toluene slush bath to liquid N_2. Products were isolated by gas chromatography, with peaks separated by a TCP column collected and further fractionated on a DC-702 column. **11** (ca. 16%) was recovered. The products obtained were 1-methyl-1,3-disilacyclobutane (**15**; 3%), 1,1,2-trimethyl-1,2-disilacyclohex-4-ene (**26**; 4%), 1-methyl-1-silacyclopent-3-ene (**28**; 3%), 1,1-dimethyl-1-silacyclopent-3-ene (**29**; 3%), 1-(2-methyl-2-silapropyl)-1-silacyclopent-3-ene (**30**; 10%), 1-methyl-1-(2-silapropyl)-1-silacyclopent-3-ene (**31**; 2%), 1-(trimethylsilyl)-1-silacyclopent-3-ene (**33**; 8%), 5-silaspiro[4.4]nona-2,7-diene (**35**; 1%), disilacyclopentadiene (**37**; 2%), 3-(trimethylsilyl)-1-silacyclopent-3-ene (**42**; 5%), 2-(trimethylsilyl)-1-silacyclopent-3-ene (**43**; 2%), 1-(trimethylsilyl)-1,3-butadiene (**44**; 5%), and 1-silacyclopent-3-ene (**45**; 2%). Spectroscopic data for **26**, **30**, **31**, **33**, **42**, **43**, and **44** are given in Table II. The properties of **26** were identical with those of an authentic sample whose synthesis was described above. **29**,[38] **35**,[39] and **45**[40] are known compounds and were identified by comparison with literature spectra. **28** was identical with an authentic sample prepared in 34% yield by flow pyrolysis of a mixture of 210 mg (1.8 mmol) of 1,1,1,2-tetramethyldisilane and 1.2 g (23 mmol, 12-fold excess) of 1,3-butadiene at 500 °C (2 torr); contact time = 6 ms. The evidence for the structure of the compound believed to be the dimer of silole **37** will be published separately.[24]

Acknowledgment. We thank Professors Tom Barton and Rob Conlin and Dr. Iain Davidson for helpful discussions and good fellowship. Professor Barton also arranged for the exact mass measurements that were carried out at Iowa State University. Many of the syntheses of starting materials were first carried out by Dewey Holten (as an undergraduate) and by Dr. Yue-Shen Chen. We are grateful to the United States Department of Energy for financial support of this project. This is technical report C00-1713-131.

Registry No. **11**, 5089-32-7; **15**, 80540-80-3; **16**, 99811-08-2; **17**, 80540-72-3; **18**, 99811-09-3; **19**, 5089-32-7; **20**, 99811-10-6; **21**, 99811-11-7; **22**, 99829-78-4; **28**, 55544-25-7; **29**, 16054-12-9; **30**, 99811-18-4; **31**, 99811-19-5; **33**, 99811-20-8; **35**, 52856-32-3; **37**, 99811-21-9; **42**, 99811-22-0; **43**, 99811-23-1; **44**, 1798-76-1; **45**, 7049-25-4; 2,2-dichlorohexamethyltrisilane, 5181-42-0; chlorotris(trimethylsilyl)silane, 5565-32-2; 1,1,2-trichlorotrimethyldisilane, 13528-88-6; 1-chloro-1,2,2-trimethyl-1,2-disilacyclohex-4-ene, 99811-12-8; 1,1,2-trimethyl-1,2-disilacyclohex-4-ene, 99811-13-9; *cis*-1,4-dibromo-2-butene, 18866-73-4; 1,2-dimethyltetrachlorodisilane, 4518-98-3; *cis*-1,2-dichloro-1,2-dimethyl-1,2-disilacyclohex-4-ene, 99811-14-0; *trans*-1,2-dichloro-1,2-dimethyl-1,2-disilacyclohex-4-ene, 99811-15-1; *cis*-1,2-dimethyl-1,2-disilacyclohex-4-ene, 99811-16-2; *trans*-1,2-dimethyl-1,2-disilacyclohex-4-ene, 99811-17-3; 1,3-butadiene, 106-99-0.

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Reaction of Acetyl Complexes with HMR_3 (M = Si, Sn). Mechanism of Acetaldehyde Formation

R. W. Wegman

Union Carbide Corporation, South Charleston, West Virginia 25303

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The thermal reaction of the acyl complexes $CH_3C(O)M(CO)_xL$ (M = Co, Mn; L = PPh_3) with $HM'R_3$ (M′ = Si, Sn; R = Bu, Ph) results in the formation of acetaldehyde and $R_3M'M(CO)_xL$. The rate law for the reaction is consistent with a pathway involving initial CO dissociation from $CH_3C(O)M(CO)_xL$, oxidative addition of the H–M′ bond, and reductive elimination of acetaldehyde. With $HSnR_3$ the rate-determining step is CO dissociation from $CH_3C(O)M(CO)_xL$. In the case of $HSiR_3$ the rate-determining step is oxidative addition of the H–Si bond.

