(3) Since the effective mass of the hole at the valence band edge is extremely small in TP compared to GP, the $\sigma$-conjugation is larger in TP. The conservation of the near trans conformation is important if the polysilanes are to be good semiconductors.

(4) The combination of a small effective hole mass and ionzation potential is an important condition in the design of a new conducting material.

**Acknowledgment.** It is our great pleasure to have discussed polysilanes with Dr. Nobuo Matsumoto and Dr. Masaie Fujino. Informal discussions with Hiroshi Kojima and Hiroaki Isaka were relaxing and supportive. We thank Dr. Takunori Mashiko for instruction in the use of the graphic program library.

**Registry No.** GP,TP, 32028-95-8.

---

# Synthesis of Dialkyl- and Alkylacylrhenium Complexes by Alkylation of Anionic Rhenium Complexes at the Metal Center. Mechanism of a Double Carbonylation Reaction That Proceeds via the Formation of Free Methyl Radicals in Solution

**Karen I. Goldberg and Robert G. Bergman***

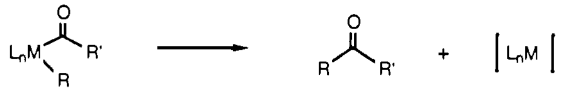
*Contribution from the Department of Chemistry, University of California at Berkeley, Berkeley, California 94720. Received June 6, 1988*

**Abstract:** The site of alkylation of salts of acylrhenates such as $Li^+[Cp(CO)_2Re(COCH_3)]^-$ (**1**) can be controlled by adjusting the hardness of the alkylating agent. Thus, treatment of **1** with the hard alkylating agent $(CH_3)_3OPF_6$ gives predominantly the classical Fischer carbene complex $Cp(CO)_2Re{=}C(OCH_3)(CH_3)$ (**2**), whereas reaction with the softer electrophile $CH_3I$ leads almost exclusively to the new metal-alkylated complex $Cp(CO)_2Re(CH_3)(COCH_3)$ (**3**). The structure of **3** has been determined by X-ray diffraction. The availability of this material, a relatively rare example of a stable alkylacylmetal complex, has provided an opportunity to study the products and mechanisms of its carbon–carbon bond-forming decomposition reactions. Thermally, the alkyl acyl complex undergoes simple reductive elimination, leading (in the presence of a metal-scavenging ligand L) to a quantitative yield of acetone and $CpRe(CO)_2(L)$. Photochemically, a more complicated reaction takes place, especially under 20 atm of CO, where $CpRe(CO)_3$ and 2,3-butanedione are formed. Strikingly, irradiation of $Cp(CO)_2Re(CH_3)_2$ (**9**) under 20 atm of CO gives products identical with those formed from **3**. Labeling experiments using $^{13}CO$ and mixtures of acetyl- and propionylrhenium complexes are inconsistent with a mechanism involving simple migratory CO insertion followed by reductive elimination. They are, however, consistent with metal–carbon bond homolysis leading to methyl and acetyl radicals, followed by carbonylation of the methyl radicals to give a second source of acetyl radicals; these reactive intermediates then dimerize to give 2,3-butanedione. Confirmation of this mechanism was obtained by trapping all the initially formed radicals with halogen donors. $BrCCl_3$ proved to be much more efficient than $CCl_4$ for this purpose: irradiation of alkyl acyl complex **3** in the presence of $BrCCl_3$ diverted the reaction completely from 2,3-butanedione production, giving instead $CH_3Br$, $CH_3COBr$, $Cp(CO)_2Re(CH_3)Br$, and $Cp(CO)_2Re(CH_3CO)Br$.

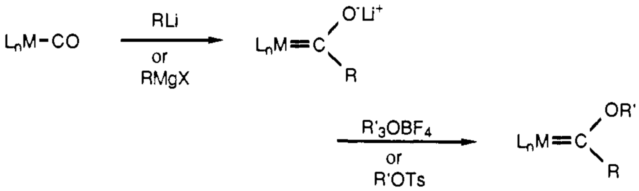
Elimination of ketones from acyl alkyl transition-metal complexes, as depicted in Scheme I, occurs rapidly compared to the similar reductive coupling of two alkyl ligands to form alkanes.[1a] The facility of this elimination reaction has hindered the isolation, characterization, and study of acyl alkyl complexes.[2]

In view of this high reactivity, acyl alkyl species have often been invoked as undetected intermediates in ketone-forming reactions. The reaction of Collman's reagent, $Na_2Fe(CO)_4$, with alkyl halides to yield ketones is postulated to proceed through such an acyl alkyl intermediate.[3] A mononuclear acetyl methyl derivative has been suggested as an intermediate in the decomposition of $[CpCo(CO)CH_3]_2$ and in the reaction of CO with $CpCo(CH_3)_2PPh_3$ to give acetone.[4] The reaction of $Cp_2TiR_2$ (R = Ph) with CO at room temperature[5] and the carbonylation reactions of $NiR_2L_2$ (R = Me, Et) to give $RCOR$[6] are presumed to go through analogous intermediates. Reductive elimination of ketone from diacyl anionic derivatives of rhenium and manganese carbonyl complexes was shown to be preceded by CO deinsertion forming acyl alkyl complexes.[2] However, only in the rhenium system were such acyl alkyl complexes isolable.

**Scheme I**



**Scheme II**



The research described in this paper was stimulated by the discovery of a potentially general procedure for preparing acy-

---

[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; references cited therein, (a) Chapter 5, (b) p 107, (c) p 244, (d) p 764.

[2] Casey, C. P.; Scheck, D. M. *J. Am. Chem. Soc.* **1980**, *102*, 2723, and references therein.

[3] Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

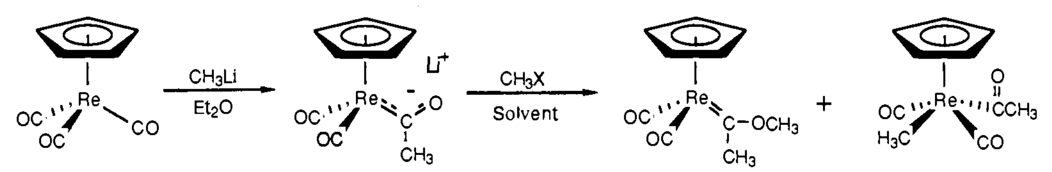
[4] (a) Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturo, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7451. (b) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 7003.

[5] Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750.

[6] Yamamoto, T.; Kohara, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2161.

0002-7863/89/1511-1285$01.50/0 © 1989 American Chemical Society

Scheme III



1 2 3

| $CH_3X$ | solvent | | | |
|---|---|---|---|---|
| $(CH_3)_3OPF_6$ | $H_2O$ | 24 | : | 74 |
| $(CH_3)_3OPF_6$ | acetone-$d_6$ | 78 | : | 22 |
| $CH_3I$ | acetone-$d_6$ | 2 | : | 98 |
| $CH_3I$ | THF-$d_8$ | 0 | : | 100 |
| $CH_3OSO_2C_6H_4CH_3$ | acetone-$d_6$ | 79 | : | 21 |
| $CH_3OSO_2C_6H_4CH_3$ | THF-$d_8$ | 69 | : | 31 |

lalkylmetal complexes by alkylation of metal acylates selectively at the metal center. This has allowed us to study the mechanism of the thermal reductive elimination of ketone from an isolable rhenium acyl alkyl complex. In contrast, ultraviolet irradiation of this acyl alkyl complex under CO yields 1,2-diketones; doubly carbonylated organic products are also formed on irradiation of the corresponding dialkylrhenium complexes. An investigation of the mechanism of this process has revealed that conventional migratory insertion steps are not involved; rather, metal–carbon bond cleavage to give acetyl and methyl radicals occurs, and under CO these reactive species are in equilibrium with one another. We report here the experiments that have led us to these conclusions.[7]

## Results and Discussion

**Synthesis and Structure of $CpRe(CO)_2(COCH_3)(CH_3)$ (3).** $CpRe(CO)_2(=C(OCH_3)(CH_3))$ (**2**) was one of the first reported metal–carbene complexes. It was prepared by protonation of the acylmetalate $CpRe(CO)_2(COCH_3)Li$ (**1**) followed by addition of $CH_2N_2$ to the resulting hydroxy carbene complex.[8] Improvements in the synthesis of alkylalkoxy (or "Fischer") carbene complexes followed quickly; the most direct pathway currently in use is that shown in Scheme II.[9] Nucleophilic addition of a Grignard or alkyllithium reagent to a metal carbonyl compound results in the formation of a metal acylate complex. Electrophilic alkylating reagents, e.g. $R_3OBF_4$ or ROTs, can then be used to alkylate the oxygen atom, leading to the desired carbene complex.

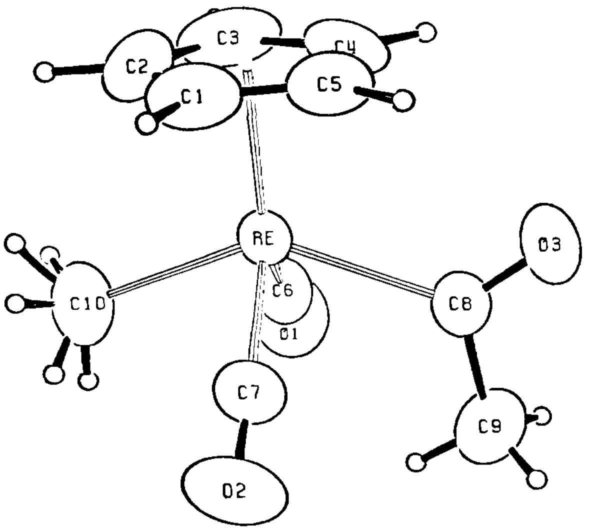


**Figure 1.** ORTEP drawing of one molecule of **3**, showing the atomic labeling scheme. Thermal ellipsoids are scaled to represent the 50% probability surface. Hydrogen atoms are given as arbitrary small spheres for clarity. The rhenium-bound methyl group is disordered; half of one hydrogen atom is located behind C10 in the view shown.

To our surprise, running the reaction of acylrhenate **1** with $(CH_3)_3OPF_6$ in $H_2O$ (as described in literature syntheses for other Fischer carbenes) resulted in a very low yield of the methylmethoxycarbene complex **2**. Instead, a structural isomer of **2**, $CpRe(CO)_2(COCH_3)(CH_3)$ (**3**), was formed in a ratio of 2.8:1 relative to **2** (Scheme III). The $^1H$ NMR spectrum of **3** in $C_6D_6$ exhibits three singlet resonances in a 5:3:3 ratio with chemical shifts attributable to a cyclopentadiene ring, an acetyl group, and a metal-bound methyl group. The $^{13}C$ NMR data are also in accord with these functionalities, and the IR spectrum in benzene reveals an acyl absorption at 1630 cm$^{-1}$, which is characteristic of an $\eta^1$-acyl ligand.[1b]

The structure of **3** was determined unambiguously in an X-ray diffraction study (performed by Dr. F. J. Hollander of the University of California at Berkeley X-ray diffraction facility (CHEXRAY)). Crystals of **3** were obtained by slow cooling of a hexane/toluene solution and exist in the space group *Pbcn*; an ORTEP drawing is shown in Figure 1. Typical of $CpML_4$ complexes, a four-legged piano stool structure is observed with a trans arrangement of the acyl and alkyl ligands. Comparison of the Re–C–O angle (122.3°) and the O–C–$CH_3$ angle (117.4°) in the acyl ligand indicates that there is no interaction of the oxygen with the rhenium, consistent with predictions of electron-counting formalisms. The metal–carbon bond distances for both the acetyl (2.192 (4) Å) and methyl ligand (2.245 (4) Å) are similar to those observed previously for rhenium, 2.05–2.22 and 2.24–2.55 Å, respectively.[10,11] Table I lists selected bond angles and distances.

The formation of **3** constitutes the first direct observation of alkylation of an acylmetalate at the metal center. Further investigation of this reaction revealed that the ratio of the two structural isomers **2** and **3** obtained (summarized in Scheme III) was dependent upon the reaction conditions, the choice of solvent, and the alkylating agent. The same type of behavior has been proposed for iron carbonyl acylates by Semmelhack and Tamura.[12] In their study, alkylation was followed by oxidation with $FeCl_3$, and the occurrence of competitive O versus Fe alkylation was deduced from the relative yields of esters and ketones obtained.

---

(7) Some of the results described here have been reported in preliminary form: Goldberg, K. I.; Bergman, R. G. *Organometallics* **1987**, *6*, 430.

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

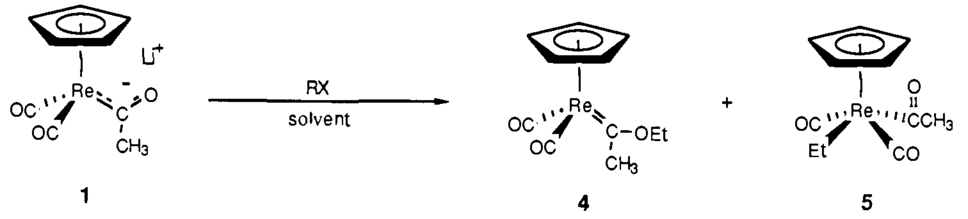
(9) (a) Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. (b) Fischer, H. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Deerfield Beach, FL, 1983; p 1.

(10) (a) Wong, W. K.; Tam, W.; Strouse, C. E.; Gladyz, J. A. *J. Chem. Soc., Chem. Commun.* **1979**, 530. (b) Astakhova, I. S.; Johannson, A. A.; Semion, V. A.; Stuchkov, Y. T.; Anibsimov, K. N.; Kolobova, N. E. *J. Chem. Soc., Chem. Commun.* **1969**, 488.

(11) (a) Long, C.; Morrisson, A. R.; McKean, D. C.; McQuillan, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 7418. (b) Aleksandrov, G. G.; Struchkov, Y. T.; Makarov, Y. V. *Zh. Strukt. Khim.* **1973**, *14*, 98. (c) Alcock, N. W. *J. Chem. Soc. A* **1967**, 2001.

(12) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099.

Scheme IV



| RX | solvent | 4 | | 5 |
|---|---|---|---|---|
| $Et_3OPF_6$ | acetone-$d_6$ | 100 | : | 0 |
| EtI | acetone-$d_6$ | 42 | : | 58 |
| EtI | THF-$d_8$ | 8 | : | 92 |

**Table I.** Selected Intramolecular Distances (Å) and Angles (deg) for 3[a]

| | | | |
|---|---|---|---|
| | Distances | | |
| Re–C6 | 1.904 (4) | C8–O3 | 1.189 (4) |
| Re–C7 | 1.899 (4) | C8–C9 | 1.512 (5) |
| Re–C8 | 2.192 (4) | C6–O1 | 1.143 (4) |
| Re–C10 | 2.245 (4) | C7–O2 | 1.161 (4) |
| Re–Cp* | 1.948 | C1–C2 | 1.387 (7) |
| Re–C1 | 2.280 (5) | C2–C3 | 1.368 (7) |
| Re–C2 | 2.315 (4) | C3–C4 | 1.406 (6) |
| Re–C3 | 2.297 (4) | C4–C5 | 1.392 (6) |
| Re–C4 | 2.253 (4) | C5–C1 | 1.387 (6) |
| Re–C5 | 2.247 (4) | | |
| | Angles | | |
| Cp*–Re–C6 | 129.38 | Re–C8–O3 | 122.3 (3) |
| Cp*–Re–C7 | 129.12 | Re–C8–C9 | 120.3 (3) |
| Cp*–Re–C8 | 112.23 | O3–C8–C9 | 117.4 (3) |
| Cp*–Re–C10 | 108.86 | Re–C6–O1 | 177.1 (4) |
| C6–Re–C7 | 101.24 (17) | Re–C7–O2 | 176.3 (4) |
| C8–Re–C10 | 138.91 (16) | C5–C1–C2 | 108.3 (4) |
| C6–Re–C8 | 78.89 (14) | C1–C2–C3 | 108.5 (4) |
| C6–Re–C10 | 74.96 (17) | C2–C3–C4 | 107.9 (4) |
| C7–Re–C8 | 78.54 (16) | C3–C4–C5 | 107.6 (4) |
| C7–Re–C10 | 76.18 (19) | C4–C5–C1 | 107.6 (4) |

[a] Cp* is the centroid of the cyclopentadiene ring.

