

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.

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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

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

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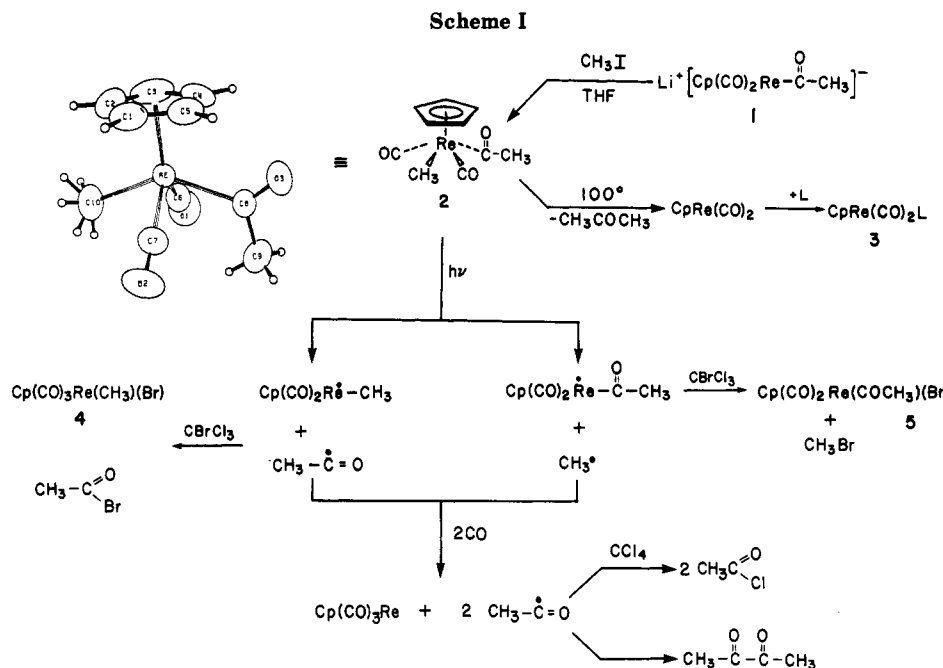
(7) This supports the argument of Semmelhack and Tamura,^{1b} who found that treatment of iron acylate salts with "hard" alkylating agents, such as fluorosulfonates, followed by oxidation gave both esters and ketones (presumably by competitive O- and Fe-alkylation, respectively), whereas reaction with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

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the reductive elimination is rate-determining.

The photochemical decomposition of **2** is not as straightforward, giving a complex mixture of organic and organometallic products in the absence of added ligand. However, irradiation of **2** at 350–380 nm under 20 atm of CO in CD_2Cl_2 at 6–8 °C leads to the clean formation of biacetyl (2,3-butanedione) (80%), CpRe(CO)_3 (100%), and acetone (8%). When the reaction was carried out under ^{13}CO , no scrambling of ^{13}CO into the starting material was observed (MS), and 92% of the CpRe(CO)_3 product contained only one ^{13}CO (6% $^{13}\text{C}_0$, 92% $^{13}\text{C}_1$, 2% $^{13}\text{C}_2$); the 2,3-butanedione formed was found by GC/MS to be 22% $^{13}\text{C}_0$, 50% $^{13}\text{C}_1$, and 28% $^{13}\text{C}_2$. Furthermore, a crossover experiment carried out by irradiation of a 53:47 mixture of $2\text{-}d_0$ and $2\text{-}d_6$ gave 2,3-butanedione having a statistical distribution of d_3 groups (obsd, 27 d_0 , 50% d_3 , 23% d_6 ; calcd, 28% d_0 , 50% d_3 , 22% d_6) with no scrambling of labels in the starting mixture.

These results argue against a mechanism involving CO migratory insertion followed by ligand addition, reductive elimination, and another ligand addition because this would be expected to lead to unlabeled 2,3-butanedione and doubly labeled CpRe(CO)_3 . They are consistent, however, with the initial formation of both methyl and acetyl radicals, provided that the methyl radicals formed can be trapped efficiently with CO to give acetyl radicals, to account for the high yield of biacetyl. Literature data are consistent with this: rate and equilibrium constants for the known $\text{CH}_3\text{•} + \text{CO} \rightleftharpoons \text{CH}_3\text{CO}\text{•}$ equilibration show that the forward reaction is reasonably rapid and the reverse rather slow ($k_1 = 3.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $k_{-1} = 1.1 \text{ s}^{-1}$; $K_{\text{eq}} = 3.1 \times 10^3 \text{ M}^{-1}$ at 7 °C).¹⁰ Pressure dependent solubility data in CH_2Cl_2 have not been reported. However, from data in other solvents, the CO concentrations present at 20-atm pressure should be on the order of 10^{-2} – 10^{-1} M .¹¹ It therefore seems reasonable that under 20 atm of CO methyl radicals in solution would be converted to CH_3CO radicals at a reasonable rate, and these could act as efficient precursors of biacetyl.