Introduction

Metal acyl complexes play a pivotal role in numerous catalytic processes. For example, in the Rh–I catalyzed carbonylation of methanol to acetic acid, reductive elimination of acetyl iodide from $CH_3C(O)Rh(CO)_2I_3^-$ leads to the formation of the intermediate acetyl iodide (eq 1).[1] In

$$CH_3C(O)Rh(CO)_2I_3^- \rightarrow CH_3C(O)I + Rh(CO)_2I_2^- \tag{1}$$

olefin hydroformylation formation of a metal acyl complex is followed by cleavage of the carbon–metal bond to yield an aldehyde.[2] With a Rh–PPh_3 catalyst it is generally accepted that $RC(O)Rh(CO)L_2$ oxidatively adds dihydrogen and then eliminates an aldehyde according to eq 2.

$$RC(O)Rh(CO)L_2 + H_2 \rightarrow RC(O)H + HRh(CO)L_2 \tag{2}$$

Cleavage of cobalt acyl complexes is somewhat less well understood. In chemistry related to olefin hydroformylation, it is thought that cleavage occurs with H_2 or $HCo(CO)_4$ (eq 3 and 4).[4]

$$RC(O)Co(CO)_4 \xrightarrow{H_2} RC(O)H + HCo(CO)_4 \tag{3}$$

$$RC(O)Co(CO)_4 \xrightarrow{HCo(CO)_4} RC(O)H + Co_2(CO)_8 \tag{4}$$

Recently the kinetics of reactions 3 and 4 with $EtOC(O)Co(CO)_4$ were reported.[5] The reactions were carried out in *n*-octane and proceed by the initial dissociation of CO from $EtOC(O)Co(CO)_4$ followed by a slower reaction of the coordinatively unsaturated $EtOC(O)Co(CO)_3$ with H_2 or $HCo(CO)_4$. The reaction of $HCo(CO)_4$ (eq 4) is approximately 12 times faster than H_2 (eq 3).

In contrast, only hydrogenolysis (eq 3) of the carbon–cobalt bond of phosphine-substituted $CH_3C(O)Co(CO)_3L$

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(L = PBu_3, PPh_2CH_3) is observed.[6,7] Attempts to react $CH_3C(O)Co(CO)_3L$ with the corresponding $HCo(CO)_3L$ results only in the decomposition of $HCo(CO)_3L$ to $[Co(CO)_3L]_2$ (eq 5), which is a well-known reaction.[8]

$$2HCo(CO)_3L \rightarrow [Co(CO)_3L]_2 + H_2 \quad (5)$$

We became interested in the chemistry of cobalt acyl complexes especially in regards to its impact on cobalt-catalyzed reductive carbonylation of methanol (eq 6).[9-13]

$$CH_3OH + CO + H_2 \rightarrow CH_3C(O)H + H_2O \quad (6)$$

In this reaction methanol is transformed into acetaldehyde, presumably via the intermediacy of an acetyl complex.[7] A simplified mechanism is shown in eq 7-11.[14]

$$HCo(CO)_4 + CH_3OH \rightarrow CH_3Co(CO)_4 + H_2O \quad (7)$$

$$CH_3Co(CO)_4 + CO \rightarrow CH_3C(O)Co(CO)_4 \quad (8)$$

$$CH_3C(O)Co(CO)_4 \xrightarrow{H_2} CH_3C(O)H + HCo(CO)_4 \quad (9)$$

$$CH_3C(O)Co(CO)_4 \xrightarrow{HCo(CO)_4} CH_3C(O)H + Co_2(CO)_8 \quad (10)$$

$$Co_2(CO)_8 + H_2 \rightarrow 2HCo(CO)_4 \quad (11)$$

Since the reductive carbonylation is best carried out in a polar solvent, i.e., methanol, we studied the reaction of the more stable $CH_3C(O)Co(CO)_3PPh_3$ with various cobalt carbonyl hydrides in polar solvents. We found that the reaction of $CH_3C(O)Co(CO)_3PPh_3$ with $HCo(CO)_4$ or $HCo(CO)_3PR_3$ (R = Bu, Ph; 1 atm of CO) carried out in THF, acetone, or 2-ethoxyethyl ether resulted only in the decomposition of the cobalt hydrides. Consequently, we examined the reaction of $CH_3C(O)Co(CO)_3PPh_3$ with HMR_3 (M = Sn, Si) in polar solvents and found that the reaction (eq 12) paralleled that normally observed with

$$CH_3C(O)Co(CO)_3PPh_3 + HMR_3 \rightarrow CH_3C(O)H + R_3MCo(CO)_3PPh_3 \quad (12)$$

cobalt hydrides in nonpolar solvents. The similarity of this reaction to eq 4 prompted us to study the kinetics of eq 12 in some detail. Also, we examined the reaction of $CH_3C(O)Co(CO)_3PPh_3$ with H_2 and, for comparison, the reaction of $CH_3C(O)Mn(CO)_5$ with HMR_3.