Acylmetalates are ambient nucleophiles analogous to organic enolate anions, and the dependence of their alkylation behavior on solvent and alkylating agent can be similarly explained.[13] In a protic solvent, such as $H_2O$, the more electronegative oxygen is solvated tightly by hydrogen bonding, rendering the less electronegative atom (the carbon or metal) more reactive toward the electrophile. In a polar aprotic solvent, a propensity for alkylation at the more electronegative site is expected. Indeed, carrying out the reaction of **1** with $(CH_3)_3OPF_6$ in $H_2O$ favored formation of the acetyl methyl complex **3**, while switching solvents to acetone-$d_6$ caused a 78:22 preference for the carbene complex **2** (Scheme III).[14]

Hard–soft acid–base theory[15] serves to rationalize the effect of alkylating agent on product determination. In acetone-$d_6$ the "hard" methylating agent $(CH_3)_3OPF_6$ favors the carbene complex **2** (O alkylation) while the "softer" alkylating agent $CH_3I$ proceeds via Re alkylation, forming predominantly (98:2) the methyl acetyl complex **3** (Scheme III). The reaction of $CH_3I$ with **1** in THF-$d_8$ resulted in 100% Re alkylation and a quantitative yield of **3**. On a preparative scale, **3** is best isolated (65%) by chromatography of the crude reaction mixture and recrystallization.

Scheme V

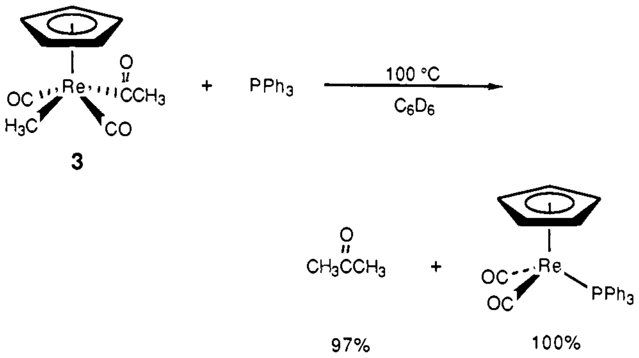


**Table II.** Observed Rate Constants for the Reaction of **3** with $PPh_3$ in $C_6D_6$ at 100 °C.

| [3] | [PPh$_3$] | $k_{obs} \times 10^5$, s$^{-1}$ | [3] | [PPh$_3$] | $k_{obs} \times 10^5$, s$^{-1}$ |
|---|---|---|---|---|---|
| $1.43 \times 10^{-2}$ | 0.142 | 6.01 | $1.50 \times 10^{-2}$ | 0.075 | 6.08 |
| $1.52 \times 10^{-2}$ | 0.307 | 6.07 | $2.16 \times 10^{-2}$ | 0.431 | 6.05 |
| $2.84 \times 10^{-2}$ | 0.285 | 6.22 | $4.79 \times 10^{-2}$ | 0.596 | 6.20 |

Alkylation of **1** with ethyl-transfer reagents showed similar site preferences (Scheme IV). The reaction of **1** with the hard alkylating agent $Et_3OPF_6$ in acetone-$d_6$ led to formation of the Fischer carbene, $CpRe(CO)_2(C(OEt)(CH_3))$ (**4**) as the exclusive product.[16] Alkylation of **1** with EtI in THF-$d_8$ favored the acyl alkyl product $CpRe(CO)_2(COCH_3)(Et)$ (**5**) by 92:8 over the carbene product **4**.[17] In acetone-$d_6$, the observed preference for **5** dropped to 58:42. The reactions of **1** with EtI were considerably slower than with $Et_3OPF_6$, requiring over 20 h at 45 °C to reach completion.

**Thermal Chemistry of 3.** While solutions of methyl acetyl complex **3** are stable at ambient temperature, thermolysis in $C_6D_6$ at 100 °C was complete within 10 h. The reaction was conveniently monitored by $^1H$ NMR spectrometry. Several organo-

---

[13] March, J. *Advanced Organic Chemistry: Reactions, Mechanisms* and *Structure*, 3rd ed.; McGraw Hill: San Francisco, CA, 1985; p 324–325.

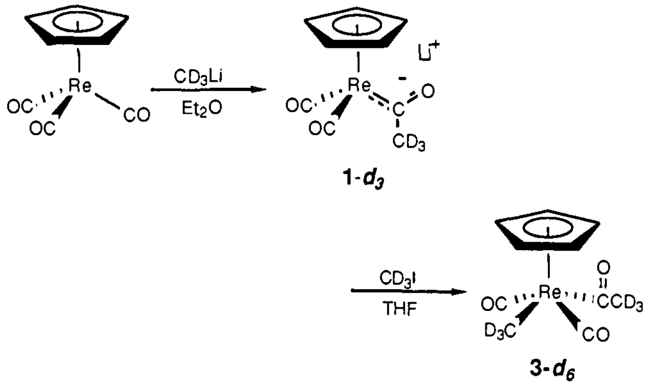
[14] While the reaction in $H_2O$ may not have been strictly homogeneous, care was taken to ensure the homogeneity of the acetone reaction. Both reactants were soluble in acetone, and the reaction was repeated several times, affording nearly identical ratios of products. We also carried out this reaction in THF-$d_8$ and observed an 85:15 ratio of **2**/**3**. However, $(CH_3)_3OPF_6$ did not appear to be soluble in this solvent, and therefore we are hesitant to draw any conclusions regarding site preferences from this result. It should also be noted that $Me_3OPF_6$ reacts over a period of several hours to polymerize THF. As pointed out by a reviewer, the nature of the metal counterion and its coordination sphere may also be important in determining the site of alkylation.

[15] (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G. *J. Chem. Ed.* **1968**, *45*, 581. (c) Pearson, R. G. *J. Chem. Ed.* **1968**, *45*, 643. (d) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *39*, 1827.

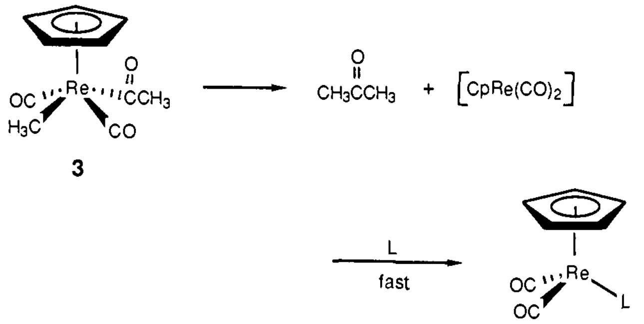
[16] Similar results were found for this reaction in THF-$d_8$ where the ratio of the carbene to the acyl alkyl species was 98:2. However, there is evidence that this THF reaction may proceed heterogeneously. Polymerization of THF by $Et_3OPF_6$ was also observed.

[17] Only $^1H$ NMR spectroscopic data are available for **5**; attempts to isolate and characterize this compound were unsuccessful. For **5**: $^1H$ NMR (THF-$d_8$) $\delta$ 5.31 (s, 5 H), 2.52 (s, 3 H), 1.97 (q, 2 H, $J$ = 7.5), 1.57 (t, 3 H, $J$ = 7.5); (acetone-$d_6$) $\delta$ 4.39 (s, 5 H), 2.50 (s, 3 H), 1.96 (q, 2 H, $J$ = 7.5), 1.55 (t, 3 H, $J$ = 7.4). It is possible that a $\beta$-elimination reaction of the ethyl group, perhaps concurrent with $\eta^5$- to $\eta^3$-isomerization of the cyclopentadienyl ring, is responsible for decomposition of **5**. This type of behavior has been observed in ($\eta^5$-cyclopentadienyl)dicarbonylrhenacyclopentane: Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129.

Scheme VI



Scheme VII



metallic products were observed, with the most abundant being CpRe(CO)$_3$ (71%). The major organic product was acetone (64%). When the thermolysis was run in the presence of PPh$_3$, the reaction was much cleaner; CpRe(CO)$_2$(PPh$_3$) and acetone were both observed in quantitative yield (Scheme V).

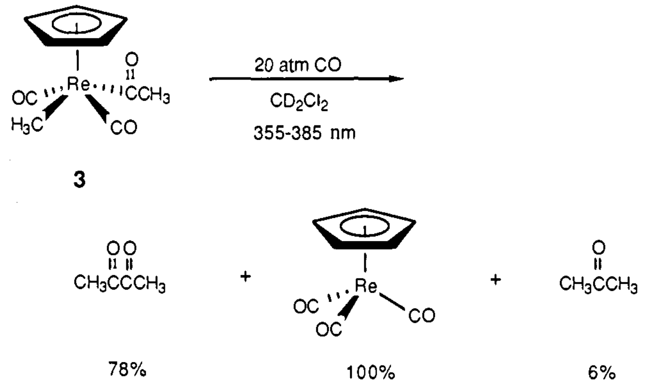
A kinetic study of the thermolysis of **3** in $C_6D_6$ in the presence of excess PPh$_3$ was undertaken. The reaction shows clean first-order kinetics to greater than 3 half-lives. The results of several runs with varying concentrations of phosphine, listed in Table II, show that a variation of [PPh$_3$] over nearly 1 order of magnitude (0.075–0.596 M) resulted in no significant change in $k_{obs}$. Thus, the reaction is first-order in [**3**] and zero-order in [PPh$_3$].

Treatment of CpRe(CO)$_3$ with $CD_3Li$ in $Et_2O$ yielded **1**-$d_3$, which was allowed to react with $CD_3I$ in THF resulting in the production of **3**-$d_6$ (Scheme VI). When an approximately 1:1 mixture of **3**-$d_6$ and **3**-$d_0$ was thermalized at 100 °C in the presence of excess phosphine, acetone-$d_6$ and acetone-$d_0$ were formed contaminated with less than 1% of acetone-$d_3$. Thus, the reaction involves intramolecular reductive elimination of acetone.

On the basis of these kinetic and labeling studies, we propose the mechanism shown in Scheme VII for the thermal decomposition of **3**. Rate-determining reductive elimination of acetone occurs to form the coordinatively unsaturated intermediate [CpRe(CO)$_2$] (or a solvated analogue of this species). This intermediate is then trapped in a fast step by L. Presumably, **3** undergoes a trans to cis isomerization prior to the reductive elimination step.[18] Our results do not distinguish whether this isomerization or the actual reductive elimination is rate-determining.

**Photochemistry of 3.** The photolysis of **3** in $C_6D_6$ is essentially complete within a 30-min irradiation time with a Hanovia 450-W lamp and a Pyrex filter at 6–8 °C. The reaction was monitored by $^1$H NMR spectrometry; several different organometallic and organic products were formed, with CpRe(CO)$_3$ (25%) and acetone (13%) identified among them. When the same irradiation was carried out under high pressures of CO (ca. 20 atm; *see cautionary note in the Experimental Section*), the reaction was cleaner; a new organic product, 2,3-butanedione, was formed in 50% yield along with CpRe(CO)$_3$ (85%) and acetone (8%). Improvement in the yield of the doubly carbonylated product was achieved with a change of solvent to $CD_2Cl_2$ and use of a filter system, which limited the irradiation wavelength to 355–385 nm; examination of the UV spectra of reactants and products demonstrated that this light range permits irradiation of the starting material ($\epsilon_{369} = 1.2 \times 10^4$ M$^{-1}$ cm$^{-1}$) with only minimal absorption by the products (CpRe(CO)$_3$, $\epsilon_{369} = 51$ M$^{-1}$ cm$^{-1}$; 2,3-butanedione, $\epsilon_{369} = 3.2$ M$^{-1}$ cm$^{-1}$). Under these conditions, the reaction is much cleaner, with 2,3-butanedione formed in 78% yield, CpRe(CO)$_3$ in 100% yield, and acetone in 6% yield (Scheme VIII).

Scheme VIII



The irradiation of **3** was also carried out in the presence of potential ligands other than CO. When **3** was irradiated in the presence of excess phosphine (L = PMe$_3$ or PPh$_3$) in $C_6D_6$, no 2,3-butanedione was observed. For L = PMe$_3$, CpRe(CO)$_2$PMe$_3$ (ca. 78%) and acetone (ca. 9%) were identified as the major products of the reaction. For L = PPh$_3$, CpRe(CO)$_2$PPh$_3$ (ca. 55%) was formed along with approximately 14% of another organometallic product, which was not identified. Several other very small signals in the region $\delta$ 0.0–3.3 were also observed when the reaction was monitored by $^1$H NMR spectrometry.

**Irradiation of 3 in the Presence of $^{13}$CO.** In order to determine the origin of the new carbonyl group in the 2,3-butanedione product, the reaction was carried out under $^{13}$CO. The sample was irradiated for 7 min (355–385 nm), resulting in approximately 50% conversion. The volatile materials were transferred under vacuum and analyzed by GC/MS. This demonstrated that the ratio of $^{13}C_0/^{13}C_1/^{13}C_2$ in the 2,3-butanedione product was 23:50:28. The nonvolatile materials (rhenium-containing species) were separated by chromatography and analyzed directly by mass spectrometry. The 98:2 $^{13}C_0/^{13}C_1$ ratio observed implies that there was virtually no exchange of $^{13}$CO into the starting material. The mass spectrum observed for the CpRe(CO)$_3$ product indicated a ratio of 6:92:2 for $^{13}C_0/^{13}C_1/^{13}C_2$ consistent with the incorporation of only one molecule of labeled CO. The overall reaction and incorporation of label are summarized in Scheme IX.

**Crossover Experiment.** In order to ascertain the molecularity of the diketone-forming reaction, the crossover experiment illustrated in Scheme X was performed. An initial mixture containing a 52:2:46 ratio of **3**-$d_0$/**3**-$d_5$/**3**-$d_6$ (MS analysis; Figure 2a) was irradiated under 20 atm of CO for 10 min (uranium filter). The volatile materials were removed and analyzed by GC/MS. The observed mass spectrum of the 2,3-butanedione product is shown in Figure 2b, along with a best fit calculation indicating a $d_0/d_2/d_3/d_5/d_6$ ratio of 28:1:54:0:16. Parts a and b of Figure 3 compare the experimental data with those expected on the basis of the starting mixture for 100% crossover (27:1:49:1:22) and those expected for 0% crossover. Clearly, the results agree with the former situation. The organometallic residue that contained unreacted starting material was analyzed directly by mass spectrometry; it showed a ratio of 49:3:49 for **3**-$d_0$/**3**-$d_5$/**3**-$d_6$ indicative of no deuterium exchange (within experimental error) in the unreacted starting material.

**Irradiation of CpRe(CO)$_2$(COEt)(CH$_3$) (6).** The propionyl methyl complex, CpRe(CO)$_2$(COEt)(CH$_3$) (**6**), was synthesized analogously to the acetyl methyl complex **3**. Addition of EtLi

---

[18] Reductive elimination has been shown to proceed in several systems only when the eliminating ligands are cis to one another. See ref 1a and references cited therein.