Further support for this picture of the mechanism was provided by the following experiments. (a) Irradiation of the dimethyl complex *trans*- $\text{Cp(CO)}_2\text{Re(CH}_3)_2$ under 20 atm CO gave clean conversion to biacetyl (80%) and CpRe(CO)_3 ; only 5% acetone and no ethane or methane were formed. When ^{13}CO was employed, the 2,3-butanedione product was found to contain >99% $^{13}\text{C}_2$ and the CpRe(CO)_3 was again found to contain only one ^{13}C . (b) Irradiation of **2** in mixtures of CCl_4 and CD_2Cl_2 under CO led to substantial amounts of acetyl chloride. As the CCl_4 concentration was increased, the yield of acetyl chloride increased smoothly at the expense of 2,3-butanedione, indicating strongly that these two products arise from the same intermediate—very likely acetyl radicals. (c) Predicting that CBrCl_3 should be a substantially more efficient radical scavenger, we hoped this halocarbon would trap both methyl radicals¹² and the initially formed rhenium radical before carbonylation or conversion to other products. This was observed in the following reaction carried out under 20 atm of CO: irradiation of **2** with CBrCl_3 gave CH_3Br (41–44%), acetyl bromide (32–39%), *trans*- $\text{Cp(CO)}_2\text{Re(CH}_3\text{)Br}$ ¹³ (4, 40–43%), *trans*- $\text{Cp(CO)}_2\text{Re(COCH}_3\text{)Br}$ ⁵ (5, 38–40%), and acetone (8–10%).¹⁴ Similarly, irradiation of $\text{Cp(CO)}_2\text{Re(CH}_3)_2$ in CCl_4 gave acetyl chloride (152% or 1.52 equiv based on 1.0 equivalent of starting Re compound), CH_3Cl (19% or 0.19 equiv), acetone (6%), and CpRe(CO)_3 (97%);¹⁵ photolysis with CBrCl_3 gave only CH_3Br (81–87%) and $\text{Cp(CO)}_2\text{Re(CH}_3\text{)(Br)}$ (78–85%). C_2Cl_6 can be detected (GC/MS) in the products of this reaction (>65%).

The radical mechanism which most reasonably accounts for our results is shown in Scheme I. Upon photolysis, the methylacetylrhodium complex **2** is promoted to an excited

(12) CBrCl_3 has been demonstrated to be an extremely efficient trap for organic radicals. The absolute rate constant for its reaction with cyclopropyl radicals is $2.8 \times 10^8 \text{ s}^{-1}$ at 298 K; $k_T(\text{CBrCl}_3)/k_T(\text{CCl}_4)$ for $\text{CH}_3\text{•} + \text{CCl}_3\text{X} \rightarrow \text{CH}_3\text{X} + \text{CCl}_3\text{•}$ is ca. 10^4 at the same temperature. (a) Johnston, L. J.; Ingold, K. U. *J. Am. Chem. Soc.* 1986, 108, 2343. (b) Macken, K. V.; Sidebottom, H. W.; *Int. J. Chem. Kinet.* 1979, 11, 511.

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(15) Less than 4% of another product was formed; we believe this to be $\text{CpRe(CO)}_2\text{(CH}_3\text{)Cl}$ on the basis of a comparison of its $^1\text{H NMR}$ (δ 5.29, 1.00) to those of the Br and I analogues.¹⁵

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state (or states) which, on the basis of the similar amounts of **4** and **5** formed in the CBrCl_3 experiment, undergo relatively nonselective cleavage of the Re-CH_3 and Re-C(O)CH_3 bonds. In the presence of CBrCl_3 , the radicals resulting from this cleavage are trapped.¹⁶ Without CBrCl_3 in solution, the $\text{CpRe(CO)}_2\text{R}^*$ ($\text{R} = \text{Me, C(O)Me}$) can go on to product CpRe(CO)_3 either by an associative (17e-19e) or a dissociative mechanism of substitution of R^* by CO . The CH_3^* radicals produced are carbonylated, and the acetyl radicals can then either combine to form 2,3-butanedione or, in the presence of sufficient concentrations of CCl_4 , react to form acetyl chloride; CCl_4 does not transfer chlorine rapidly enough ($k = 8.2 \text{ M}^{-1} \text{ s}^{-1}$ at 7°C)¹² to compete with carbonylation of the methyl radicals. This mechanism also accounts for the statistical distribution of isotopes in the reaction of **2** with ^{13}CO ; acetyl radicals are known to undergo rapid interchange of acyl groups with 1,2-diketones.¹⁷

In summary, we have found that the cyclopentadienyl rhenium complexes discussed here undergo thermal and photochemical decomposition by different mechanisms; the latter process involves M-C bond homolysis, leading to methyl and acetyl radicals. The methyl radicals react competitively with CO and CBrCl_3 ; CCl_4 reacts more slowly and scavenges only the acetyl radical product of CH_3^* carbonylation. It seems possible that some other organometallic "double carbonylation" reactions may take place by similar nonchain radical mechanisms;¹⁸ in addition, our results suggest that CBrCl_3 is substantially more useful than CCl_4 as a diagnostic reagent for organic and organometallic radical intermediates.¹⁹

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(16) Many instances are known in which photolysis of metal alkyl complexes leads to metal and alkyl radicals that can be trapped (e.g., by CCl_4 or spin traps); there is considerably less evidence for generation of acyl radicals in acyl metal complex irradiations. See, for example, ref 19 and: (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: San Francisco, 1979. (b) Alt, H. G. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 766. (c) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* 1976, 14, 345. (d) Hudson, A.; Lappert, M. F.; Lednor, P. W.; MacQuitty, J. J.; Nicholson, B. K. *J. Chem. Soc., Dalton Trans.* 1981, 2159.