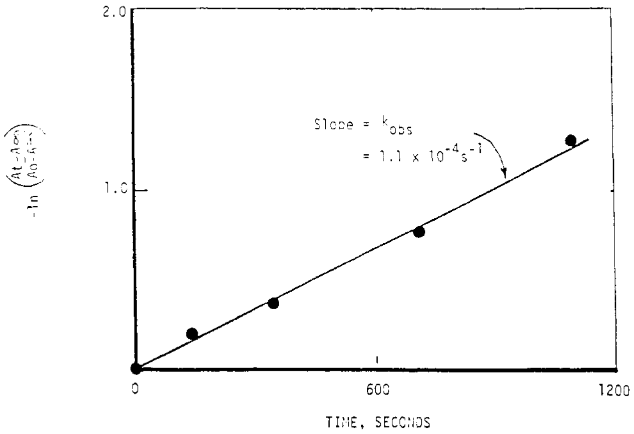

Figure 1. First-order rate plot for the reaction of $CH_3C(O)Co(CO)_3PPh_3$ with $HSnBu_3$ where $[CH_3C(O)Co(CO)_3PPh_3]_0$ = 0.01 M and $[HSnBu_3]_0$ = 0.14 M at 25 °C and 1 atm of CO. A = absorbance for 1690 cm^{-1} band due to $CH_3C(O)Co(CO)_3PPh_3$.

Results and Discussion

Metal hydrides HMR_3 (M = Si, Ge, Sn; R = alkyl) react with $Co_2(CO)_8$ at 20 °C affording the complexes $R_3MCo(CO)_4$ and H_2.[15-17] In the case of $HSiR_3$, $HCo(CO)_4$ has been identified as an intermediate.[18] Further reaction of $HCo(CO)_4$ with $HSiR_3$ yields $R_3SiCo(CO)_4$ and H_2. Similarly, $HCo(CO)_3PBu_3$ and $HMo(CO)_3C_5H_5$ react with $HSnBu_3$ to yield $Bu_3SnCo(CO)_3PBu_3$ and $Bu_3SnMo(CO)_3C_5H_5$, respectively.[19] As mentioned in the Introduction, the reaction of HMR_3 (M = Sn, Si) with $CH_3C(O)Co(CO)_3PPh_3$ affords the complex $R_3MCo(CO)_3PRh_3$ and acetaldehyde as shown by eq 13. The reaction pro-

$$CH_3C(O)Co(CO)_3PPh_3 + HMR_3 \rightarrow R_3MCo(CO)_3PPh_3 + CH_3C(O)H \quad (13)$$

ceeds at a reasonable rate under mild reaction conditions. It is conveniently monitored by IR; CO stretches for $CH_3C(O)Co(CO)_3PPh_3$ and $R_3MCo(CO)_3PPh_3$ are well separated.[20] In the kinetic studies the absorption at 1690 cm^{-1} due to the acyl stretch of $CH_3C(O)Co(CO)_3PPh_3$ was followed as a function of time. A typical first-order rate plot for the reaction of $CH_3C(O)Co(CO)_3PPh_3$ with excess $HSnBu_3$ is shown in Figure 1. In this case the products are acetaldehyde and $Bu_3SnCo(CO)_3PPh_3$. These data were obtained at 25 °C and 1 atm of CO with initial concentrations of $CH_3C(O)Co(CO)_3PPh_3$ and $HSnBu_3$ equal to 0.01 and 0.14 M, respectively. The plot is linear for up to 4 half-lifes, indicating that the rate of product formation is first order in $CH_3C(O)Co(CO)_3PPh_3$ concentration. The slope of this plot equals the pseudo-first-order rate constant k_{obsd}. Varying the initial $HSnBu_3$ concentration (25 °C, 1 atm of CO) over the range 0.14–0.61 M had little, if any, effect on the value of k_{obsd}, indicating a zero-order dependence on the $HSnBu_3$ concentration. Thus, at 25 °C and 1 atm of CO $k_{obsd} = (1.12 \pm 0.06) \times 10^{-4}\ s^{-1}$. CO inhibits the reaction only to a small extent. For example, at 25 °C and 6.8 atm of CO k_{obsd} is $9.6 \times 10^{-5}\ s^{-1}$. When the reaction is carried out under Ar (no added CO), k_{obsd} is $1.1 \times 10^{-4}\ s^{-1}$. Similarly, $HSnPh_3$ reacts with $CH_3C(O)Co(CO)_3PPh_3$ according to eq 13, generating acetaldehyde and $Ph_3SnCo(CO)_3PPh_3$. The reaction is first order in $CH_3C(O)Co(CO)_3PPh_3$ concentration and zero order in $HSnPh_3$ concentration with $k_{obsd} = 1.11 \times 10^{-4}\ s^{-1}$ at 1 atm of CO and 25 °C. Increasing the CO pressure to 6.8 atm (25 °C) decreased k_{obsd} to $9.1 \times 10^{-5}\ s^{-1}$.