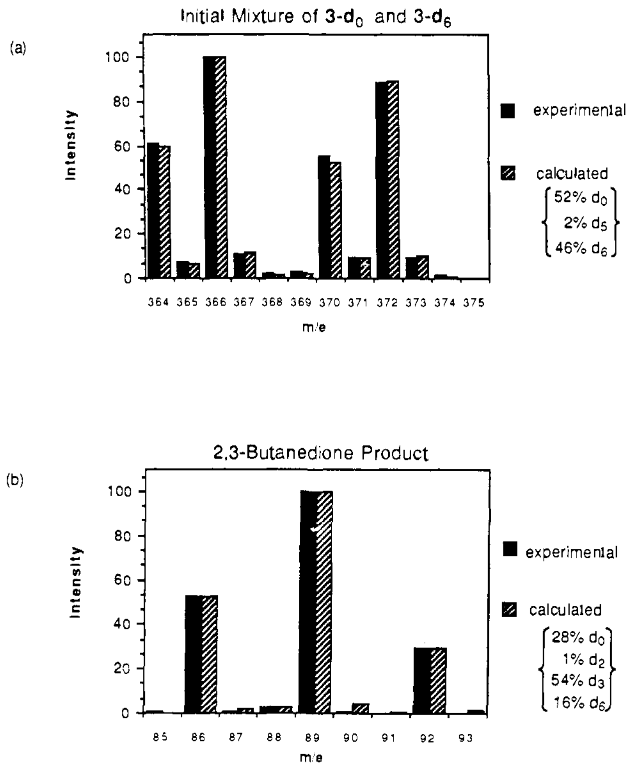


**Figure 2.** For the irradiation of 3-$d_0$/3-$d_6$ mixture under 20 atm of CO: (a) Observed and best fit calculation mass spectrum of the molecular ion region of **3** for the initial mixture of 3-$d_0$ and 3-$d_6$. (b) Observed and best fit calculation mass spectrum for the molecular ion region of 2,3-butanedione for the 2,3-butanedione product.

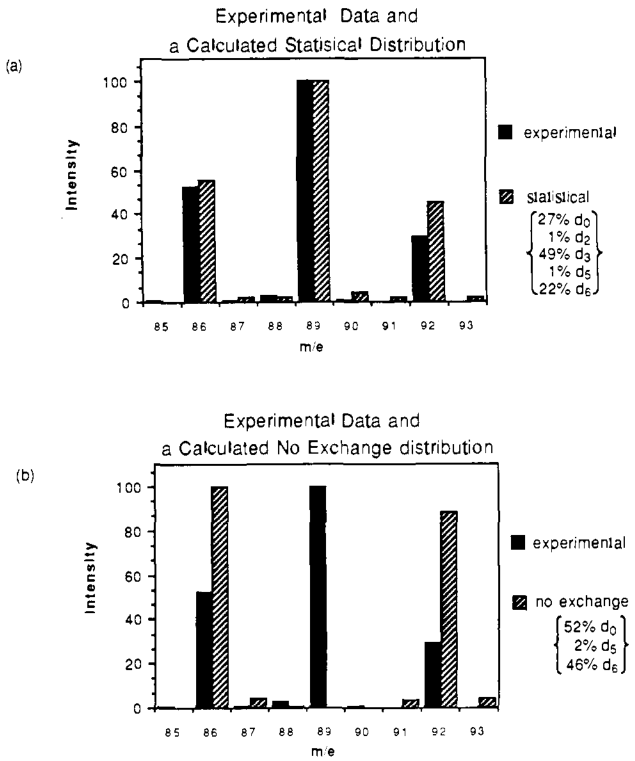
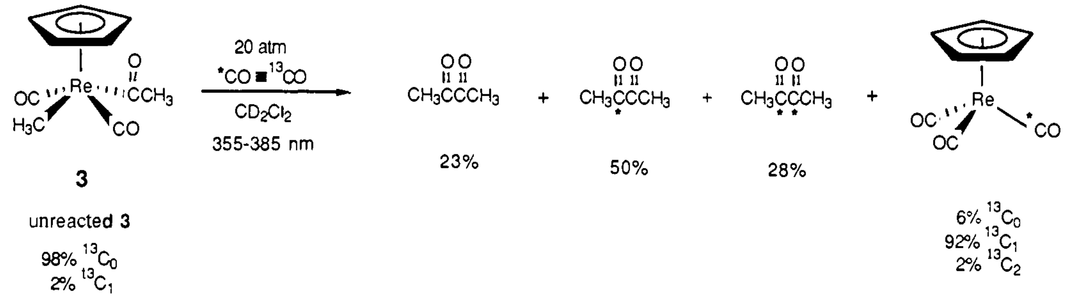


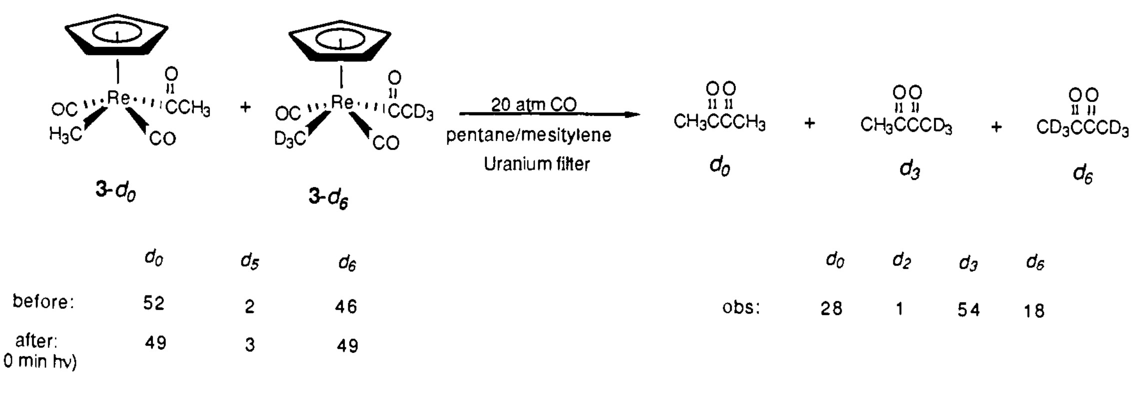
**Figure 3.** Comparison of the mass spectral experimental data for the 2,3-butanedione product obtained in the irradiation of 3-$d_0$ and 3-$d_6$ mixture under 20 atm of CO with (a) a calculated statistical distribution of the label and (b) a distribution based on no exchange from the starting composition of 3-$d_0$ and 3-$d_6$.

to CpRe(CO)$_3$ was followed by alkylation of the propionylrhenate salt with CH$_3$I to give **6**. A statistical distribution of diketone products was observed upon irradiation of a solution of propionyl methyl complex **6** in C$_6$D$_6$ under 20 atm of CO (Scheme XI). The organic products 3,4-hexanedione, 2,3-pentanedione, and 2,3-butanedione, identified by comparison with $^1$H NMR spectra of commercial samples, were formed in a 1:1.83:1.23 ratio. The only detectable organometallic product was CpRe(CO)$_3$. Significantly, when the irradiation of the acetyl methyl complex **3** was carried out under CO in the presence of 1 equiv of 3,4-hexanedione to only 18% conversion, the following products (yields corrected for percent conversion) were observed: CpRe(CO)$_3$ (100%), 2,3-butanedione (34%), 2,3-pentanedione (68%), and acetone (10%) (Scheme XII). These yields are calculated on the basis of rhenium starting material **3**. The ratio of the acetyl methyl complex **3** to 3,4-hexanedione remained constant. In a

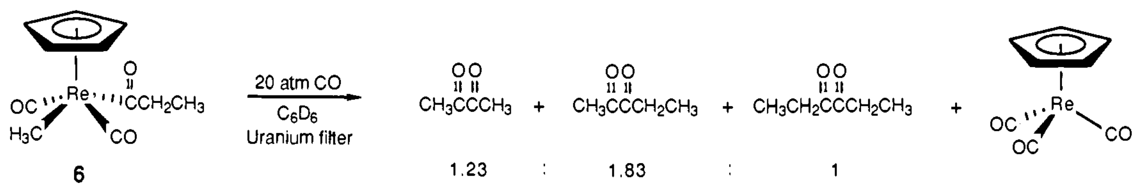
**Scheme IX**



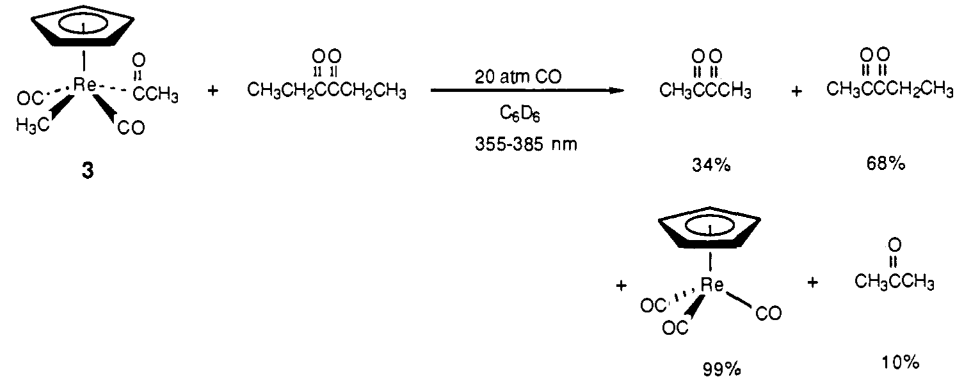
**Scheme X**



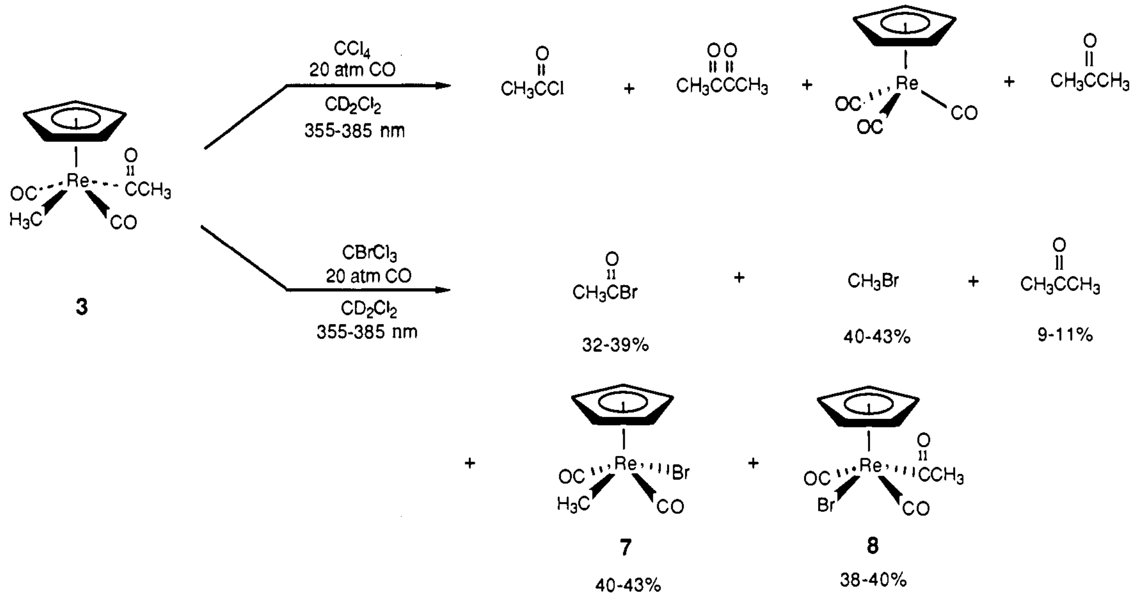
Scheme XI



Scheme XII



Scheme XIII



control experiment, no 2,3-pentanedione was formed when a 1:1 mixture of 2,3-butanedione and 3,4-hexanedione was irradiated under 20 atm of CO (uranium glass filter; 10 min).

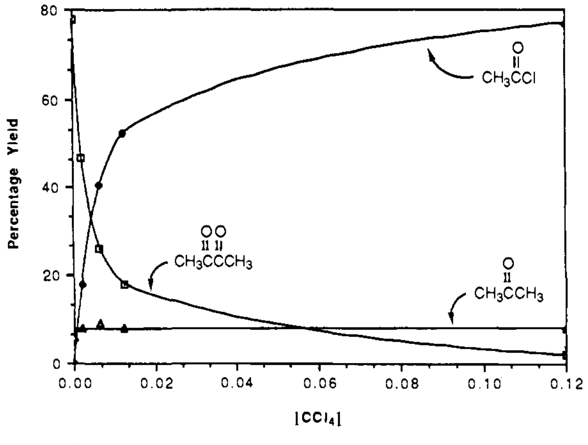
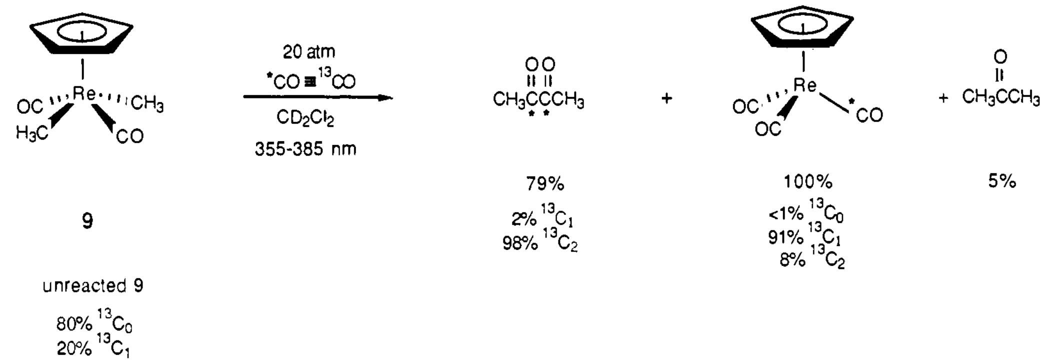


Figure 4. Graph of the percentage yields of 2,3-butanedione (squares), acetyl chloride (divided by 2; diamonds), and acetone (triangles) versus the concentration of $CCl_4$ for the irradiation of **3** under 20 atm of CO in $CD_2Cl_2$.

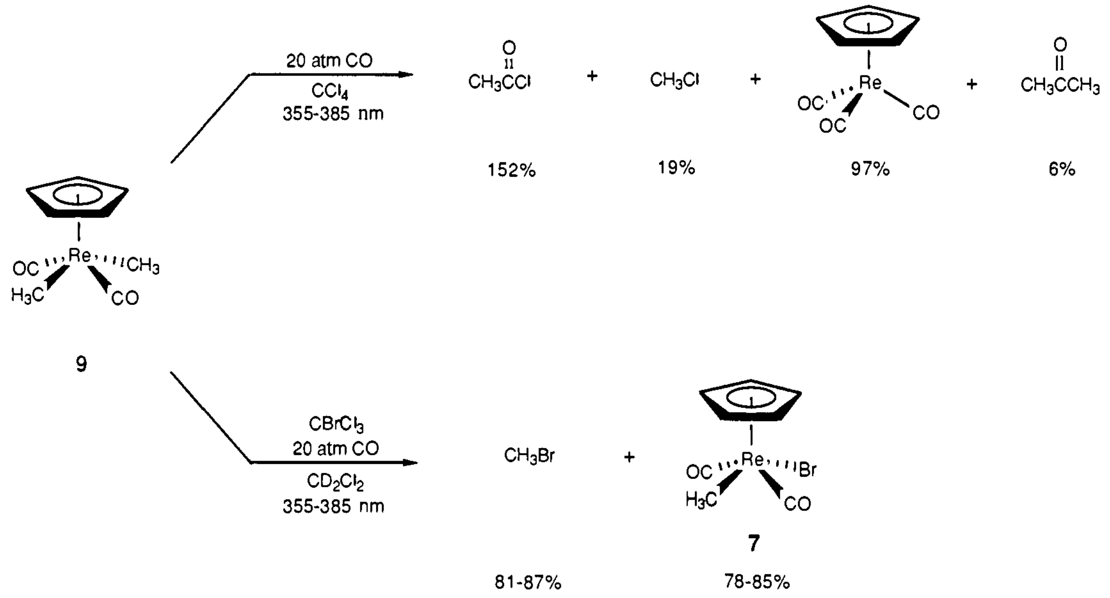
**Irradiation of 3 under 20 atm of CO in the Presence of $CCl_4$ and $CBrCl_3$.** An attempt to trap radical species generated in the photolysis reaction was made by adding $CCl_4$ to the reaction solution. This resulted in the formation of acetyl chloride with yields dependent on the concentration of trapping agent (Scheme XIII). A series of experiments were carried out by irradiating solutions of **3** under 20 atm of CO in $CD_2Cl_2$ with concentrations of $CCl_4$ varying from 0–0.1 M. Monitoring the progress of the reactions by $^1H$ NMR integration against an internal standard allowed calculation of the yields for the various products. The yields, corrected for percent conversion, remained essentially constant within experimental error throughout the irradiation. $CpRe(CO)_3$ was produced quantitatively in all cases. A plot of the yields of organic products as a function of $[CCl_4]$ is shown in Figure 4 and shows that, as the $CCl_4$ concentration was increased, the yield of acetyl chloride increased smoothly at the expense of 2,3-butanedione. This result strongly suggests that these two products arise from the same intermediate. Note that the small yield of acetone is not affected by the $CCl_4$ concentration.

