β -hydrogen comes close to Th in this case, and the calculated $P(\text{Th}-\text{H}_\beta)$ is weakly positive (0.036). The versatile ethyl coordination mode means hydrogen atoms (or C-H bonding electrons) in either the α - or the β -position can approach Th *without difficulty*. The same would be true for γ -hydrogens when present. This argument should provide a theoretical basis for understanding important aspects of C-H activation or cyclometalation chemistry involving actinide centers.⁹

Acknowledgment. We thank Prof. Tobin J. Marks for informing us of his experimental results prior to publication and helpful comments.

(9) (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357-7360. (b) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Ibid.* **1979**, *101*, 7728-7729; *Inorg. Chem.* **1981**, *20*, 2991-2995. (c) See ref 2b and references therein.

Preparation and Structure of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCH}_2$, an Analogue of a Vinylidene Cluster Complex: Reduction of the Unique Carbonyl of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCO}$

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Summary: The reaction of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCO}$ with BH_3 in THF results in the reduction of the unique carbonyl to form a methylene group, giving a triosmium borylidene carbonyl, $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCH}_2$, which is an electronic and structural analogue of the triosmium vinylidene cluster $\text{H}_2(\text{CO})_9\text{Os}_3\text{CCH}_2$.

The unique carbonyl of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCO}$ (**I**) is bound to a boron atom that caps an equilateral triangle of osmium atoms.¹ A recent calculation² indicates that the oxygen

(1) Shore, S. G.; Jan, D.-Y.; Hsu, L.-Y.; Hsu, W.-L. *J. Am. Chem. Soc.* **1983**, *105*, 5923.

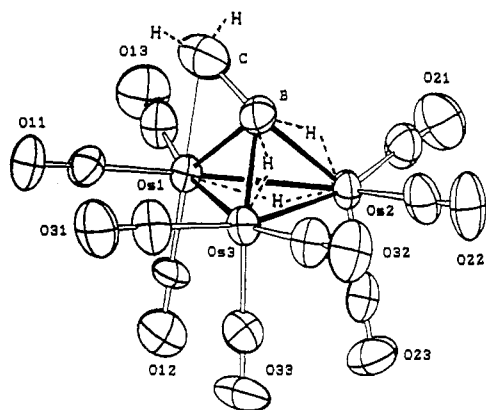
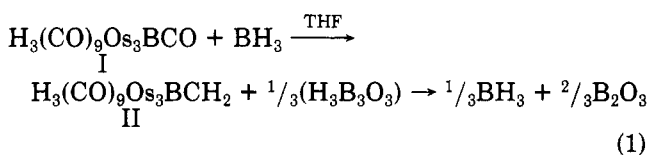


Figure 1. Structure of $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCH}_2$.

of this carbonyl has the most negative Mulliken atomic charge ($-0.246e$) of any of the oxygens in the molecule, thereby suggesting to us that it could be the favored site for reaction with an electrophilic group. Indeed we find that the reaction of I with BH_3 in THF results in the reduction of this carbonyl to form a methylene group to give a triosmium borylidene carbonyl, $\text{H}_3(\text{CO})_9\text{Os}_3\text{BCH}_2$ (II). This cluster is of interest not only because it is an electronic and structural analogue of the triosmium vinylidene cluster $\text{H}_2(\text{CO})_9\text{Os}_3\text{CCH}_2^3$ (III) but also because of its possible relationship to an intermediate that might be formed in the methanation of CO in the presence of a metal boride since some metal borides are known to function as methanation catalysts.⁴

The overall preparative reaction for II is represented by eq 1. This reaction is believed to occur through initial



addition of BH_3 to the oxygen of the unique carbonyl followed by transfer of two hydrides to the carbon and then elimination of HBO to form II and the boroxine trimer $\text{H}_3\text{B}_3\text{O}_3$ that is known to decompose into B_2O_3 and B_2H_6 .⁵

In a typical synthesis of II an excess quantity of B_2H_6 (0.858 mmol) was condensed into THF solution (2 mL) of I (0.108 mmol, 0.0934 g). The solution was stirred at room temperature for 30 min during which time the color of the solution changed from bright yellow to light yellow with concomitant formation of a white precipitate of B_2O_3 . After the volatile components were pumped away at room temperature, the residue was extracted with hexane, leaving behind the B_2O_3 . Upon evaporation of hexane from the filtrate, a light yellow, apparently air stable, solid was obtained that was recrystallized from Et_2O in 80% yield (0.086 mmol, 0.073 g). The FT/ICR mass spectrum of II shows a parent ion peak that corresponds to the molecular formula $^{11}\text{B}^{12}\text{C}_{10}^{1}\text{H}_5^{16}\text{O}_9^{192}\text{Os}_3$ m/z (obsd) 856, m/z (calcd) 856. The sequential loss of each of the nine carbonyls from the molecular ion was visible in the mass spectrum. IR spectrum (ν_{CO} , cyclohexane): 1985 m, 1993 w, 2015 s, 2034 s, 2054 s, 2076 s, 2107 cm^{-1} .