The reaction of $HSiR_3$ (R = Et, Ph) with $CH_3C(O)Co(CO)_3PPh_3$ yielded somewhat different kinetic results. The reaction proceeds analogously to eq 13 yielding acet-

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aldehyde and $R_3SiCo(CO)_3PPh_3$. A temperature of 50 °C is required in order to obtain reasonable rates. Since there is little, if any, difference in the observed rate with $HSiEt_3$ or $HSiPh_3$ we studied only the reaction of $HSiEt_3$ with $CH_3C(O)Co(CO)_3PPh_3$ in detail. Under pseudo-first-order conditions in $HSiEt_3$ concentration (≥10-fold excess) the reaction is first order in $CH_3C(O)Co(CO)_3PPh_3$ concentration. As shown in Figure 2, k_{obsd}, the pseudo first-order rate constant, increases with increasing $HSiEt_3$ concentration. For example, at 50 °C and 1 atm of CO k_{obsd} varies from 1.2 to $4.22 \times 10^{-5}\ s^{-1}$ over the initial $HSiEt_3$ concentration range of 0.188–1.13 M. The reaction is somewhat inhibited by added CO, however, the exact dependence on the CO concentration was not determined.

Scheme I

$$CH_3C(O)Co(CO)_3PPh_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3C(O)Co(CO)_2PPh_3 + CO \quad (14)$$

$$CH_3C(O)Co(CO)_2PPh_3 + HMR_3 \xrightarrow{k_2} CH_3C(O)Co(CO)_2(H)(MR_3)PPh_3 \quad (15)$$

$$CH_3C(O)Co(CO)_2(H)(MR_3)PPh_3 \rightarrow CH_3C(O)H + R_3MCo(CO)_2PPh_3 \quad (16)$$

$$R_3MCo(CO)_2PPh_3 + CO \rightarrow R_3MCo(CO)_3PPh_3 \quad (17)$$

A mechanism that accounts for the observed reaction of $CH_3(O)Co(CO)_3PPh_3$ with HMR_3 is shown in Scheme I. Scheme I is similar to the mechanism proposed for the reaction of $EtOC(O)Co(CO)_4$ with $HCo(CO)_4$.[5] The initial step (eq 14) involves CO dissociation from $CH_3COCo(CO)_3PPh_3$ to generate the 16-electron coordinatively unsaturated intermediate $CH_3COCo(CO)_2PPh_3$. The inhibition by CO requires that this step be reversible. Oxidative addition of HMR_3 (eq 15) followed by reductive elimination of acetaldehyde (eq 16) and addition of CO results in the observed products. With the assumption of a steady-state concentration for the intermediate $CH_3COCo(CO)_2PPh_3$, the rate equations (18) and (19) can be derived

$$\frac{-d[CH_3COCo(CO)_3PPh_3]}{dt} = \text{rate} = \frac{k_1k_2[HMR_3][CH_3COCo(CO)_3PPh_3]}{k_{-1}[CO] + k_2[HMR_3]} \quad (18)$$

$$\frac{-d[CH_3COCo(CO)_3PPh_3]}{dt} = \text{rate} = k_{obsd}[CH_3COCo(CO)_3PPh_3] \quad (19)$$