Predicting that $CBrCl_3$ should be a more effective radical scavenger and might trap an initially formed metal radical or any short-lived organic radicals, the irradiation of **3** under 20 atm of

Scheme XIV



Scheme XV



CO in $CD_2Cl_2$ in the presence of this halide was performed. This resulted in production of methyl bromide (40–43%), acetyl bromide (32–39%), $CpRe(CO)_2(CH_3)Br$[19] (7; 40–43%), $CpRe(CO)_2(COCH_3)(Br)$ (8; 38–40%), and acetone (9–11%) (Scheme XIII). No 2,3-butanedione was detected. These yields are based on 10–16% conversion, as $CpRe(CO)_2(COCH_3)(Br)$ appears to be somewhat photosensitive.

**Photochemistry of $CpRe(CO)_2(CH_3)_2$ (9).** Similar results were obtained in photochemical experiments with $CpRe(CO)_2(CH_3)_2$[19] (**9**). When **9** was irradiated under 20 atm of CO in $CD_2Cl_2$ with a uranium filter, clean conversion to 2,3-butanedione (79%) and $CpRe(CO)_3$ (100%) with a small amount of acetone (5%) was observed by $^1H$ NMR (Scheme XIV). When $^{13}CO$ was employed and the reaction was taken to ca. 50% conversion with 355–385-nm light, the 2,3-butanedione product was found to be 98% $^{13}C_2$ and 2% $^{13}C_1$ (GC/MS). The starting material recovered from the reaction was analyzed by mass spectrometry and found to be 80% $^{13}C_0$ and 20% $^{13}C_1$ by a best fit calculation to the molecular ion region. The organometallic product $CpRe(CO)_3$, also analyzed by mass spectrometry, contained <1% $^{13}C_0$, 91% $^{13}C_1$, and 8% $^{13}C_2$. These results are summarized in Scheme XIV.

Trapping experiments similar to those performed with **3** were undertaken using **9**. Irradiation of **9** in $CCl_4$ under 20 atm of CO led to acetyl chloride (1.52 equiv based on 1 equiv of starting **9**), methyl chloride (19%), acetone (6%), and $CpRe(CO)_3$ (97%; Scheme XV).[20] Irradiation of **9** under 20 atm of CO in the presence of the more effective halogen atom donor $CBrCl_3$ gave only $CH_3Br$ (81–87%) and $CpRe(CO)_2(CH_3)Br$ (**7**; 78–85%). At high conversions, $CpRe(CO)_2Br_2$[21] was also observed along with greater yields of $CH_3Br$. $C_2Cl_6$ was detected by GC/MS in the products of this reaction.

**Discussion of Photolytic Reductive Elimination Mechanism.** Upon our initial observation of the formation of 2,3-butanedione in the photolysis of **3** under CO, we considered a simple mechanism involving CO insertion[22] followed by reductive elimination, the latter step being similar to that observed for the formation of the carbon–carbon bond in the thermolysis reaction. In this mechanism (Scheme XVI), formation of an electronically excited state (**3***) followed by insertion of CO into the metal–metal bond and trapping by L would yield diacyl complex (**A**). Reductive elimination of 2,3-butanedione from this species results in an unsaturated rhenium fragment (**B**), which is trapped by ligand to give the final organometallic product (C). Note that insertion of CO could also take place into the metal–acyl bond of **3***, followed by

---

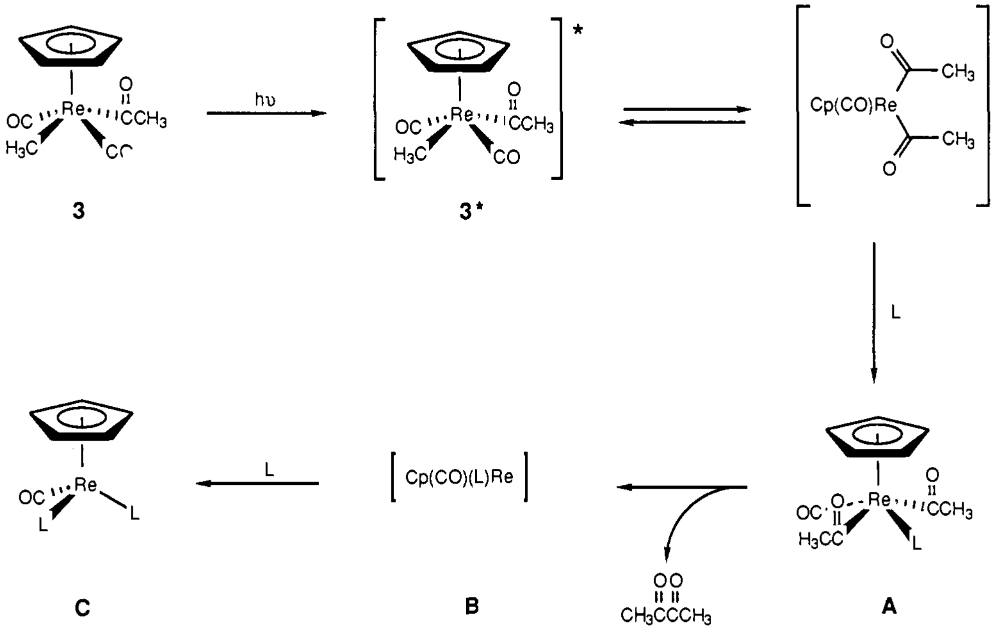
(19) Nesmeyanov, A. N.; Kolobova, N. E.; Makarov, Y. V.; Anisimov, K. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1974**, *44*, 2179.

(20) Less than 4% of another product was formed; we believe this to be $CpRe(CO)_2(CH_3)Cl$ on the basis of a comparison of its $^1H$ NMR spectrum ($\delta$ 5.29, 1.00) to those of the known Br and I analogues.[19]

(21) King, R. B.; Reimann, R. H. *Inorg. Chem.* **1976**, *15*, 179.

(22) For reviews of this very general reaction of metal alkyls, see: (a) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195. (b) Flood, T. C. In *Topics in Organic and Organometallic Stereochemistry*; Geoffroy, G. L., Ed.; Wiley: New York, 1981. (c) Alexander, J. J. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; Wiley: New York, 1985; Vol. 2, Chapter 5. For examples of reactions in which the primary photoproducts of metal methyl derivatives have been converted thermally to acetyl derivatives, see: (d) Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177. (e) Barnett, K. W.; Treichel, P. M. *Inorg. Chem.* **1967**, *6*, 294. (f) Alt, H. G.; Eichner, M. E. *J. Organomet. Chem.* **1981**, *212*, 397. (g) Reference 30a and references cited therein. For recent studies of double carbonylation reactions that do not proceed via radicals and references to related papers in this area, see: (h) Sen, A.; Chen, J.-T. *J. Am. Chem. Soc.* **1984**, *106*, 1506. (i) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Hoffmann, R.; Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4467.

Scheme XVI



reductive elimination from an α-ketoacetyl methyl complex. However, much less precedent exists for CO insertion into a metal–acyl bond.[23]

Early in our study, however, observations were made that raised significant doubts about this mechanism. For example, the pathway outlined in Scheme XVI attaches no special significance to the identity of the incoming ligand, implying that photolysis in the presence of any ligand L should result in the formation of 2,3-butanedione. However, photochemical reactions with $PMe_3$ and $PPh_3$ were unsuccessful. The mechanism in Scheme XVI also implies that when the reaction is carried out under $^{13}CO$, the 2,3-butanedione produced should contain no $^{13}C$ label and the $CpRe(CO)_3$ product should be doubly labeled. The results of our $^{13}CO$ experiment are not consistent with this mechanism: the $CpRe(CO)_3$ incorporated only one molecule of $^{13}CO$. Even more dramatically, as was summarized earlier in Scheme IX, the 2,3-butanedione product contained a total of only 1 mol of $^{13}CO$, and the labeled carbon was distributed so as to give an essentially statistical ratio of unlabeled and single- and double-labeled analogues of this compound.

A similar statistical distribution of diketone products was formed in the isotope crossover experiment (Scheme X) and upon irradiation of the propionyl methyl complex **6** (Scheme XI). While these results might be explained on the basis of some bimolecular mechanism, the observation of a similar statistical mixture upon irradiation of **3** in the presence of 3,4-hexanedione requires a different interpretation. Another possibility is that the reaction is intramolecular but that subsequent label scrambling occurs in the diketone products. This might occur by photochemical carbon–carbon bond breaking, leading to acyl radicals, which could recombine to form scrambled diketones. This was ruled out by the following observations: (a) 3,4-Hexanedione and 2,3-pentanedione are reported to undergo intramolecular rearrangement, rather than C–C cleavage, upon irradiation.[24] (b) In agreement with this, we observed no 2,3-pentanedione upon irradiation of 3,4-hexanedione and 2,3-butanedione under 20 atm of CO. (c) The statistical distribution of diketone products is observed even at very low conversions.

In contrast to the above mechanisms, the direct photochemical generation of acetyl radicals provides a plausible explanation for our results. It is known that acetyl radicals undergo rapid exchange of acyl groups with 1,2-diketones (eq 1).[25] Thus, the

$$R'C^{\bullet}(O) + RC(O)C(O)R \rightleftharpoons R'C(O)C(O)R + RC^{\bullet}(O) \qquad (1)$$

occurrence of acetyl radicals along the reaction path could account for the statistical distributions observed even at low conversion.

The presence of acetyl radicals was also supported by the high yields of acetyl chloride produced upon irradiation of **3** under CO in the presence of $CCl_4$. Evidence that acetyl radicals trapped by $CCl_4$ might be intermediates on the reaction path leading to 2,3-butanedione was derived from the dependence of the yields of 2,3-butanedione and acetyl chloride on the concentration of $CCl_4$, one increasing at the expense of the other. We propose that the trapping of acetyl radicals by $CCl_4$ to give acetyl chloride competes with the combination of acetyl radicals to yield 2,3-butanedione.

The high yields of 2,3-butanedione and acetyl chloride require that both the acetyl and methyl groups in **3** can serve as sources of acetyl radicals. This suggests that metal–methyl and metal–acetyl bond cleavages occur competitively and that the methyl radicals formed under the reaction conditions are trapped efficiently by CO to produce acetyl radicals (eq 2). Literature data

$$CH_3^{\bullet} + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3CO^{\bullet} \qquad (2)$$

on the kinetics and thermodynamics of the carbonylation of methyl radicals clearly support this conclusion. For the equilibrium shown in eq 2, the rate constant for the forward reaction $k_1$ is $3.4 \times 10^3$ $M^{-1}\ s^{-1}$ at 7 °C. The reverse rate constant $k_{-1}$ is 1.1 $s^{-1}$, giving an equilibrium constant $K_{eq} = 3.1 \times 10^3\ M^{-1}$ at 7 °C for this process.[26] Although no pressure-dependent solubility data have been reported for CO in $CH_2Cl_2$, from data collected in other solvents, the CO concentration present at 20 atm of CO pressure can be estimated to be on the order of $10^{-2}$–$10^{-1}$ M.[27] It therefore

---

[23] Sheridan, J. B.; Han, S.-H.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1987**, *109*, 8097, and references cited therein.

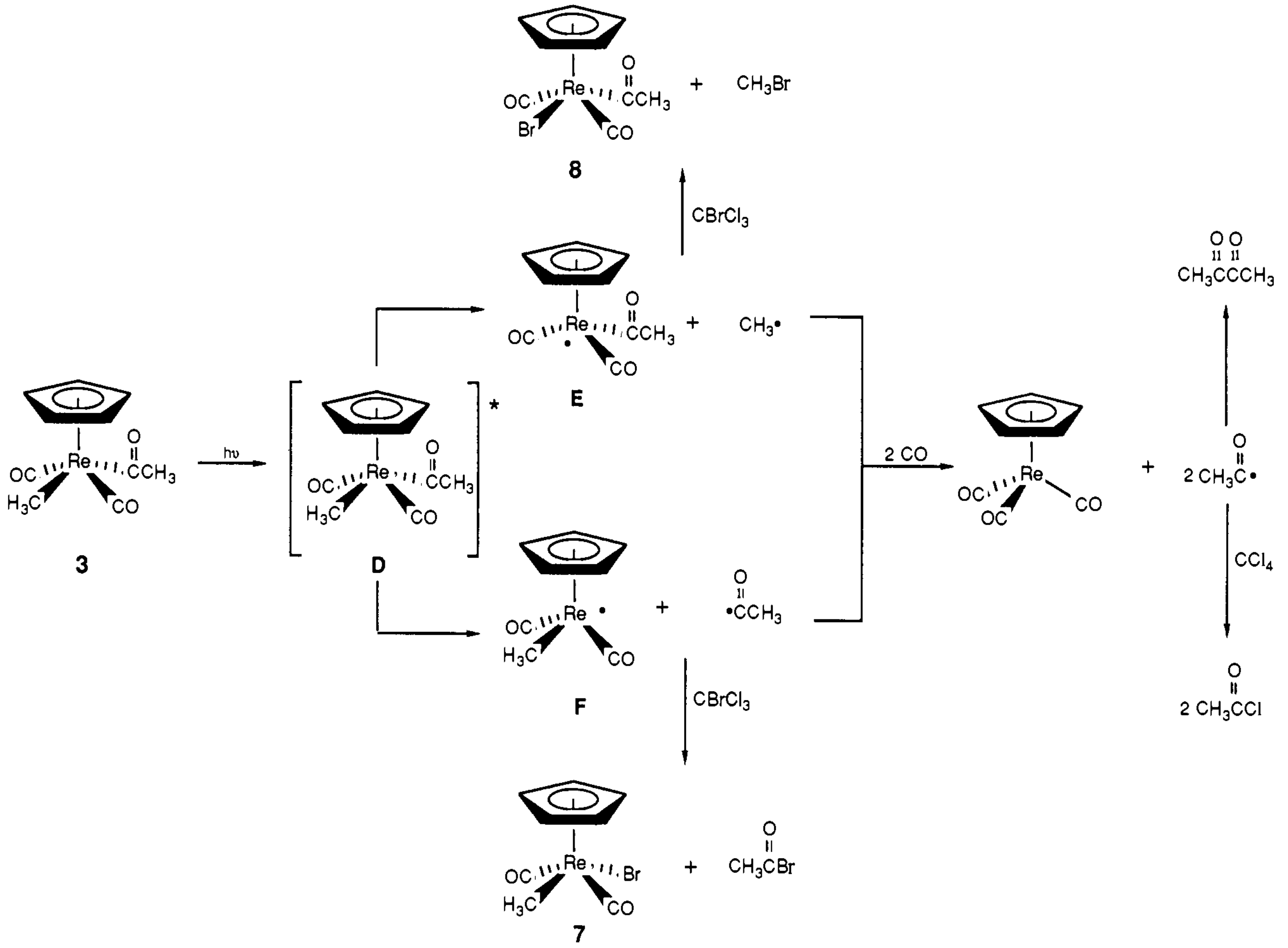
[24] Irradiation of long-chain aliphatic α-diketones results in production of cyclobutanols, presumably by an internal abstraction/cyclization reaction. In some cases, acyloin and pinacol products are observed as well. (a) Monroe, B. M. *Adv. Photochem.* **1971**, *8*, 77, and references therein. (b) Urry, W. H.; Trecker, D. J.; Winey, D. A. *Tetrahedron Lett.* **1962**, 609. (c) Urry, W. H.; Trecker, D. J. *J. Am. Chem. Soc.* **1962**, *84*, 118.

[25] (a) Kelder, J.; Cerfontain, F. W.; van der Wielen, F. W. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 712. (b) Acyl exchange has also been observed with vicinal triones. Urry, W. H.; Pai, M.-S. H.; Chen, C. Y. *J. Am. Chem. Soc.* **1964**, *86*, 5342.