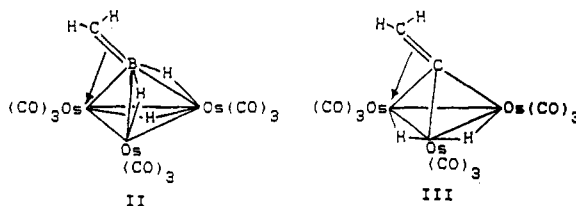
(2) Barreto, R. D.; Fehlner, T. P.; Hsu, L.-Y.; Jan, D.-Y.; Shore, S. G. *Inorg. Chem.* **1986**, *25*, 3572.

(3) (a) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415. (b) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Chem. Commun.* **1973**, 277.

(4) (a) Bartholomew, C. H.; Uken, A. H. *Appl. Catal.* **1982**, *4*, 19. (b) Uken, A. H.; Bartholomew, C. H. *J. Catal.* **1980**, *65*, 402.

(5) Porter, R. F.; Gupta, S. K. *J. Phys. Chem.* **1964**, *68*, 280.

Scheme I



The molecular structure of II (Figure 1) was determined from a single-crystal X-ray diffraction study.⁶ Although the hydrogen atoms were not located, the position of the Os(1)–H–Os(2) hydrogen was inferred by the fact that the distance Os(1)–Os(2) = 2.929 (1) Å is significantly longer than the other metal–metal distances: Os(1)–Os(3) = 2.827 (1) Å and Os(2)–Os(3) = 2.815 Å. Also the presence of an Os(1)–H–Os(2) bond is inferred by the larger angles observed for Os(2)–Os(1)–C(13) = 114 (1)° and Os(1)–Os(2)–C(21) = 113 (1)° compared to Os(3)–Os(1)–C(11) = 89(1)° and Os(3)–Os(2)–C(22) = 89 (1)°. The positions of the remaining hydrogen atoms are readily assigned from the *nmr* spectra of II. In the proton NMR spectrum (toluene- d_8 , 25 °C, δ 0.00 (Me₄Si)), there are two signals that are assigned to the CH₂ protons, 3.74 (1 H, m) and 3.49 (1 H, m) ppm, and three signals that are assigned to the bridging hydrogens, –12.26 (1 H, br), –13.45 (1 H, br), and –20.39 (1 H, d (2.5 Hz)) ppm. The two broad signals sharpen when ¹¹B decoupling is applied and also with decreasing temperature (–30 °C). These are the hydrogens that bridge boron. The signal at highest field is assigned to the proton bridging Os(1) and Os(2). The ¹¹B NMR spectrum (toluene- d_8 , 25 °C, δ 0.00 (BF₃OEt₂)) consists of a single broad resonance at 53.5 ppm that sharpens with proton decoupling.

The arrangement of non-hydrogen atoms in II closely resembles that observed for $\text{H}_2(\text{CO})_9\text{Os}_3\text{CCH}_2^3$ (III). Structural parameters involving the CH₂B unit are Os(1)–C = 2.325 (17) Å, B–C = 1.498 (19) Å, B–Os(1) = 2.287(12) Å, B–Os(2) = 2.270 (11) Å, B–Os(3) = 2.216 (14) Å, Os(1)–C–B = 69.8 (8)°, Os(1)–B–C = 72.5 (8)°, Os(1)–B–Os(2) = 80.3 (4)°, Os(1)–B–Os(3) = 77.9 (4)°, Os(2)–B–Os(3) = 77.7(4)°. Deviation from perpendicularity of the B–C vector from the Os₃ plane is 60°. The B–C distance cited above is about 0.1 Å shorter than observed³ B–C single bond distances (ca. 1.6 Å) and is slightly longer than the B–C bond in I (1.469 (15) Å), a bond which is believed to have significant double-bond character.^{1,2}

At this point it is a matter of taste as to whether the bonding of the BCH₂ unit in II to the metal cluster is described as a μ -BCH₂ bridge or as a tilted CH₂ in B=CH₂ group that binds to Os(1) through a three-center bond, similar to that considered for III⁷ (scheme I), even though the “short” B–C distance appears to favor this latter de-