where

$$k_{obsd} = \frac{k_1k_2[HMR_3]}{k_{-1}[CO] + k_2[HMR_3]} \quad (20)$$

If the rate-determining step is CO dissociation (eq 14) and at 1 atm of CO $k_2[HMR_3] > k_{-1}[CO]$, then k_{obsd} simplifies to k_1 and eq 19 would predict that the rate is zero order in HMR_3 concentration and first order in $CH_3C(O)Co(CO)_3PPh_3$ concentration. The results with $HSnR_3$ are consistent with a rate-determining CO loss from $CH_3C(O)Co(CO)_3PPh_3$. The slight CO inhibition observed at the higher CO pressure is presumably due to the back reaction of eq 14. In the case of rate-determining HMR_3 oxidative addition (eq 15) eq 20 can be rearranged to yield eq 21. Equation 21 predicts that a plot of $1/k_{obsd}$ vs. $1/[HMR_3]$ will be linear, and as shown in Figure 3 for $HSiEt_3$ this is the case. The y intercept of Figure 3 equals $1/k_1$ which leads to a value of $k_1 = 2.0 \times 10^{-4}\ s^{-1}$ at 50 °C. Note, k_1 is the CO dissociation rate constant for $CH_3COCo(CO)_3PPh_3$ (eq 14). In the case of $HSnR_3$ $k_1 = k_{obsd} = 1.1 \times 10^{-4}\ s^{-1}$ at 25 °C. The k_1 values obtained with $HSiR_3$ and $HSnR_3$ are in reasonable agreement when the temperature difference is taken into account.

$$1/k_{obsd} = \frac{k_{-1}[CO]}{k_1k_2[HMR_3]} + 1/k_1 \quad (21)$$

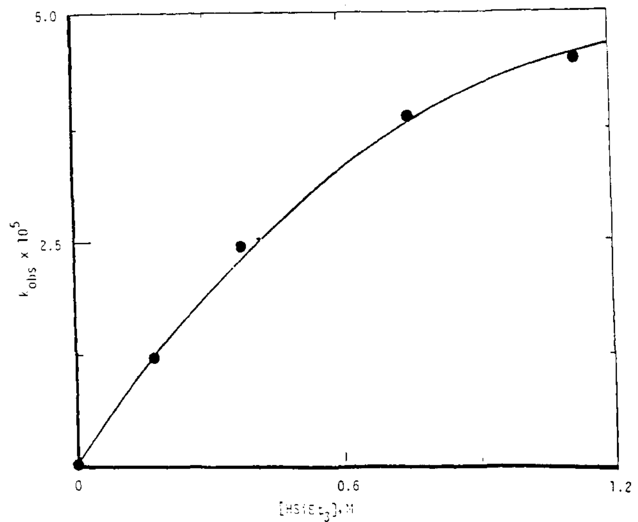


Figure 2. Pseudo-first-order rate constant, k_{obsd}, as a function of $[HSiEt_3]_0$ for the reaction of $CH_3C(O)Co(CO)_3PPh_3$ (0.01 M) with $HSiEt_3$ at 50 °C and 1 atm of CO.

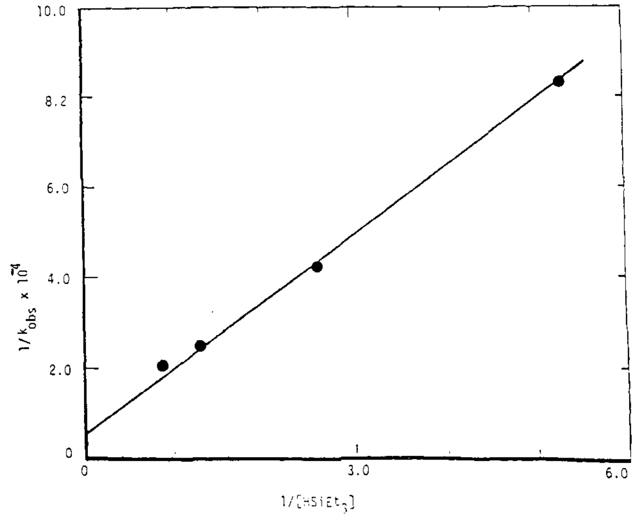
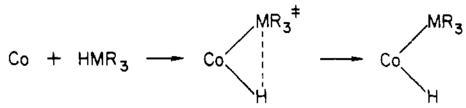


Figure 3. Plot of $1/k_{obsd}$ vs. $1/[HSiEt_3]$ for the reaction of $CH_3C(O)Co(CO)_3PPh_3$ with $HSiEt_3$ at 50 °C and 1 atm of CO.

Thus, the reaction of $CH_3C(O)Co(CO)_3PPh_3$ with HMR_3 proceeds via (a) rate-determining CO loss from $CH_3C(O)Co(CO)_3PPh_3$ for M = Sn or (b) rate-determining HMR_3 oxidative addition for M = Si. The change in the rate-determining step is presumably due to the stronger H–Si bond (77 kcal mol^{-1}) relative to the H–Sn bond (60 kcal mol^{-1}).[21] This would suggest that in the transition state leading to oxidative addition (eq 16) significant breakage of the H–M bond has occurred (eq 22). The kinetic isotope effect was not measured.