[26] Watkins, K. W.; Word, W. W. *Int. J. Chem. Kinet.* **1974**, *6*, 855.

[27] See for example: (a) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1. (b) Tonner, S. P.; Wainwright, M. S.; Trinm, D. L.; Cant, N. W. *J. Chem. Eng. Data* **1983**, *28*, 59. (c) Velekis, E.; Hacker, D. S. *J. Chem. Eng. Data* **1984**, *29*, 36.

**Scheme XVII**



seems reasonable that, under 20 atm of CO, methyl radicals in solution would be converted to acetyl radicals with high efficiency.

Rate data can also be found for the reaction of $CCl_4$ with methyl radicals (eq 3, where X = Cl), allowing calculation of $k_2 = 8.2$ $M^{-1}\ s^{-1}$ at 7 °C.[28]

$$CH_3^\bullet + CXCl_3 \xrightarrow{k_2} CH_3X + {}^\bullet CCl_3 \qquad (3)$$

Thus, even at high concentrations of $CCl_4$, this reaction may not be completely competitive with the carbonylation reaction under 20 atm of CO. However, the reaction of methyl radicals with $CBrCl_3$ is much faster than that with $CCl_4$; $k_2(CBrCl_3)/k_2(CCl_4)$ for eq 3 is on the order of $10^4$ at 25 °C.[28] Consistent with these rate data, the irradiation of acetyl methyl complex **3** in the presence of $CBrCl_3$ resulted in trapping of acetyl and methyl radicals, and irradiation of the dimethyl complex **4** under the same conditions resulted in trapping of methyl radicals exclusively. Not only were the organic fragments trapped by $CBrCl_3$ but also the metal fragments reacted with this reagent.[29] This supports the hypothesis that the methyl and acetyl radicals are produced by direct homolytic cleavage of the metal–carbon bonds of the starting alkyl and acyl complexes upon irradiation.[30]

The mechanism that accounts most reasonably for all of our results is shown in Scheme XVII. Upon irradiation, the acetyl methyl complex **3** is promoted to an excited state (or states) (**D**). On the basis of the similar amounts of $CpRe(CO)_2(COCH_3)(Br)$ and $CpRe(CO)_2(CH_3)Br$ formed in the $CBrCl_3$ experiment, **D** undergoes relatively unselective cleavage of the Re–$CH_3$ and Re–$COCH_3$ bonds, leading to E and **F**. In the presence of $CBrCl_3$, these radicals are trapped by halogen atom transfer, leading to **7**, **8**, and organic halides. Without $CBrCl_3$ in solution, the $CpRe(CO)_2R^\bullet$ (R = $CH_3$, $COCH_3$) can go on to product $CpRe(CO)_3$ by either an associative (17e → 19e → 18e) or dissociative mechanism of substitution of $R^\bullet$ by CO.[31] The methyl radicals are carbonylated and 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.

---

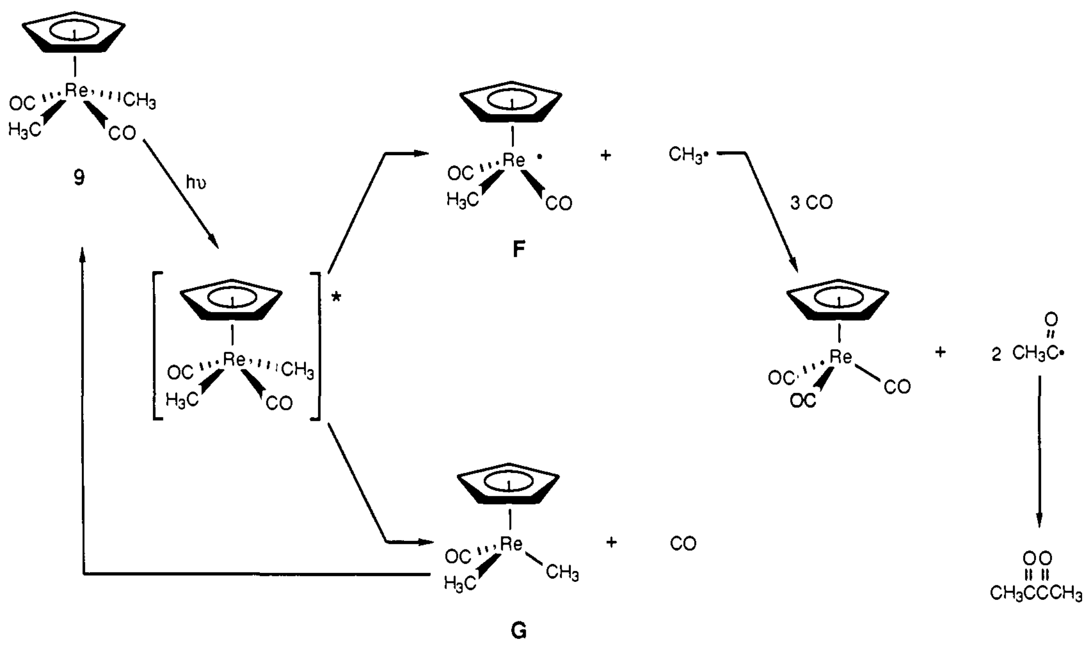
[28] Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511.

[29] $CCl_4$ has been used extensively to trap organometallic radicals, and bimolecular rate constants $k_T$ for halogen abstraction by organometallic radicals from $CX_4$, $CHX_3$, $CH_2X_2$, and $C_6H_5CH_2X$ (X = Cl or Br) have been estimated[29e] or more recently, directly measured.[29a–d] The order of increasing $k_T$ corresponds roughly to a decrease in the C–X bond dissociation energy,[29b] supporting our observation that $CBrCl_3$ 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.

[30] 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 29 and (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: San Francisco, CA, 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. (e) Pourreau, D. B.; Geoffroy, G. L. *Adv. Organomet. Chem.* **1986**, *24*, 249.

[31] Mechanistic studies of substitution reactions of 17e species have provided evidence for associative pathways. However, in these cases, 2e ligands were the leaving groups and the overall transformation was 17e → 19e → 17e. (a) Reference 1c. (b) Stiegman, A. E.; Tyler, D. R. *Comments Inorg. Chem.* **1986**, *5*, 215, and references therein. (c) Trogler, W. C. *Int. J. Chem. Kinet.* **1987**, *19*, 1025, and references therein. It would be of interest to uncover reactions in which organic radicals are displaced from stable paramagnetic metal complexes, so that the mechanisms of such processes might be examined directly.

Scheme XVIII



The consistent presence of 8–10% acetone in the products of the irradiation of **3** under 20 atm of CO and in all of the trapping experiments suggests that this product arises from an independent pathway. Perhaps a fraction of the excited state reacts by a direct reductive elimination mechanism.

The mechanism set out for the photochemical reactions of **3** is easily extrapolated to the case of the dimethyl complex **9** (Scheme XVIII). The trapping and labeling experiments are consistent with initial Re–methyl bond homolysis from the excited state, yielding **F** and a methyl radical. As explained above, **F** undergoes a substitution reaction of $CH_3$• by CO to give $CpRe(CO)_3$. The methyl radicals undergo carbonylation, and combination of the acetyl radicals yields 2,3-butanedione. It should be noted in that in the irradiation of **9** with $^{13}CO$ considerably more incorporation of labeled CO into the starting material was observed than for the acetyl methyl complex **3**. Thus, another primary pathway for the decomposition of the initial excited state is likely to be loss of CO, to give **G**. In the presence of high concentrations of CO, this pathway is expected to be reversible. Other examples of competitive ligand loss and metal–carbon bond homolysis have been reported previously.[32]

## Conclusions

By exploring analogies in alkylation reactivity of enolate anions and acylmetalate complexes, we have increased the availability of acylalkylrhenium complexes. It is hoped that the potential generality of our synthetic method will allow the synthesis of new stable acyl alkyl complexes in other transition-metal systems.

Our investigations have shown that the thermal and photochemical decompositions of the cyclopentadienylrhenium acyl alkyl complexes proceed by different pathways. Both of these processes, however, can lead to carbon–carbon bond formation. Thermally, simple intramolecular reductive elimination occurs, leading to the formation of ketones in high yield. In contrast, ultraviolet irradiation causes single metal–carbon bond cleavage at both the metal–alkyl and metal–acyl bonds, leading to methyl and acetyl radicals at comparable rates. In the presence of CO, the methyl radicals are carbonylated to give additional acyl radicals; combination of these radicals leads to the efficient formation of vicinal diketones. Our results show that $CBrCl_3$ is substantially more useful than $CCl_4$ as a reagent for trapping both organic and organometallic radical intermediates. In addition, it seems likely that some other organometallic "double carbonylation" reactions[33] may take place by nonchain radical mechanisms similar to the one elucidated in this work.

## Experimental Section

**General Procedures.** Unless otherwise noted, all manipulations were carried out under an inert atmosphere in a Vacuum Atmospheres 553-2 drybox with attached M6-40-1H Dritrain or by using standard Schlenk or vacuum-line techniques.

$^1H$ NMR spectra were obtained on either the 250-, 300-, 400-, or 500-MHz Fourier Transform spectrometers at the University of California at Berkeley NMR facility. The 250- and 300-MHz instruments were constructed by Rudi Nunlist and interfaced with either a Nicolet 1180 or 1280 computer. The 400- and 500-MHz instruments were commercial Bruker AM Series spectrometers. $^1H$ NMR spectra were recorded relative to residual protiated solvent. $^{13}C$ NMR spectra were obtained at either 75.4, 100.6, or 125.7 MHz on the 300-, 400-, or 500-MHz instruments, respectively, and chemical shifts were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane, and all coupling constants are reported in hertz.

IR spectra were obtained on a Perkin-Elmer Model 283 infrared spectrometer or on a Perkin-Elmer Model 1550 or 1750 FT-IR spectrometer using potassium bromide solution cells (0.1- or 0.025-mm path length) or potassium bromide ground pellets. UV/vis spectra were recorded on a Hewlett-Packard Model 8450A spectrometer. Mass spectroscopic (MS) analyses were obtained at the University of California at Berkeley mass spectrometry facility on AEI MS-12 and Finnigan 4000 mass spectrometers. GC/MS results were obtained either with a gas chromatograph in series with the Finnigan 4000 or with a Hewlett-Packard 5890A gas chromatograph in series with a Hewlett-Packard 5970 mass selective detector using a 30-m column (0.25 mm i.d., 0.25-m film thickness; DB1701 from J&W Scientific). Elemental analyses were obtained from the University of California at Berkeley Microanalytical Laboratory. Melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected.

Best fit mass spectra of the molecular ion regions were calculated by a matrix least-squares analysis[34] using computer-generated or hand-calculated individual spectra of the differently labeled complexes. A

---

(32) In the irradiation of $(CO)_5MnCH_3$, evidence was reported for both CO dissociation and metal–alkyl bond homolysis pathways. See reviews cited in ref 30.

(33) (a) Booth, G.; Chatt, J. *J. Chem. Soc. A* **1966**, 634. (b) Bauld, N. L. *Tetrahedron Lett.* **1963**, *27*, 1841. (c) Ryand, M.; Kwang-Myeong, S.; Sawa, Y.; Tsutsumi, S. *J. Organomet. Chem.* **1966**, *5*, 305. (d) Yamamoto, T.; Kohara, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2161. (e) Ozawa, F.; Yamamoto, A. *Chem. Lett.* **1981**, 289. (f) Nudelman, N. S.; Outumuro, P. *J. Org. Chem.* **1982**, *47*, 4347. (g) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic Press: New York, 1974; Vol. 1, p 166. (h) Reference 1d.

(34) Hamilton, W. C. *Statistics in Physical Science*; Ronald Press: New York, 1964.

small amount of $^{13}C^{18}O$ was found in the $^{13}CO$ purchased from Cambridge Isotopes; incorporation of this isotopic combination was also accounted for in the $^{13}CO$ labeling experiments.

Kinetic experiments were run in flame-sealed NMR tubes, and the samples were heated in a Neslab Model EX-250 HT high-temperature oil bath. Photolyses were performed in an apparatus consisting of a 450-W Conrad–Hanovia mercury immersion lamp with an Ace 7830-60 power supply and an Ace 7874B-38 immersion well. The immersion well was secured in a stainless steel beaker filled with water cooled to 5–10 °C by a Lauda K-4/RD refrigerated bath circulator. Photolysis experiments were performed with either Pyrex, uranium glass, or a combination of Corning CS 0-52 and Corning CS 7-60 filters (355–385 nm).

Sealed NMR tubes were prepared by fusing Wilmad 505-PP and 504-PP tubes to ground-glass joints, which were then attached to a vacuum line with Kontes stopcocks or, alternatively, the tubes were attached via cajon adapters directly to Kontes vacuum stopcocks.[35] High-pressure valve NMR tubes refer to Wilmad Cat. No. 522-PV. Known-volume bulb vacuum transfers were accomplished with an MKS Baratron attached to a high-vacuum line.

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. $PPh_3$ (Aldrich) was recrystallized from $CH_2Cl_2/Et_2O$, and $PMe_3$ (Strem) was dried over NaK or a Na mirror and vacuum transferred prior to use. Ferrocene (Aldrich) was sublimed prior to use. $CH_3Li$ (Fluka, approx. 1.6 M in $Et_2O$) was stored at −30 °C and titrated prior to use. $CD_3Li$ was prepared by the reaction of Li wire with $CD_3I$ in $Et_2O$ under an Ar atmosphere. EtLi was isolated as a solid from a benzene solution (Organometallics) by lyophilization of solvent. KH was isolated by filtration from a mineral oil solution (Aldrich) and washed with hexanes. $CpRe(CO)_3$ was synthesized from $Re_2(CO)_{10}$ according to published procedure.[36] $CpRe(CO)_2(COCH_3)Li$ (**1**), prepared by the method of Fischer et al.,[8] was isolated by collection of the yellow precipitate from the reaction on a fine frit and was stored at −30 °C (yields 85–90%). Although **1** was dried under high vacuum ($10^{-4}$ atm), small variable amounts of $Et_2O$ always remained behind. $CpRe(CO)_2H_2$ was prepared by the method of Yang and Bergman.[17]

Pentane and hexane (UV grade, alkene free) were distilled from $LiAlH_4$ under nitrogen. Benzene, toluene, mesitylene, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was either distilled under $N_2$ or vacuum transferred from $CaH_2$. Carbon tetrachloride and bromotrichloromethane were dried with $P_2O_5$ and stored over 4-Å sieves. Methyl and ethyl iodide were dried and stored under 4-Å sieves with Cu and protected from light. 3,4-Hexanedione was vacuum transferred from $CaCl_2$. Acetone-$d_6$ was dried over 4-Å sieves and other deuteriated solvents for use in NMR experiments were dried as their protiated analogues but were vacuum transferred from the drying agent.