(6) Crystal data for $\text{H}_2(\text{CO})_9\text{Os}_3\text{BCH}_2$: space group $P\bar{1}$, $a = 7.933$ (4) Å, $b = 9.162$ (2) Å, $c = 12.162$ (1) Å, $\alpha = 85.07$ (2)°, $\beta = 88.35$ (3)°, $\gamma = 69.17$ (1)°, $V = 823.1$ Å³, $\rho(\text{calcd}) = 3.42$ g cm⁻³ for M , 850.5, $Z = 2$, $\mu = 231.7$ cm for Mo K α . Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP 11/44 computer using the SDP (Structure Determination Package). The structure was solved by the direct method MULTAN 11/82 and difference Fourier syntheses. $R_F = 0.048$ and $R_{wF} = 0.068$ (209 parameters refined, including the extinction coefficient) for 2810 reflections [$I \geq 3.0 \sigma(I)$] of 3415 unique reflections collected in the range of $4^\circ \leq 2\theta \leq 55^\circ$.

(7) Deeming, A. J.; Hasso, S.; Underhill, M.; Canty, A. J.; Johnson, B. F. G.; Jackson, W. G.; Lewis, J.; Matheson, T. W. *J. Chem. Soc., Chem. Commun.* **1974**, 807.

(8) (a) Saturnino, D. J.; Yamauchi, M.; Clayton, W. R.; Nelson, W. R.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063. (b) Hsu, L. Y.; Mariategui, J. F.; Niedenzu, K.; Shore, S. G. *Inorg. Chem.*, in press.

scription. A theoretical investigation by Schilling and Hoffman⁹ of the related cluster $(\text{CO})_9\text{Co}_3\text{CCH}_2^+$ indicates that the preferred conformation is away from the upright position. It has been suggested⁹ that the related ionic complexes: $\text{H}_3(\text{CO})_9\text{M}_3\text{CCH}_2^+$ ($\text{M} = \text{Ru}, \text{Os}$),⁷ $(\text{CO})_9\text{Co}_3\text{CCHR}^+$,¹⁰ and more recently $\text{H}(\text{CO})_9\text{Fe}_3\text{CCH}_2$,¹¹ have similar tilting of the CH_2 unit as observed in III. NMR evidence has been provided¹² for tilted ground-state structures in $\text{Co}_3(\text{CO})_9\text{CCHR}^+$. Other vinylidene clusters have also been identified as having structural arrangements similar to III: $(\text{CO})_9\text{Co}_2\text{RuCCRH}$ ($\text{R} = \text{H}, \text{Me}, t\text{-Bu}, \text{Ph}$)¹³ and $(\text{CO})_9\text{Co}_2\text{FeCCH}_2$.¹⁴

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Supplementary Material Available: Listings of selected bond distances, selected bond angles, positional parameters, and anisotropic thermal parameters (5 pages); a listing of structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

(9) Shilling, E. R.; Hoffman, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

(10) (a) Seyferth, D.; Williams, G. H.; Halgren, J. E. *J. Am. Chem. Soc.* **1973**, *95*, 266. (b) Seyferth, D.; Williams, G. H.; Traficante, D. D. *Ibid.* **1974**, *96*, 604. (c) Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

(11) (a) Louridichi, M.; Mathieu, R. *Organometallics* **1986**, *5*, 2067. (b) Louridichi, M.; Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231.

(12) Eddln, R. T.; Norton, J. R.; Mislow, K. *Organometallics* **1982**, *1*, 561.

(13) Eckerhardt, R.; Wolfgang, B.; Vahrenkamp, H. *Chem. Ber.* **1985**, *118*, 2858.

(14) Ros, J.; Mathieu, R. *Organometallics* **1983**, *2*, 771.

Electrophilic Alkylation of an Acylmetalate Complex at the Metal Center Leading to a Stable Methylacetylirhenium Complex. Photochemical Decomposition To Give 2,3-Butanedione via a Mechanism Involving Carbonylation of Free Methyl Radicals

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Summary: Alkylation of the rhenium metalate $\text{Li}[\text{CpRe}(\text{CO})_2(\text{COCH}_3)]$ (**1**) can be controlled to give either the Fischer carbene complex $\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{OCH}_3)(\text{CH}_3)$ or the new alkyl aryl complex $\text{Cp}(\text{CO})_2\text{Re}(\text{COCH}_3)(\text{CH}_3)$ (**2**). Photochemical decomposition of **2** under 20 atm of CO leads to 2,3-butanedione; evidence is presented that the diketone is produced by formation and carbonylation of free methyl radicals.