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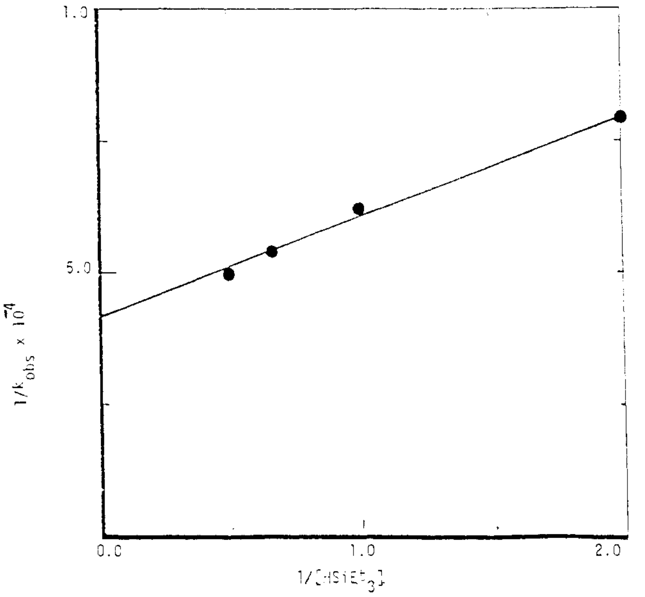

Figure 4. Plot of $1/k_{obsd}$ vs. $1/[HSiEt_3]$ for the reaction of $CH_3C(O)Mn(CO)_5$ with $HSiEt_3$ at 25 °C and 1 atm of CO.

The chemistry of $CH_3COMn(CO)_5$ has been well studied; however, little has been reported concerning the reaction of $CH_3COMn(CO)_5$ with HMR_3.[22] We examined this reaction and found that in the presence of excess HMR_3 (10-fold) acetaldehyde is produced according to eq 23.

$$CH_3COMn(CO)_5 + HMR_3 \rightarrow CH_3C(O)H + R_3MMn(CO)_5 \quad (23)$$

Under pseudo-first-order conditions in HMR_3 concentration the reaction is first order in $CH_3COMn(CO)_5$ concentration. A detailed analysis was not carried out for $HSnR_3$. In a typical experiment $CH_3COMn(CO)_5$ (0.05 M) and $HSnBu_3$ (0.5 M) react at 25 °C and 1 atm of CO with $k_{obsd} = 3.5 \times 10^{-5}\ s^{-1}$. Varying the $HSnBu_3$ concentration had negligible effect on the observed rate. The reaction is slower for $HSiEt_3$. At 25 °C under 1 atm of CO k_{obsd} increases from 1.27 to $1.99 \times 10^{-5}\ s^{-1}$ with increasing $HSiEt_3$ concentration from 0.5 to 2.0 M. The rate increase is not linear, and plotting $1/k_{obsd}$ vs. $1/[HSiEt_3]$ yields a straight line as shown in Figure 4.

Scheme II

$$CH_3COMn(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3COMn(CO)_4 + CO \quad (24)$$

$$CH_3COMn(CO)_4 + HMR_3 \xrightarrow{k_2} CH_3COMn(CO)_4(H)MR_3 \quad (25)$$

$$CH_3COMn(CO)_4(H)MR_3 + CO \rightarrow CH_3C(O)H + R_3MMn(CO)_5 \quad (26)$$

The above results are similar to those observed with $CH_3COCo(CO)_3PPh_3$ and suggest a mechanism (Scheme II), which is analogous to Scheme I. For $HSnBu_3$ $k_{obsd} = k_1$, the CO dissociation rate constant, and is $3.5 \times 10^{-5}\ s^{-1}$ (25 °C). For $HSiEt_3$ its concentration dependence and the relationship shown in Figure 4 indicates k_{obsd} equals eq 27.

$$k_{obsd} = \frac{k_1 k_2[HSiEt]}{k_{-1}[CO] + k_2[HSiEt_3]} \quad (27)$$

k_1, k_{-1}, and k_2 are defined in Scheme II. The y intercept of Figure 4 is $1/k_1$ and is 4.1×10^4 s, giving k_1 a value of $2.5 \times 10^{-5}\ s^{-1}$ (25 °C). The k_1 values for equation 24 obtained with $HSnBu_3$ and $HSiEt_3$ are in good agreement.