**Reaction of 1 with $(CH_3)_3OPF_6$ in $H_2O$.** The procedure used was modified from a reported procedure for the reaction of $Cr(CO)_6$ with $CH_3Li$ followed by treatment with $(CH_3)_3OBF_4$.[37] The rhenium starting material was $CpRe(CO)_3$, and the acylmetalate **1** was generated and carried through to the alkylation reaction with $(CH_3)_3OPF_6$. A Schlenk tube was charged with $CpRe(CO)_3$ (0.500 g, 1.49 mmol) and $Et_2O$ (10 mL). To this stirring solution was added 0.86 mL of a 1.74 M $CH_3Li/Et_2O$ solution (1.49 mmol) dropwise. The reaction turned yellow during the addition; stirring for 1.5 h resulted in formation of a fine yellow precipitate. The $Et_2O$ was removed under vacuum, and oxygen-free $H_2O$ (3.5 mL, four vacuum–$N_2$ flushes) was added to the residue. The solid did not completely dissolve, as it turned from yellow to orange. Trimethyloxonium hexafluorophosphate was added in small portions to the stirring nonhomogeneous solution until the reaction mixture tested acidic (pH = 4–5; amount added 0.461 mg, 2.24 mmol). A 10% benzene/hexane solution (150 mL) was added in 50-mL portions to extract the products, and this solution was filtered through a bed of flame-dried $Na_2SO_4$ on a medium frit. The filtrate was concentrated under vacuum. A $^1H$ NMR of the residue was recorded in $C_6D_6$; resonances due to **2** and **3** integrated in a 1:2.8 ratio. Several other unidentified Cp-containing products were noted along with some remaining starting material, $CpRe(CO)_3$. Various purification techniques were attempted with small portions of this product mixture, and it was found that chromatography (silica, 5% benzene/hexane) was effective in separation of the products. Quantities of **2** and **3** sufficient for spectral analysis were thus obtained. For **2**: $^1H$ NMR ($C_6D_6$) $\delta$ 4.80 (s, 5 H), 4.05 (s, 3 H), 1.98 (s, 3 H); (THF-$d_8$) $\delta$ 5.57 (s, 5 H), 4.14 (s, 3 H), 2.34 (s, 3 H); (acetone-$d_6$) $\delta$ 5.64 (s, 5 H), 4.14 (s, 3 H), 2.36 (s, 3 H). $^{13}C$ NMR (gated, $C_6D_6$) $\delta$ 289.5 (s), 204.3 (s), 88.7 (d, $J = 178$), 64.8 (q, $J = 145$), 49.5 (q, $J = 127$). IR (hexane) 1960, 1890, 1220 $cm^{-1}$. Literature values:[8] $^1H$ NMR ($C_6D_6$) $\delta$ 4.91, 4.16, 2.06. IR (Nujol) 1972, 1894, 1204 $cm^{-1}$. For **3**: vide infra.

**Reaction of 1 with Alkylating Agents.** In a typical experiment, a medium-walled NMR tube was charged with **1** (6.8 mg, $1.9 \times 10^{-2}$ mmol) and $(CH_3)_3OPF_6$ (4.1 mg, $2.0 \times 10^{-2}$). Acetone-$d_6$ was vacuum transferred into the tube, and the tube was sealed under vacuum. The sample was thawed at −78 °C for 0.5 h and then warmed to −40 °C for 0.5 h. The reaction appeared homogeneous at −40 °C. A $^1H$ NMR spectrum was recorded at 22 °C with the ratio of **2**/**3** integrating to 78:22. The reaction was repeated three times with both different batches of **1** and $(CH_3)_3OBF_4$ instead of the $PF_6$ salt. No significant variation in the ratio was observed (79:21, 76:24, 78:22). Reactions of **1** with other alkylating agents (MeI, MeOTs, EtI, $Et_3OPF_6$) in THF-$d_8$ and acetone-$d_6$ were performed and analyzed similarly (see text for alkylation product ratios). Exceptions: (1) The alkylating agents MeI and EtI were added by vacuum transfer to frozen solutions of **1**. (2) Excess amounts of MeI, EtI, and MeOTs and/or elevated temperatures (45 °C) were employed to increase rates of reaction. All experiments were checked for reproducibility.

**Preparative-Scale Synthesis of $CpRe(CO)_2(COCH_3)(CH_3)$ (3).** A 100-mL flask fitted with a stir bar and a vacuum stopcock was charged with **1** (409 mg, 1.14 mmol). THF (30 mL) and $CH_3I$ (1 mL) were vacuum transferred into the flask (−196 °C). The reaction was thawed and allowed to stir for 2 days at room temperature, protected from light. The solvent and excess $CH_3I$ were removed under vacuum. The residue was triturated with pentane and filtered in air. The pentane was removed by rotary evaporation, and chromatography [Alumina III, benzene/hexane (1:4)] yielded a nearly colorless fraction. The solvent was removed under vacuum, and recrystallization of the residue by slow cooling of a hexane/toluene solution to −60 °C yielded 263 mg of **3** as cream-colored needlelike crystals. Removal of the solvent from the mother liquor under vacuum and recrystallization of the residue as above yielded a second crop of 18 mg (67%, total yield): $^1H$ NMR ($C_6D_6$) $\delta$ 4.39 (s, 5 H), 2.68 (s, 3 H), 0.67 (s, 3 H); (THF-$d_8$) $\delta$ 5.32 (s, 5 H), 2.52 (s, 3 H), 0.78 (s, 3 H); (acetone-$d_6$) $\delta$ 5.40 (s, 5 H), 2.51 (s, 3 H), 0.78 (s, 3 H); $^{13}C$ NMR (gated, $C_6D_6$) $\delta$ 221.8 (s), 200.0 (s), 93.7 (d, $J = 182$), 55.2 (q, $J = 127$), −36.4 (q, $J = 136$). IR ($C_6D_6$) 2004 (m), 1932 (s), 1630 (m) $cm^{-1}$. MS (70 eV) 364/366 ($M^+$, $^{185}Re/^{187}Re$). MP 93–94 °C. Anal. Calcd for $C_{10}H_{11}O_3Re$: C, 32.84; H, 3.03. Found: C, 32.74; H, 3.01.

**Crystal and Molecular Structure Determination of 3.** Long golden needlelike crystals of the compound were obtained by slow cooling to −30 °C from hexane/toluene. Fragments cleaved from some of these crystals were mounted on glass fibers with poly(cyanoacrylate) cement. The X-ray structure determination was carried out by Dr. F. J. Hollander of the University of California at Berkeley X-ray Diffraction Facility (CHEXRAY). Preliminary precession photographs indicated orthorhombic Laue symmetry and yielded preliminary cell dimensions.

The crystal used for data collection was then transferred to our Enraf-Nonius CAD-4 diffractometer[38] and centered in the beam. Automatic peak search and indexing procedures yielded the orthorhombic reduced primitive cell. Systematic absences were consistent only with the space group *Pbcn*. The structure analysis was carried out with data reduction formulae identical with those described in detail in an earlier study.[38] The final cell parameters and specific data collection parameters are listed in Table III.

The 1641 raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards showed a monotonic isotropic decrease to 95% of the original intensity. The data were corrected for this decay. Inspection of the azimuthal scan data showed a variation $I_{min}/I_{max} = 0.59$ for the average curve and good agreement between curves. An empirical correction for the absorption, based on the azimuthal scan data, was applied to the intensities because the crystal had decayed completely between data collection and the attempt to measure it for analytical correction. Removal of systematically absent data left 1392 unique data.

---

(35) Bergman, R. G.; Buchanan, J. M.; McGhee, W. D.; Periana, R. A.; Seidler, P. F.; Trost, M. K.; Wenzel, T. T. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; p 227.

(36) Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1958**, 4314.

(37) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954.

(38) For a description of the X-ray diffraction and analysis protocols used, see: (a) Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834. (b) Roof, R. B., Jr. *A Theoretical Extension of the Reduced-Cell Concept in Crystallography*; Publication LA-4038, Los Alamos Scientific Laboratory: Los Alamos, NM 1969. (c) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

**Table III.** Crystal and Data Collection Parameters for **3**

Empirical formula: $C_{10}H_{11}O_3Re$

(A) Crystal Parameters at 25 °C[a,b]

$a$ = 20.7239 (26) Å
$b$ = 12.3440 (14) Å
$c$ = 8.3708 (7) Å
$V$ = 2141.4 (7) Å$^3$
$\mu$(calc) = 114.8 cm$^{-1}$
size of cryst = 0.14 × 0.19 × 0.43 mm
space gp *Pbcn*
formula wt = 365.40 amu
$Z$ = 8
$d$(calc) = 2.27 g cm$^{-1}$

(B) Data Measurement Parameters

radiatn Mo K$\alpha$ ($\lambda$ = 0.710 73 Å)
monochromator: highly oriented graphite ($2\theta$ = 12.2°)
Detector: crystal scintillation counter, with PHA
reflctns measd: $+h,+k,+l$
$2\theta$ range: 3°–45°
scan type: $\theta$–$2\theta$
scan width: $\Delta\theta = 0.5 + 0.347 \tan\theta$
scan speed: 0.6–6.7 ($\theta$, °/min)
bckgd: measd over 0.25 ($\Delta\theta$) added to each end of the scan
aperture to cryst = 173 mm; vertical aperture = 3.0 mm
horizontal aperture = 2.0 + 1.0 tan $\theta$ mm (variable)
no. of reflctns collcd: 1641
no. of unique reflctns: 1392
intensity standards: (635), (482), (14, 3, 1): measd every 1 h of X-ray exposure time; over the data collcn period, 5% decrease in intens obsd
orientn: 3 reflctns checked after every 250 measmnts; cryst orientn redetermined if any reflctns offset from their predicted positions by more that 0.1°; reorientn not necessary during data collcn

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo K$\alpha$ components of 24 reflections with $2\theta$ near 30°. [b] In this and all tables of X-ray structure data, the esd's of all parameters are given in parentheses, right-justified to the least significant digit(s) given.

The structure was solved by Patterson methods and refined via standard least-squares and Fourier techniques. In a difference Fourier map calculated following refinement of all non-hydrogen atoms with anisotropic thermal parameters, peaks corresponding to the exact positions of most of the hydrogen atoms were found. Hydrogens were included in the structure factor calculations in their expected positions based on idealized bonding geometry but were not refined in least squares. The hydrogens on the methyl group C10 were clearly disordered and were calculated on the basis of 50–50 disorder. All hydrogens were assigned isotropic thermal parameters 1–2 Å$^2$ larger than the equivalent $B_{iso}$ of the atom to which they were bonded. Inspection of the low-angle high-intensity data showed that they were strongly affected by secondary extinction. A secondary extinction parameter was refined in the final cycles of least squares and converged to a value of 9.1 (2) × 10$^{-8}$, corresponding to a correction of 20% to the largest structure factor.

The final residuals for 128 variables refined against the 1111 data for which $F^2 > 3\sigma F^2$ were $R$ = 1.65%, w$R$ = 2.06%, and GOF = 1.39. The $R$ value for all 1392 data points was 2.86%. Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed very low intensity and relatively high residuals for the two parity groups eeo and eoe but otherwise no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.72 e/Å$^3$, and all the top peaks were near the rhenium atom. The positional parameters of the refined atoms, a corresponding listing of thermal parameters, and a listing of $F_o$ and $F_c$ are given in the supplementary material to the preliminary communication describing part of this work.[7]

**Preparation of $CpRe(CO)_2(C(OEt)(Me))$ (4).** To a yellow-golden solution of **1** (154 mg, 4.3 × 10$^{-1}$ mmol) in 10 mL of THF was added $Et_3OPF_6$ (110 mg, 4.4 × 10$^{-1}$ mmol), resulting in an almost immediate color change to orange. The reaction was allowed to stir under $N_2$ for 4 h at which time solvent was removed under vacuum. Hexane-soluble products were separated by addition of 25 mL of the solvent and filtration through glass wool. A very bright yellow solution resulted. Solvent was removed by vacuum transfer, and the residue was recrystallized from hexane (−40 °C) to yield 64.2 mg of **4** (39% yield). A second crop of 23.4 mg (53%, total yield) was obtained by concentration of the mother liquor and cooling to −40 °C: $^1$H NMR ($C_6D_6$) $\delta$ 4.84 (s, 5 H), 4.58 (q, 2 H, $J$ = 7.1), 2.03 (s, 3 H), 1.18 (t, 3 H, $J$ = 7.1); (THF-$d_8$) $\delta$ 5.55 (s, 5 H), 4.47 (q, 2 H, $J$ = 7.1), 2.34 (s, 3 H), 1.44 (t, 3 H, $J$ = 7.1); (acetone-$d_6$) $\delta$ 5.62 (s, 5 H), 4.45 (q, 2 H, $J$ = 7.0), 2.37 (s, 3 H), 1.45 (t, 3 H, $J$ = 7.0). $^{13}$C NMR ($C_6D_6$) $\delta$ 287.7, 204.4, 190.0, 86.6, 74.2, 49.8, 14.5. IR (hexane) 1960 (s), 1887 (s), 1212 (m) cm$^{-1}$. HRMS (Et) 378.0402, 380.0425. Calcd for $C_{11}H_{13}O_3{}^{185}Re$ and $C_{11}H_{13}O_3{}^{187}Re$: 378.0394, 380.0423.

**Thermolysis of 3 without Added Ligand.** An NMR tube was charged with 0.54 mL of a $C_6D_6$ solution of **3** (2.2 × 10$^{-2}$ M) and $Cp_2Fe$ (1.0 × 10$^{-2}$ M, internal standard). The solution was degassed via three freeze–pump–thaw cycles, and the tube was sealed under vacuum. The tube was heated at 100 °C for 8.5 h and monitored at intervals by $^1$H NMR spectrometry. Integration against the ferrocene resonance showed that acetone ($\delta$ 1.54) was formed in 63% yield and that the major organometallic product was $CpRe(CO)_3$ ($\delta$ 4.32; 71%). These products were identified by comparison of their $^1$H NMR spectra with authentic samples.

**Thermolysis of 3 with Excess $PPh_3$.** An NMR tube was charged with **3** (5.3 mg, 1.4 × 10$^{-2}$ mmol) and $PPh_3$ (42.0 mg, 0.16 mmol). $C_6D_6$ (0.53 mL) was vacuum transferred into the tube, and dioxane (6.7 × 10$^{-3}$ mmol, internal standard) was added by known-volume bulb vacuum transfer. The tube was sealed under vacuum. After an initial $^1$H NMR spectrum was recorded, the tube was heated at 100 °C for 10.25 h. Integration against the dioxane standard revealed that $CpRe(CO)_2(PPh_3)$ [$\delta$ 7.56 (m), 4.53 (s)][39] was formed in 100% yield and acetone ($\delta$ 1.54) in 97% yield. These products were identified by their $^1$H NMR spectra. Literature values[17] for $CpRe(CO)_2(PPh_3)$: $^1$H NMR ($C_6D_6$) $\delta$ 7.56 (m, 6 H), 7.07 (m, 9 H), 4.53 (s, 5 H).

**Kinetics of Thermolysis of 3.** A standard solution of **3** (8.26 × 10$^{-2}$ M) and ferrocene (4.08 × 10$^{-2}$ M, internal standard) was made up in hexane. An appropriate volume of this solution was syringed into an NMR tube sealed to a ground-glass joint, and the hexane was removed under vacuum. Triphenylphosphine was weighed into the tube, and $C_6D_6$ was vacuum transferred into the tube, which was then sealed under vacuum. A kinetic experiment was performed by immersing the tube in a oil bath at 100.0 ± 0.5 °C. At given intervals, the tube was taken out of the bath and immediately placed in a dry ice/acetone slush. A $^1$H NMR spectrum was recorded at room temperature, and the NMR tube was then returned to the bath. The cyclopentadienyl resonance intensity of **3** was integrated against the internal standard signal. At least 12 data points over greater than 3 half-lives were obtained in this manner. The kinetic results are summarized in Table II.

**Preparation of 3-$d_6$.** This material was prepared analogously to **3**-$d_0$ (yield 37%): $^1$H NMR ($C_6D_6$) $\delta$ 4.41. $^2$H NMR ($C_6H_6$) $\delta$ 2.59, 0.06. MS (EI) 370/372 (M$^+$, $^{185}$Re/$^{187}$Re).

**Thermal Crossover Experiment.** In 0.74 mL of toluene-$d_8$ was dissolved **3**-$d_0$ (4.0 mg, 1.1 × 10$^{-2}$ mmol) and **3**-$d_6$ (4.1 mg, 1.1 × 10$^{-2}$ mmol). An aliquot was removed, and after vacuum evaporation of the solvent the residue was submitted for mass spectral analysis. The molecular ion region for **3** was found to be consistent with **3**-$d_0$ (48%), **3**-$d_5$ (3%), and **3**-$d_6$ (49%) by a best fit calculation. The remaining solution was pipetted into an NMR tube containing $PPh_3$ (55 mg, 2.1 × 10$^{-1}$ mmol). The solution was degassed via four freeze–pump–thaw cycles, and the tube was sealed under vacuum. The reaction was heated for 3.25 h (50% conversion) at 100 °C after which the tube was attached to a

---

(39) The additional resonance at $\delta$ 7.07 is obscured by the free $PPh_3$ resonances.

vacuum line and cracked open.[35] The volatile materials were removed by vacuum transfer and were analyzed by GC/MS. The results of a best fit calculation of the data in the molecular ion region of acetone are 50% $d_0$, 4% $d_5$, and 45% $d_6$.