Transition-metal alkyl acyl complexes $(\text{M}(\text{COR})(\text{R}))$ have been proposed as intermediates in various ketone forming processes such as that involving the reaction of Collman's reagent $\text{Na}_2\text{Fe}(\text{CO})_4$ with alkyl halides¹ and the elimination of acetone from $[(\text{CpCo}(\text{CO})(\text{CH}_3))_2]$.² As

Casey has pointed out, due to the ease with which alkyl acyl complexes undergo reductive elimination to give ketones, only a small number of isolated examples are known.³ We wish to report that reaction of the acyl metalate $\text{Li}[\text{CpRe}(\text{CO})_2(\text{COCH}_3)]$ (**1**) with alkylating agents can be controlled to give either the conventional Fischer carbene product $\text{Cp}(\text{CO})_2\text{Re}=\text{C}(\text{OCH}_3)(\text{CH}_3)$ ⁴ by O-alkylation or the alkyl acyl complex *trans*- $\text{Cp}(\text{CO})_2\text{Re}(\text{COCH}_3)(\text{CH}_3)$ ⁵ (**2**) by alkylation at the metal center. With a reasonably stable and fully characterized alkyl acyl complex in hand, we have found that thermal elimination in the presence of either CO or phosphines leads to acetone, but carbonylation induced by UV irradiation leads to good yields of 2,3-butanedione (biacetyl). We provide evidence here that these two transformations proceed by different mechanisms: the thermal reaction appears to involve a conventional reductive elimination pathway, but the photochemical reaction involves the generation and carbonylation of free organic radicals.

By analogy to the chemistry of organic enolates,⁶ treatment of lithium acyl metalate **1** with the relatively "hard" alkylating agent trimethyloxonium hexafluorophosphate $((\text{CH}_3)_3\text{OPF}_6)$ in THF gives the expected Fischer carbene complex and the new alkyl acyl complex **2** (Scheme I) in a 6:1 ratio by NMR. In contrast, use of the "softer" electrophile CH_3I gives **2** quantitatively, and it may be isolated pure in 65% yield by chromatography followed by recrystallization. We believe this constitutes the first direct observation of metal alkylation of an acyl metalate.⁷ The structure of **2** has been confirmed by X-ray diffraction; an ORTEP diagram is shown in Scheme I.⁸

Although **2** is quite stable in solution at ambient temperature, thermolysis in C_6D_6 at 100 °C in a sealed tube produced acetone in 93% yield (NMR).⁹ This reaction proceeds most cleanly in the presence of excess L ($\text{L} = \text{PPh}_3, \text{PMe}_3, \text{or CO}$); here acetone and $\text{CpRe}(\text{CO})_2\text{L}$ were produced in essentially quantitative yield. A crossover experiment carried out by thermolysis of 2- d_0 and 2- d_6 in the presence of excess PPh_3 yielded acetone- d_0 and acetone- d_6 with less than 1% acetone- d_3 (GC/MS). A kinetic study of this reductive elimination in the presence of excess PPh_3 showed that the reaction rate is first order in [**2**] and zero order in [L], with $k_1 = 6.1 \times 10^{-5} \text{ s}^{-1}$ at 100 °C. On the basis of these results, we propose that the process occurs by simple rate-determining reductive elimination of acetone from **2** to form the coordinatively unsaturated intermediate $\text{CpRe}(\text{CO})_2$, and this fragment is then trapped in a fast step by L. Presumably **2** undergoes a *trans* to *cis* isomerization before reductive elimination of acetone; our data do not distinguish whether this isomerization or

(3) Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723 and references therein. Saunders, D. R.; Stephenson, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1984**, 539.

(4) Fischer, E. O.; Riedel, A. *Chem. Ber.* **1968**, *101*, 156.

(5) Spectroscopic and analytical data are provided in the supplementary material.

(6) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, 2nd ed.; McGraw Hill: San Francisco, 1977; p 338.

(7) This supports the argument of Semmelhack and Tamura,^{1b} who found that treatment of iron acylate salts with "hard" alkylating agents, such as fluorosulfonates, followed by oxidation gave both esters and ketones (presumably by competitive O- and Fe-alkylation, respectively), whereas reaction with softer electrophiles such as EtI led only to ketone (via exclusive Fe-alkylation).

(8) The structure was determined by Dr. F. J. Hollander of the UC Berkeley College of Chemistry X-ray Diffraction Facility (CHEXRAY). Details of the structure determination are provided as supplementary material. The rhenium-bound methyl group is disordered; half of a hydrogen is located behind C-10 in the ORTEP view shown in Scheme I.

(9) The Fischer carbene formed by O-alkylation of **1** is stable in C_6D_6 at 100 °C.

(1) (a) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342. (b) Semmelhack, M. F.; Tamura, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 4099.

(2) Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturo, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7451.