The reaction of $CH_3COMn(CO)_5$ with PR_3 (eq 28) is

$$CH_3COMn(CO)_5 + PR_3 \rightarrow CH_3COMn(CO)_4PR_3 + CO \quad (28)$$

thought to proceed via a mechanism similar to Scheme II.[23] The rate-determining step is CO dissociation from $CH_3COMn(CO)_5$ followed by rapid reaction of PR_3 with $CH_3COMn(CO)_4$. k_1, measured by this reaction, is $3.1 \times 10^{-5}\ s^{-1}$ (30 °C).[23]

The reaction of $CH_3C(O)Co(CO)_3PPh_3$ (0.02 M in THF) with H_2 was examined via high-pressure infrared spectroscopy. At low H_2 pressure (100 psi) and 50 °C there is no apparent reaction. Increasing the H_2 pressure to 500 psi (50 °C, $[H_2] \approx 0.2$ M) results in the slow hydrogenolysis of the carbon–cobalt bond to yield acetaldehyde and $HCo(CO)_3PPh_3$ (eq 29). At 500 psi of H_2 the $CH_3C(O)Co(CO)_3PPh_3$ conversion is less than 10% after 1.0 h. The rate of the reaction increases with increasing H_2 pressure. For example, at 2000 psi of H_2 ($[H_2] \approx 0.9$ M) and 50 °C the $CH_3C(O)Co(CO)_3PPh_3$ conversion is nearly 100% after 15 min. With an initial CO pressure of 500 psi no reaction is observed at H_2 partial pressures of 500–2000 psi, demonstrating the powerful inhibiting effect that CO has on the reaction. High-pressure hydrogenolysis has been reported for the cobalt acyl complexes $CH_3C(O)Co(CO)_3PBu_3$,[6] $CH_3C(O)Co(CO)_3P(CH_3Ph_2)_3$,[7] and $EtOC(O)Co(CO)_4$.[5]

$$CH_3C(O)Co(CO)_3PPh_3 + H_2 \rightarrow CH_3C(O)H + HCo(CO)_3PPh_3 \quad (29)$$

Although quantitative data were not obtained, the results are consistent with a mechanism involving initial CO dissociation from $CH_3C(O)Co(CO)_3PPh_3$ followed by oxidative addition of H_2 (eq 30–33). This mechanism is similar to Scheme I and the mechanism proposed for the reaction of $EtOC(O)Co(CO)_4$ with H_2.[5] In the latter case the postulated rate-determining step is the bimolecular reaction of H_2 with coordinatively unsaturated $EtOC(O)Co(CO)_3$. Due to the dependence on H_2 pressure (concentration) it is reasonable to assign eq 31 as the rate-determining step in the reaction of H_2 with $CH_3C(O)Co(CO)_3PPh_3$.

$$CH_3C(O)Co(CO)_3PPh_3 \rightarrow CH_3C(O)Co(CO)_2PPh_3 + CO \quad (30)$$

$$CH_3C(O)Co(CO)_2PPh_3 + H_2 \rightarrow CH_3C(O)Co(CO)_2(H)_2PPh_3 \quad (31)$$

$$CH_3C(O)Co(CO)_2(H)_2PPh_3 \rightarrow CH_3C(O)H + HCo(CO)_2PPh_3 \quad (32)$$

$$HCo(CO)_2PPh_2 + CO \rightarrow HCo(CO)_3PPh_3 \quad (33)$$

Conclusion

Our results support the notion that cleavage of the carbon–cobalt bond in $CH_3C(O)Co(CO)_3PPh_3$ proceeds by the mechanism outlined in Scheme I: (i) initial CO dissociation from $CH_3C(O)Co(CO)_3PPh_3$, (ii) oxidative addition of the reducing agent, and (iii) reductive elimination of acetaldehyde. The rate of acyl group cleavage depends on the nature of the reducing agent. In particular, the rate decreases according to $HSnR_3 > HSiR_3 > H_2$ which correlates to increasing strength of the bond, $H–Sn < H–Si < H–H$, involved in the oxidative addition step. A change

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in the rate-determining step occurs between H–Sn (60 kcal mol^{-1}) and H–Si (77 kcal mol^{-1}). In the former case CO dissociation from $CH_3C(O)Co(CO)_3PPh_3$ is rate limiting and in the latter oxidative addition is rate limiting.

Experimental Section

Materials. THF and 2-ethoxyethyl ether were distilled from Na/benzophenone prior to use. $HSnBu_3$, $HSnPh_3$, $HSiEt_3$, and $HSiPh_3$ were obtained from Aldrich and used without further purification. These compounds were stored under N_2 at 0 °C. $HCo(CO)_4$,[24] $HCo(CO)_3PBu_3$,[25] $HCo(CO)_3PPh_3$,[25] $CH_3C(O)Co(CO)_3PPh_3$,[26] and $CH_3C(O)Mn(CO)_5$[23] were synthesized according to standard literature procedures.