**Irradiation of 3 under 20 atm of CO.** A medium-walled NMR tube was charged with **3** (4.8 mg, $1.3 \times 10^{-2}$ mmol). $CD_2Cl_2$ (0.38 mL) was vacuum transferred into the NMR tube. Dioxane ($4.9 \times 10^{-3}$ mmol) was added by vacuum transfer via a known-volume bulb. The CO was added by pressurizing a 508.51-mL known-volume bulb with 525 Torr and then opening it to the NMR tube. The tube was sealed 2 cm above the liquid nitrogen level. The vapor pressure of CO at −196 °C is 469 Torr,[40] and knowing the total volume of the apparatus between the known-volume bulb and the point of the tube seal allowed calculation of the amount of CO added to the tube as 1.25 mmol. At room temperature, assuming no solubility of CO, this amount would correspond to approximately 20 atm of CO in the area of tube above the solution. (*Note: The tube was thawed cautiously and slowly to room temperature, with the experimenter protected by a safety shield. Light bouncing of the tube in a stainless steel beaker tested for stress in the glass and seal. In one instance even after testing, a tube prepared in this manner exploded in the NMR probe. Extreme caution is advised.*) After an initial spectrum was recorded to determine the relative intensities of the resonances of **3** versus the dioxane signal, the tube was irradiated with 355–385-nm light for a total of 22 min. This amount of time corresponded to 100% conversion as monitored by $^1H$ NMR spectrometry. The yields of products calculated by integration against the internal standard ($Cp_2Fe$) were the following: $CH_3COCOCH_3$ ($\delta$ 2.29), 78%; $CH_3COCH_3$ ($\delta$ 2.12), 6%; $CpRe(CO)_3$ ($\delta$ 5.40), 102%, they remained constant within experimental error throughout the irradiation when corrected for percent conversion. The products were identified by comparison of the $^1H$ NMR spectra to those of authentic samples. The identity of the organic products was confirmed in a separate experiment by GC retention times.

**Irradiation of 3 in the Presence of $PMe_3$ and $PPh_3$.** An NMR tube was charged with **3** (4.0 mg, $1.1 \times 10^{-2}$ mmol) and $Cp_2Fe$ (1.2 mg, $6.4 \times 10^{-3}$ mmol, internal standard). For L = $PPh_3$, L (28 mg, 0.11 mmol) was added directly to the tube. $C_6D_6$ (0.53 mL) was vacuum transferred into the tube. For L = $PMe_3$, L ($8.8 \times 10^{-2}$ mmol) was added by vacuum transfer from a known-volume bulb. The irradiation of the samples (Pyrex filter) was monitored by $^1H$ NMR spectrometry, and yields were calculated by integration against the internal standard resonance. For L = $PMe_3$, after 97% conversion, the products $CpRe(CO)_2PMe_3$ [$\delta$ 4.56 (d, 5 H, $J$ = 0.5), 1.20 (d, 9 H, $J$ = 9.5); 78%] and acetone ($\delta$ 1.54; 9%) were noted along with several unidentified signals barely visible above the base line. Literature values[41] for $CpRe(CO)_2PMe_3$: $^1H$ NMR ($C_6D_6$) $\delta$ 4.56 (d, 5 H, $J$ = 0.6), 1.20 (d, 9 H, $J$ = 9.4). For L = $PPh_3$ after 88% conversion, $CpRe(CO)_2PPh_3$ (Cp resonance at $\delta$ 4.53; 55%) and another Cp-containing product ($\delta$ 4.25; 14%) were observed along with a number of very small signals from $\delta$ 0 to 3.3.

**Irradiation of 3 in the Presence of $^{13}CO$.** A high-pressure valve, heavy-walled NMR tube was charged with **3** (8 mg, $2.2 \times 10^{-2}$ mmol). Mesitylene (0.07 mL) was added to dissolve **3**, and then pentane was added to a total volume of 0.29 mL (the pentane/mesitylene mixture was chosen for favorable GC/MS conditions and solubility reasons). Degassing was accomplished via three freeze–pump–thaw cycles. The tube was pressurized with ca. 25 atm of $^{13}CO$ in the following manner: A stainless steel vessel with valves at both ends, having a known 3.0-mL volume, was attached directly to a low dead-volume regulator on a $^{13}CO$ lecture bottle. Small inside diameter stainless steel tubing was used to attach the known-volume vessel to the valve NMR tube while flushing the apparatus with a low flow of $^{13}CO$. The known-volume vessel was then pressurized with 75 psi of $^{13}CO$ and opened to the NMR tube, with the latter cooled to −196 °C. As in the unlabeled CO experiment, knowledge of the pressures and volumes involved allowed calculation of the amount of $^{13}CO$ added. The tube was irradiated for 7 min with a filter admitting 355–385-nm light. The tube was then degassed via three freeze–pump–thaw cycles, and then the more volatile materials (excluding most of the mesitylene) were transferred under vacuum to another tube and sealed under vacuum. GC/MS analysis of the 2,3-butanedione produced in the reaction led to a best fit calculation of $^{13}C_0$ (23%), $^{13}C_1$ (50%), and $^{13}C_2$ (28%). The mesitylene was removed from the remaining nonvolatile material under high vacuum, and the residue was chromatographed (Alumina III, hexane/benzene). The first fraction contained the product $CpRe(CO)_3$, which was analyzed directly by mass spectrometry. The best fit calculation to the data was $^{13}C_0$ (6%), $^{13}C_1$ (92%), and $^{13}C_2$ (2%). The second fraction containing unreacted **3** was also stripped and analyzed directly by mass spectrometry to yield a best fit calculation to the data of $^{13}C_0$ (98%) and $^{13}C_1$ (2%).

**Irradiation of 3 under 20 atm of CO, Crossover Experiment.** A high-pressure valve NMR tube was loaded with **3**-$d_0$ (3.0 mg, $8.2 \times 10^{-3}$ mmol) and **3**-$d_6$ (3.0 mg, $8.2 \times 10^{-3}$ mmol). Mesitylene (0.13 mL) and pentane (0.11 mL) were added by vacuum transfer (as above, this mixed solvent system was chosen for solubility and favorable GC/MS conditions). An aliquot of this solution was removed under $N_2$; the solvent was evaporated under vacuum and the residue analyzed by mass spectrometry. A best fit calculation to the molecular ion region of the spectrum indicated that the ratio of **3**-$d_0$/**3**-$d_5$/**3**-$d_6$ in the initial mixture was 52:2:46.

The remaining solution was degassed via five freeze–pump–thaw cycles, and then the tube was connected directly to a CO cylinder regulator and pressurized to 300 psi (20 atm). The tube was then irradiated for 10 min at 6–8 °C through a uranium glass filter. The CO was removed by six freeze–pump–thaw cycles. The volatile materials were transferred under vacuum and analyzed by GC/MS at 17-eV ionizing voltage. A best fit calculation to the molecular ion region indicated a $d_0/d_2/d_3/d_6$ ratio of 28:1:54:16. The nonvolatile material was analyzed directly by mass spectrometry, and the ratio of $d_0/d_5/d_6$ was found to be 49:3:49 by a best fit calculation to the molecular ion region of **3**.

**$CpRe(CO)_2(COEt)(CH_3)$ (6).** $CpRe(CO)_3$ (500 mg, 1.49 mmol) was dissolved in 5 mL of $Et_2O$. EtLi (82 mg, 2.28 mmol) was added as a solution in 3 mL of $Et_2O$. The reaction was allowed to stir for 45 min, and then the yellow precipitate that had formed was filtered off and washed with cold $Et_2O$ (−30 °C). In this way, $CpRe(CO)_2(COEt)Li$ (260 mg, 47% yield) was isolated, dried under high vacuum, and stored at −30 °C: $^1H$ NMR (THF-$d_8$) $\delta$ 5.02 (s, 5 H), 2.56 (q, 2 H, $J$ = 7.5), 0.80 (t, 3 H, $J$ = 7.5). A 50-mL round-bottomed flask was fitted with a vacuum stopcock charged with $CpRe(CO)_2(COEt)Li$ (166 mg, 0.447 mmol) and THF (10 mL) and a stir bar. The solution was degassed via three freeze–pump–thaw cycles, and $CH_3I$ (0.4 mL) was added by vacuum transfer from a graduated vessel. The resulting mixture was stirred and protected from light for 12 h, and then the solvent and excess $CH_3I$ were removed under vacuum. In air, the residue was taken up in 50 mL of benzene and filtered. After removing the solvent by rotary evaporation, the residue was chromatographed on Alumina III (4:1 hexane/benzene). After a small initial yellow fraction, a colorless fraction was collected and the solvent removed. The residue was recrystallized by slow cooling from hexane/toluene to −60 °C, yielding 85 mg of **6** as off-white needlelike crystals (50% yield): $^1H$ NMR ($C_6D_6$) $\delta$ 4.43 (s, 5 H), 2.94 (q, 2 H, $J$ = 7.2), 1.04 (t, 3 H, $J$ = 7.2), 0.69 (s, 3 H). $^{13}C$ NMR ($C_6D_6$ $\delta$ 224.5, 200.3, 93.5, 62.0, 10.4, −36.3. IR ($C_6D_6$) 2001 (m), 1929 (s), 1634 (m). Anal. Calcd for $C_{11}H_{13}O_3Re$: C, 34.82; H, 3.45. Found: C, 34.94; H, 3.43.

**Irradiation of 6 under CO.** A medium-walled NMR tube was charged with $CpRe(CO)_2(COCH_2CH_3)(CH_3)$ (**6**; 4.1 mg, $1.1 \times 10^{-2}$ mmol), and $C_6D_6$ (0.36 mL) was vacuum transferred into the tube. The tube was pressurized with 20 atm of CO and sealed as described in the analogous reaction with **3**. The tube was irradiated for 10 min through a uranium glass filter. The only organometallic product detectable by $^1H$ NMR was $CpRe(CO)_3$ ($\delta$ 4.32). The organic products, $CH_3CH_2COCOCH_2CH_3$ [$\delta$ 2.35 (q, $J$ = 7.2), 0.82 (t, $J$ = 7.2)], $CH_3CH_2COCOCH_3$ [$\delta$ 2.30 (q, $J$ = 7.2), 1.84 (s), 0.79 (t, $J$ = 7.2)], and $CH_3COCOCH_3$ [$\delta$ 1.79 (s)], identified by comparison to spectra of commercial samples, were formed in the ratio 1:1.83:1.23. In a separate experiment, the identities of these products were confirmed by GC/MS.

**Irradiation of 3 under 20 atm of CO in the Presence of 3,4-Hexanedione.** A medium-walled NMR tube was charged with **3** (4.4 mg, $1.2 \times 10^{-2}$ mmol), and $C_6D_6$ (0.38 mL) was vacuum transferred into the tube. 3,4-Hexanedione ($1.2 \times 10^{-2}$ mmol) and dioxane ($8.6 \times 10^{-3}$ mmol, internal standard) were added by vacuum transfer via a known-volume bulb. The tube was pressurized with CO and sealed as described for the irradiation of **3** under 20 atm of CO. An initial $^1H$ NMR spectrum was recorded to establish the concentrations of **3** and 3,4-hexanedione relative to the internal standard; the two reactants were observed in the ratio 1.1:1. The tube was irradiated with 355–385-nm light for 85 s, corresponding to 18% conversion. The yields of products based on **3** and corrected for percent conversion were the following: $CpRe(CO)_3$, 100%; $CH_3COCOCH_3$, 34%; $CH_3CH_2COCOCH_3$, 68%; acetone, 10%. The ratio of the remaining **3** to 3,4-hexanedione was 1.1:1.

**Irradiation of 3 under CO with Varying Concentrations of $CCl_4$.** Four medium-walled NMR tubes were charged with similar quantities of **3** (4.2–4.6 mg, 1.2–$1.3 \times 10^{-2}$ mmol). $CD_2Cl_2$ (~0.38 mL) was vacuum transferred into each tube. An appropriate amount of tetramethylsilane (3.0–$3.2 \times 10^{-2}$ mmol, internal standard) was added by vacuum transfer via a known-volume bulb. Different amounts of $CCl_4$ ($1.9 \times 10^{-3}$, $6.4 \times 10^{-3}$, $1.2 \times 10^{-2}$, $1.2 \times 10^{-1}$ mmol) were also added by this technique. The tubes were pressurized with CO and sealed as for the irradiation of **3** under 20 atm of CO. Measurement of the total volumes of solution

---

(40) *CRC Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1979.

(41) Cramer, R.; Seiwell, L. P. *J. Organomet. Chem.* **1975**, *92*, 245.

after thawing the tubes allowed the molarity of the $CCl_4$ to be calculated as $4.9 \times 10^{-3}$, $1.6 \times 10^{-2}$, $3.3 \times 10^{-2}$, and $3.1 \times 10^{-1}$ M. Initial spectra were recorded to establish the relative concentrations of **3** and the internal standard. The tubes were irradiated with 355–385-nm light, and the reactions were monitored at appropriate intervals by $^1H$ NMR spectrometry. The yields, corrected for percent conversion, remained constant within experimental error throughout the photolyses. Yields of the organic products are plotted as a function of $[CCl_4]$ in Figure 4. The organometallic product, $CpRe(CO)_3$, was produced in quantitative yield.

**Irradiation of 3 under 20 atm of CO with $CBrCl_3$.** A medium-walled NMR tube was charged with **3** (5.0 mg, $1.4 \times 10^{-2}$ mmol). $CD_2Cl_2$ (0.38 mL) was vacuum transferred into the tube. $CBrCl_3$ ($5.5 \times 10^{-1}$ mmol) and dioxane ($5 \times 10^{-3}$ mmol, internal standard) were added by vacuum transfer via a known-volume bulb. The tube was pressurized and sealed under CO as described for the irradiation of **3** under 20 atm of CO. After an initial $^1H$ NMR spectrum was taken to determine the relative intensities of the resonances of **3** versus that of the internal standard, the tube was irradiated with 355–385-nm light. The reaction was monitored at various intervals by $^1H$ NMR spectrometry. For conversion times less than 2 min (10–16% conversion), yields of products were calculated by NMR integration against the internal standard and normalized to conversion percentage: $CH_3COBr$ ($\delta$ 2.82), 32%; $CH_3Br$ ($\delta$ 2.66), 43% (identified by comparison of their $^1H$ NMR spectra to those of commercial samples); $CpRe(CO)_2(CH_3)Br$ (**7**)[19] [$\delta$ 5.36 (s, 5 H), 1.10 (s, 3 H)], 43% (identified by comparison of its $^1H$ NMR spectrum to an authentic sample; $CpRe(CO)_2(COCH_3)Br$ (**8**), 40% (identified by comparison of its $^1H$ NMR spectrum with that of an authentic sample prepared and characterized as described below); $CH_3COCH_3$, 9%. At greater conversion times, decomposition of $CpRe(CO)_2(COCH_3)Br$ was noted. This experiment was repeated, and the yields at 15% conversion were as follows: $CH_3COBr$, 39%; $CH_3Br$, 40%; **7**, 40%; **8**, 38%; $CH_3COCH_3$, 11%.