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(19) CCl_4 has been used extensively to trap organometallic radicals, and bimolecular rate constants, k_T , of halogen abstraction by organometallic radicals from CX_4 , CHX_3 , CH_2X_2 , and $\text{C}_6\text{H}_5\text{CH}_2\text{X}$ ($\text{X} = \text{Cl}$ or Br) have been estimated^{19a} or more recently, directly measured.^{19a-d} The ordering of increasing k_T roughly corresponds to a decrease in the C-X bond dissociation energy,^{19b} supporting our observation that CCl_3Br is more efficient than CCl_4 at trapping metal radicals. (a) Lee, K.-W.; Hanckel, J. M.; Brown, T. L. *J. Am. Chem. Soc.* 1986, 108, 2266. (b) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* 1985, 4, 42 and references therein. (c) Hanckel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* 1986, 25, 1852. (d) Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* 1982, 104, 1842. (e) Laine, R. M.; Ford, P. C. *Inorg. Chem.* 1977, 16, 388. (f) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* 1983, 105, 5934.

Supplementary Material Available: Spectroscopic and analytical data for **2** and **5**, experimental details of the X-ray diffraction study of **2** including crystal and data collection parameters, tables of positional parameters, general temperature factors, and intramolecular distances and angles (10 pages); a listing of F_o and F_c for **2** (8 pages). Ordering information is given on any masthead page.

Synthesis and Protonation Reactions of Trimethylphosphine-Substituted Carbyne Complexes of Molybdenum and Tungsten. The Tungsten Alkylidene Complexes $[(\text{W}=\text{CHR})\text{Cl}_2(\text{CO})(\text{PMe}_3)_2]$ as Precursors for Carbyne Complexes Containing Weakly Coordinated Ligands

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Summary: Efficient procedures for the synthesis of the tungsten carbyne complexes $[(\text{W}=\text{CR})\text{Cl}(\text{CO})(\text{PMe}_3)_3]$ (**2**, $\text{R} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{CH}_3$ -4) and $[(\text{M}=\text{CPh})\text{Br}(\text{PMe}_3)_4]$ (**3**, $\text{M} = \text{W}$, and **5**, $\text{M} = \text{Mo}$) are described. Reaction of complex **3** with HBr gives the hydrido complex $[(\text{W}=\text{CPh})\text{Br}_2(\text{H})(\text{PMe}_3)_3]$. Reaction of complexes **2** with HCl gives the tungsten alkylidene complexes $[(\text{W}=\text{CHR})\text{Cl}_2(\text{CO})(\text{PMe}_3)_2]$ (**7**) that can be deprotonated to give coordinatively labile anionic tungsten carbyne complexes $[(\text{W}=\text{CR})\text{Cl}_2(\text{CO})(\text{PMe}_3)_2]^-$. Dehydrochlorination of **7** in the presence of ligands provides substituted tungsten carbyne complexes $[(\text{W}=\text{CR})\text{Cl}(\text{CO})(\text{PMe}_3)_2\text{L}]$ ($\text{L} = \text{pyridine, P(OMe)}_3, \text{CNCMe}_3$). The crystal structure of the benzylidene complex $[(\text{W}=\text{CHPh})\text{Cl}_2(\text{CO})(\text{PMe}_3)_2]$ is reported.

Bis(donor ligand)-substituted carbyne complexes¹ of the group 6 transition metals have become easily accessible through the recent development of simple synthetic procedures.² The bis(pyridine)-substituted complexes $[(\text{M}=\text{CR})\text{X}(\text{CO})_2(\text{py})_2]$ ($\text{X} = \text{Cl, Br}$; $\text{py} = \text{pyridine}$; $\text{M} = \text{Cr, Mo, W}$; $\text{R} = \text{alkyl, aryl}$) are particularly useful systems since they combine increased thermal stability—compared to the tetracarbonylmetal carbyne complexes $[(\text{M}=\text{CR})\text{X}(\text{CO})_4]$ —and a high degree of reactivity—due to coordinative lability of the two pyridine ligands. The lability of the pyridine ligands is essential in the synthesis of stable tungsten alkene carbyne complexes such as $[(\text{W}=\text{CPh})\text{Cl}(\text{maleic anhydride})(\text{CO})(\text{py})_2]$.⁴ On the other hand, reaction of $[(\text{W}=\text{CPh})\text{Cl}(\text{CO})_2(\text{py})_2]$ with alkynes leads to alkyne polymerization without detectable metal alkyne carbyne complexes as intermediates.⁵ Our interest in this latter type of metal complex led us to develop more strongly stabilized metal carbyne complexes containing only one weakly coordinated ligand. Availability of such

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