Kinetic Experiments. All manipulations were carried out under N_2 with standard Schlenk procedures. In a typical reaction known amounts of $CH_3C(O)Co(CO)_3PPh_3$ and HMR_3 were dissolved in known volumes of THF in separate flasks in a vacuum Atmospheres Corp. inert-atmosphere box. The sealed flasks were removed from the box and cooled to 0 °C. The $CH_3C(O)Co(CO)_3PPh_3$ and HMR_3 solutions were transferred via syringe into a Pyrex tube approximately 15 cm in height at 1.0 cm in diameter equipped with a septum and stopcock. The solution (0 °C) was then gently purged with CO and maintained under a constant pressure of CO. The tube was then placed in a temperature bath thermostated ±0.5 °C of the desired reaction temperature. After thermal equilibration (15 min) an initial IR spectrum was obtained (= 0 min). Following this IR spectra were recorded as a function of time. The rate of $CH_3C(O)Co(CO)_3PPh_3$ disappearance was determined by monitoring the acyl absorption at 1690 cm^{-1}. The liquid products were analyzed with a Hewlett-Packard Model 5880 gas chromatograph equipped with a 20 × $^1/_8$ in., 60/80 mesh Chromosorb 101 column. The following program was utilized: initial temperature = 80 °C; 6 °C/min increase for 12 min followed by 8.0 °C/min increase up to a final temperature of 290 °C.

In the initial part of the reaction the amount of acetaldehyde found corresponded well to the amount of $CH_3C(O)Co(CO)_3PPh_3$ reacted. In some cases toward the end of the reaction ethanol was observed presumably a result of reduction of acetaldehyde by HMR_3. Similar procedures were utilized for the reaction of $CH_3C(O)Mn(CO)_5$ with HMR_3. The products $R_3MCo(CO)_3PPh_3$[20,27] and $R_3MMn(CO)_5$[28] were determined by their characteristic IR spectra.

A description of the high-pressure infrared equipment including the high-pressure infrared cell and spectrometer together with the usual operation procedure has already appeared.[29]

Registry No. $CH_3C(O)Co(CO)_3PPh_3$, 14054-68-3; $CH_3C(O)Mn(CO)_5$, 13963-91-2; $HSnBu_3$, 688-73-3; $HSnPh_3$, 892-20-6; $HSiEt_3$, 617-86-7; $HSiPh_3$, 789-25-3; acetaldehyde, 75-07-0.

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New Synthetic Strategies for Organometallic Complexes with Thiolate Ligands

Paul M. Treichel* and Paul C. Nakagaki

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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Reactions between several carbonylmetalate anions ($PPN[Mn(CO)_5]$ and $PPN[M(CO)_3(\eta\text{-}C_5H_5)]$; $PPN^+ = Ph_3PNPPh_3^+$; M = Mo, W) and organic disulfides (RSSR; R = Ph, Me, CF_3) initially give the metal thiolate complexes $Mn(SR)(CO)_5$ and $M(SR)(CO)_3(\eta\text{-}C_5H_5)$. The tungsten species are stable and isolable. The molybdenum and manganese compounds are not stable; the former rapidly lose CO and form thiolate bridge dimers (a known reaction) while the later is converted, within this reaction system, to a mixture of $Mn_2(\mu\text{-}SR)_2(CO)_8$ and $PPN[Mn_2(\mu\text{-}SR)_3(CO)_6]$. Reactions between these carbonylmetalate anions and $[Me_2SSMe]BF_4$ yield the same mononuclear metal thiolate complexes which, when appropriate, lose CO and dimerize. If an excess of this sulfonium reagent is present, a further reaction may also occur to produce unstable complexes with monodentate organic disulfide ligands ($[Mn(CO)_5(RSSR)]^+$ and $[M(RSSR)(CO)_3(\eta\text{-}C_5H_5)]^+$). The reaction of $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ with $[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$ gives $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$. This reaction is much faster than the reaction of $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ with MeSSMe, indicating that coordination of the disulfide to the metal has substantially enhanced its reactivity toward nucleophilic attack.

Introduction

Metal carbonyl complexes with thiolate (RS^-) ligands form a well-defined subset among organometallic compounds.[1] Generally in these compounds the thiolate group is found to function as a bridging ligand linked to two or three metal atoms. Complexes with terminal thiolate ligands are also encountered although they are often unstable relative to CO loss and formation of thiolate-bridged dimeric species. Known manganese carbonyl thiolate complexes include $Mn(SR)(CO)_5$, $Mn_2(\mu\text{-}SR)_2(CO)_8$, $Mn_4(\mu_3\text{-}SR)_4(CO)_{12}$,[2] and $[Mn_2(\mu\text{-}SR)_3(CO)_6]^-$, the last series of complexes being recently prepared in our research labs[3] and elsewhere.[4] Thiolate derivatives of

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(1) The last general review in this area is quite old, see: Abel, E. W.; Crosse, B. C. *Organomet. Chem. Rev.* **1967**, *2*, 443.

(2) A summary of references to these compounds is provided in: Treichel, P. M. In "Comprehensive Organometallic Chemistry"; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: London, 1982; Vol. 3, pp 103–110.

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