**$CpRe(CO)_2(COCH_3)Br$ (8).** A 50-mL Schlenk flask fitted with a stir bar and vacuum stopcock was charged with **1** (100 mg, 0.280 mmol) and pyridinium hydrobromide perbromide (89.5 mg, 0.28 mmol). THF (5 mL) was vacuum transferred into the flask, and the reaction was allowed to stir at −78 °C for 1 h. The mixture was warmed to room temperature, and the THF was removed under vacuum. The residue was triturated with $Et_2O$ in air. The $Et_2O$ was removed under vacuum, and the residue was chromatographed (Alumina III, hexane/$Et_2O$). The yellow-orange fraction was stripped and recrystallized from $Et_2O$ layered with pentane at −70 °C to yield 44 mg of **8** (36%): $^1H$ NMR ($C_6D_6$) $\delta$ 4.50 (s, 5 H), 2.52 (s, 3 H); $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ 212.3, 195.3, 95.0, 55.0. IR ($Et_2O$) 2037 (m), 1972 (s), 1663 (m) $cm^{-1}$. MS (EI) 428/430/432 ($M^+$, $^{185}Re$, $^{79}Br$/$^{185}Re$, $^{81}Br$; $^{187}Re$, $^{79}Br$/$^{187}Re$, $^{81}Br$). MP 102–103.5 °C (dec). Anal. Calcd for $C_9H_8BrO_3Re$: C, 25.12; H, 1.87. Found: C, 25.04; H, 1.81.

**$CpRe(CO)_2(CH_3)_2$ (9).** The synthesis of $CpRe(CO)_2(CH_3)_2$ from $CpRe(CO)_2H_2$ was carried out by a modification of the route described by Hoyano and Graham[42] in consideration of the work of Yang and Bergman[43] on the nature of $CpRe(CO)_2H^-K^+$. $CpRe(CO)_2H_2$ (500 mg, 1.62 mmol) was placed in a 50-mL flask with 10 mL of THF and a stir bar. To this stirring solution was added a slurry of KH (441 mg, 11.0 mmol) in 5 mL of THF. The reaction was allowed to stir for 16 h and then filtered through a fine frit. The excess KH was washed with 200 mL of THF. The filtrate and washings were combined and reduced under vacuum to 12 mL. $CH_3I$ (7 mL) was added by vacuum transfer. The resulting mixture was allowed to warm slowly to room temperature and then stirred at room temperature for 20 min. The solvent and excess $CH_3I$ were removed under vacuum. The residue was triturated with 125 mL of pentane and filtered. The filtrate was evaporated in vacuo, leaving crude *trans*-$CpRe(CO)_2(CH_3)H$; 3 mL of THF was added to this residue. A slurry of KH (420 mg, 10.5 mmol) in 3 mL of THF was added. The reaction bubbled vigorously and turned a yellow color. After stirring for 20 min, the reaction mixture was filtered through a fine frit. The excess KH was washed with 75 mL of THF. The filtrate and combined washings were reduced in volume to 4 mL. $CH_3I$ (5 mL) was added by vacuum transfer, and the reaction was warmed slowly to room temperature. After the solution was stirred at room temperature for 0.5 h, the solvent and excess $CH_3I$ were removed under vacuum. In the air, the residue was triturated with 50 mL of pentane and filtered. The solvent was removed from the filtrate by rotary evaporation and chromatography of the residue (Alumina III, hexane) yielded a slightly yellow fraction, which was collected. The solvent was removed in vacuo from this fraction and recrystallization of the residue from hexane by slow cooling to −60 °C yielded 410 mg of **9** as light yellow square crystals (75%): $^1H$ NMR ($CDCl_3$) $\delta$ 5.01 (s, 5 H), 0.73 (s, 6 H). IR (cyclohexane) 2009 (m), 1939 (s) $cm^{-1}$. Literature values:[42] $^1H$ NMR ($CDCl_3$) $\delta$ 5.05 (s, 5 H), 0.77 (s, 6 H). IR (heptane) 2009 (m); 1940 (s).

**Irradiation of 9 under CO.** A medium-walled NMR tube was charged with the dimethyl complex **9** (4.2 mg, $1.2 \times 10^{-2}$ mmol). $CD_2Cl_2$ (0.38 mL) was vacuum transferred into the tube. Dioxane ($1.9 \times 10^{-2}$ mmol, internal standard) was added by vacuum transfer from a known-volume bulb. The tube was pressurized and sealed under 20 atm of CO as described for the irradiation of **3** under CO. After an initial $^1H$ NMR spectrum was recorded to determine the relative amounts of **9** and the internal standard, the tube was irradiated through a uranium filter for 10 min, corresponding to 90% conversion. On the basis of this conversion, yields calculated from the integrated intensities of the $^1H$ NMR signals for the various products were the following: $CH_3COCOCH_3$, 79%; $CH_3COCH_3$, 5%; $CpRe(CO)_3$, 100%.

**Irradiation of 9 under $^{13}CO$.** A pressure valve heavy-walled NMR tube was charged with $CpRe(CO)_2(CH_3)_2$ (8.0 mg, $2.4 \times 10^{-2}$ mmol). The NMR tube was evacuated and pentane (0.26 mL; chosen for favorable GC/MS conditions) was vacuum transferred into the tube. The tube was attached to a $^{13}CO$ lecture bottle and pressurized as described for the analogous experiment with **3**. The tube was irradiated for 7 min with 355–385-nm light. After degassing via six freeze–pump–thaw cycles, the volatile materials were removed by vacuum transfer. GC/MS analysis of the volatile fraction showed that the 2,3-butanedione produced was $^{13}C_1$ (2%) and $^{13}C_2$ (98%). The nonvolatile residue was chromatographed (Alumina III/hexane). The solvent was removed in vacuo from the first fraction, containing recovered starting material, and the residue was analyzed directly by mass spectrometry. A best fit calculation of the data in the molecular ion region was consistent with a ratio of 80% $^{13}C_0$ and 20% $^{13}C_1$. $CpRe(CO)_3$ was isolated from the second fraction and was also analyzed directly by mass spectrometry. The data were consistent with a best fit calculation of the molecular ion region as <1% $^{13}C_0$, 91% $^{13}C_1$, and 8% $^{13}C_2$.

**Irradiation of 9 under 20 atm of CO in $CCl_4$.** A medium-walled NMR tube was charged with **9** (4.5 mg, $1.3 \times 10^{-2}$ mmol). $CCl_4$ (0.38 mL) was vacuum transferred into the tube. Tetramethylsilane ($6.7 \times 10^{-3}$ mmol, internal standard) was added by vacuum transfer from a known-volume bulb. The tube was pressurized and sealed under CO as described for the irradiation of **3** under 20 atm of CO. An initial $^1H$ NMR spectrum was recorded to establish the relative concentrations of **9** and the internal standard. The tube was then irradiated with 355–385-nm light, and the reaction was monitored at intervals by $^1H$ NMR spectrometry. Yields of the products were calculated as 152% (1.52 equiv based on 1 equiv of starting material) $CH_3COCl$, 19% (0.19 equiv) $CH_3Cl$, 6% acetone, 97% $CpRe(CO)_3$, and <4% of another product [$\delta$ 5.29 (5 H), 1.0 (3 H)] believed to be $CpRe(CO)_2(CH_3)Cl$ by comparison with its $^1H$ NMR spectrum to the known Br and I analogues.[19]

**Irradiation of 9 under 20 atm of CO with $CBrCl_3$.** A medium-walled NMR tube was charged with $CpRe(CO)_2(CH_3)_2$ (**9**; 5.0 mg, $1.5 \times 10^{-2}$ mmol), and $CD_2Cl_2$ (0.38 mL) was vacuum transferred into the tube. $CBrCl_3$ ($3.1 \times 10^{-1}$ mmol) and dioxane ($9.0 \times 10^{-3}$ mmol, internal standard) were added by vacuum transfer via a known-volume bulb. The tube was pressurized and sealed under CO as described for the analogous reaction of **3**. After an initial $^1H$ NMR spectrum was taken to establish the relative concentrations of **9** and the internal standard, the tube was irradiated with 355–385-nm light. $^1H$ NMR spectrometry was used to monitor the reaction; all products were identified by their $^1H$ NMR spectrum, and yields were calculated by integration against the internal standard. Yields of $CH_3Br$ ($\delta$ 2.66) and $CpRe(CO)_2(CH_3)Br$ (**7**)[19] ($\delta$ 5.36, 1.10) were 87% and 85%, respectively, at early conversion (5–16%). This experiment was repeated, and the yields at 12% conversion were $CH_3Br$, 81%, and **7**, 78%. At conversions greater than 50%, significantly higher yields of $CH_3Br$ were noted along with declining yields of **7**, and finally the appearance of *trans*-$CpRe(CO)_2Br_2$ ($\delta$ 5.78; identified by comparison of its $^1H$ NMR spectrum with that of an authentic sample prepared by the method of Yang and Bergman[43]). After degassing of the sample and removal of the volatile materials in vacuo, GC/MS was used to identify $C_2Cl_6$ in the volatile fraction by a computer matching of its mass spectrum with that published in the NBS libraries.[44] $C_4Cl_6$ (2 $\mu$L) was added as a standard, and response factors were tested on known samples. The yield of $C_2Cl_6$ was found to be >65%.

**Acknowledgment.** We are grateful for financial support of this work from the National Science Foundation through Grant No. 8420979. We also acknowledge fellowship support to K.I.G. from the National Science Foundation and from AT&T Bell Laboratories through their Graduate Research Program for Women.

---

[42] Hoyano, J. K.; Graham, W. A. G. *Organometallics* **1982**, *1*, 783.

[43] Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500.

[44] NBS Libraries (Revision E) are available from Hewlett-Packard for use on their instruments.

**Supplementary Material Available.** Tables of positional parameters, anisotropic thermal parameters, and a listing of $F_o$ and $F_c$ for the X-ray diffraction study of **3** were provided as supplementary information with the communication that reported part of the results discussed in this paper.[7] Ordering information is given on any current masthead page.

**Registry No. 1**, 12306-94-4; **2**, 12307-24-3; **3**, 106402-85-1; **3**-$d_6$, 118378-25-9; **4**, 118378-21-5; **5**, 118378-22-6; **6**, 118378-23-7; **7**, 41618-24-0; **8**, 118378-24-8; **9**, 80952-46-1; $CpRe(CO)_3$, 12079-73-1; $CpRe(CO)_2(PPh_3)$, 42766-75-6; $CH_3COCOCH_3$, 431-03-8; $CH_3COCH_3$, 67-64-1; $CpRe(CO)_2PMe_3$, 84521-32-4; $CpRe(CO)_2(COEt)Li$, 118378-26-0; $CH_3CH_2COCOCH_2CH_3$, 4437-51-8; $CH_3CH_2COCOCH_3$, 600-14-6; $CCl_4$, 56-23-5; $CBrCl_3$, 75-62-7; $CpRe(CO)_2H_2$, 80952-45-0; *trans*-$CpRe(CO)_2(CH_3)H$, 118455-81-5; $CpRe(CO)_2(CH_3)Cl$, 118378-27-1; $CH_3COCl$, 75-36-5; $CpRe(CO)_2Br_2$, 57194-43-1.

---

# Synthesis, Characterization, and DNA-Binding Properties of (1,2-Diaminoethane)platinum(II) Complexes Linked to the DNA Intercalator Acridine Orange by Trimethylene and Hexamethylene Chains

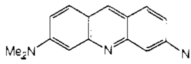
**Bruce E. Bowler,[1a] Kazi J. Ahmed,[1a] Wesley I. Sundquist,[1a] L. Steven Hollis,[1b] Edward E. Whang,[1a] and Stephen J. Lippard*[,1a]**

*Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.* *Received June 16, 1988*

**Abstract:** We report the syntheses of intercalator-linked platinum complexes, $[Pt\{AO(CH_2)_nen\}Cl_2]Cl$, where $(CH_2)_n$ is a polymethylene chain having $n = 6$ (**9**) or $n = 3$ (**20**) linking the DNA intercalator acridine orange (AO) to the Pt-binding ligand ethylenediamine (en). Single-crystal X-ray diffraction studies of the oxalate (ox) derivative of **9**, $[Pt\{AO(CH_2)_6en\}(ox)](NO_3)\cdot 7H_2O$ (**10**), and of the ligand precursors, $[AO(CH_2)_6OH]I$ (**5**) and $[AO(CH_2)_3OH]I$ (**15**), revealed the molecular structures and crystal packing of these compounds. In **10**, infinite "head-to-tail" stacking of the acridine orange rings occurs while the {Pt(en)(ox)} groups stack in a pairwise fashion. In compounds **5** and **15**, there are head-to-tail stacked acridine orange dimers with only weak interactions between the dimers. Visible absorption spectroscopy has been used to compare the effects of different chain lengths and substituents on the stacking interactions of these modified acridine orange compounds in solution. The tendency of molecules to aggregate in acidic aqueous solution follows the order $[Pt\{AO(CH_2)_3en\}Cl_2]^+ \gg [Pt\{AO(CH_2)_6en\}Cl_2]^+ > AO \gg [AO(CH_2)_6(en)]^+ > [AO(CH_2)_3(en)]^+$. The interaction of compounds **9** and **20** with DNA has also been studied by absorption spectroscopy. These results, together with the previously reported covalent binding to, and superhelical unwinding of, DNA by **9**, support a model in which the platinum moiety binds covalently to DNA while the AO moiety is intercalated one or two base pairs away.

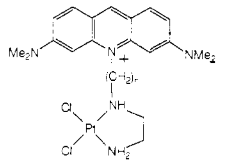
We have recently been investigating the DNA-binding properties of organic intercalators and platinum complexes in the presence of one another. In part, our interest stems from the clinical success of the antitumor drug *cis*-diamminedichloroplatinum(II), *cis*-DDP,[2] which has stimulated much work on the interaction of platinum complexes with DNA, the proposed site of platinum antitumor activity.[3,4] Most chemotherapy protocols use *cis*-DDP in combination with one or more intercalative drugs, such as actinomycin,[5] and we wondered whether simultaneous binding of these two different classes of drugs might affect their individual interactions with DNA. Previously, we found that, at high drug-to-nucleotide ratios, the intercalator ethidium bromide can alter the mode and position of platinum binding to DNA.[6-8] These and studies by others[9] revealed that ethidium bromide can modulate *cis*-DDP binding to its preferred d(GpG) sites on DNA.

An important facet of this work has been the design and synthesis of a new class of bifunctional molecules comprised of the DNA intercalator acridine orange (AO) linked to the platinum complex, $[Pt(en)Cl_2]$, by trimethylene and hexamethylene chains. The acridine orange moiety binds to DNA in a reversible noncovalent intercalative fashion,[10] whereas the $[Pt(en)Cl_2]$ fragment binds covalently and essentially irreversibly to DNA. There is considerable precedent for combining several such functionalities into a single molecule in order to probe DNA sequence and structure. DNA footprinting and affinity cleaving agents,[11] metallointercalator DNA structure probes,[12] intercalator-linked oligonucleotides,[13] metallointercalator-modified DNA-binding



Acridine Orange

AO



$[Pt\{AO(CH_2)_6en\}Cl_2]^+$

---

(1) (a) Massachusetts Institute of Technology. (b) Engelhard Corp.

(2) Hacker, M. P., Douple, E. B., Krakoff, I. H., Eds. *Platinum Coordination Compounds in Cancer Chemotherapy*; Nijhoff: Boston, 1984.

(3) Sherman, S. E.; Lippard, S. J. *Chem. Rev.* **1987**, *87*, 1153-1181.

(4) (a) Reedijk, J. *Pure Appl. Chem.* **1987**, *59*, 181-192. (b) Lippard, S. J. *Pure Appl. Chem.* **1987**, *59*, 731-742.

(5) Loehrer, P. J.; Einhorn, L. H. *Ann. Intern. Med.* **1984**, *100*, 704-713.

(6) Merkel, C. M.; Lippard, S. J. *Cold Spring Harbor Symp. Quant. Biol.* **1982**, *47*, 355-360.

(7) Tullius, T. D.; Lippard, S. J. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3489-3492.

(8) Bowler, B. E.; Lippard, S. J. *Biochemistry* **1986**, *25*, 3031-3038.

(9) Malinge, J.-M.; Schwartz, A.; Leng, M. *Nucleic Acids Res.* **1987**, *15*, 1779-1797.

(10) Berman, H. M.; Young, P. R. *Annu. Rev. Biophys. Bioeng.* **1981**, *10*, 87-114.

(11) Dervan, P. B. *Science* **1986**, *232*, 464-471.

(12) Barton, J. K. *Science* **1986**, *233*, 727-734.

0002-7863/89/1511-1299$01.50/0 © 1989 American Chemical Society