H_3PO_4 for boron and phosphorus, respectively. Proton shifts are given with respect to the resonance signal of proton impurity in CD_2Cl_2, which was taken as 5.28 ppm. Shifts to lower fields are assigned positive values. Generally, reactions were run in 9–10 mm o.d. Pyrex tubes or in 10 mm o.d. resealable NMR sample tubes (products of J. Young, Ltd.) and were monitored on the NMR instrument by observing ^{11}B spectra.

Reaction of $B_3H_7{\cdot}P(CH_3)_3$ with $N(CH_3)_3$. A 1.0-mmol sample of $N(CH_3)_3$ was condensed into a reaction tube containing 0.50 mmol of $B_3H_7{\cdot}P(CH_3)_3$ (prepared from B_4H_{10} and $P(CH_3)_3$[12]) and approximately 1 mL of CH_2Cl_2. The reactants were mixed well at −80 °C and then allowed to warm slowly. When the temperature reached about 20 °C, the reactants had been completely converted to a mixture of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ and $BH_3{\cdot}N(CH_3)_3$ (−8.3 ppm).[13] The solvent and the BH_3 adduct were pumped out at −45 and 0 °C, respectively, and the remaining solid residue was sublimed under high vacuum at room temperature onto a 0 °C cold finger.

Samples of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ for reaction studies were prepared by allowing the initial mixture of reactants to stand at room temperature for 15 min and then by removing the solvent and the $BH_3{\cdot}N(CH_3)_3$ as described above. The solid residues thus obtained were sufficiently pure for general use.

Reaction of $B_3H_7{\cdot}N(CH_3)_3$ with $P(CH_3)_3$. A 1.05-mmol sample of $P(CH_3)_3$ was condensed onto a frozen CH_2Cl_2 solution containing 0.49 mmol of $B_3H_7{\cdot}N(CH_3)_3$, and the solution was mixed thoroughly at −80 °C. Trimethylamine–borane(3) and $B_2H_4{\cdot}2P(CH_3)_3$ (−37.5 ppm)[14,15] slowly formed in the reaction mixture at room temperature. The reaction was nearly complete after 3 h at this temperature.

Reaction of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ with HCl. Anhydrous HCl (0.25 mmol) was condensed into a reaction tube containing 0.18 mmol of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ and approximately 1 mL of CH_2Cl_2 frozen at −196 °C. As the mixture was allowed to melt, the reaction occurred immediately. The ^{11}B NMR spectrum of the reaction mixture indicated the formation of $BH_3{\cdot}N(CH_3)_3$ and $BH_2Cl{\cdot}P(CH_3)_3$ (−18.8 ppm)[14] with traces of $BH_3{\cdot}P(CH_3)_3$ (−37.1 ppm)[4] and $BH_2Cl{\cdot}N(CH_3)_3$ (−7.8 ppm).[13]

Reaction of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ with B_4H_{10}. A 0.55-mmol sample of B_4H_{10} was condensed into a 10-mm NMR tube containing 0.50 mmol of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ and approximately 1 mL of CH_2Cl_2. The reactants were mixed well at −80 °C and then allowed to slowly warm. At −60 °C the formation of $B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_3H_8{}^-$ was observed. Then, the tube was warmed to room temperatures to ensure that the reaction had gone to completion. The solution was then cooled to −10 °C, and the solvent and unchanged B_4H_{10} were removed by pumping. The resulting white solid residue, $B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_3H_8{}^-$, was redissolved in CD_2Cl_2 for the NMR study.

Reaction of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ with B_2H_6. A 0.81-mmol sample of B_2H_6 was condensed into a reaction tube containing 0.52 mmol of $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$ and approximately 1 mL of CH_2Cl_2. The reactants were mixed well at −80 °C, and then the tube was allowed to warm slowly. At −65 °C the formation of $B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_2H_7{}^-$ was observed. At −45 °C the reaction was faster, and the formation of $BH_3{\cdot}N(CH_3)_3$ and $B_3H_7{\cdot}P(CH_3)_3$ (−15.6 and −45.0 ppm)[16] was observed. When the temperature reached 25 °C, only the signals of $BH_3{\cdot}N(CH_3)_3$, $B_3H_7{\cdot}P(CH_3)_3$, and B_2H_6 were present.

Acknowledgment. We gratefully acknowledge the support of this work by the U.S. Army Research Office through Grant DAAG 29-85-K-0034. Financial support to R.E.D. from the National Science Foundation (Minority Graduate Fellowship, 1981–1984) is appreciated. The NMR instrument was acquired with the use of instrumentation funds that were provided by the National Science Foundation and the Department of Defense.

Registry No. $B_2H_4{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3$, 97551-46-7; $B_3H_7{\cdot}P(CH_3)_3$, 97012-38-9; $B_3H_7{\cdot}N(CH_3)_3$, 57808-48-7; $BH_3{\cdot}N(CH_3)_3$, 75-22-9; $B_2H_4{\cdot}2P(CH_3)_3$, 67113-98-8; $BH_3{\cdot}P(CH_3)_3$, 1898-77-7; $BH_2Cl{\cdot}P(CH_3)_3$, 64160-46-9; HCl, 7647-01-0; B_4H_{10}, 18283-93-7; $B_3H_6{\cdot}N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_3H_8{}^-$, 112925-44-7; B_2H_6, 19287-45-7; $B_3H_6N(CH_3)_3{\cdot}P(CH_3)_3{}^+B_2H_7{}^-$, 112968-02-2.

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Contribution from the Department of Chemistry,
Brookhaven National Laboratory, Upton, New York 11973

Ketone-like Derivatization Reactions of Metal Carbonyls. Attempts To Measure the Equilibrium Constant for Ketalization of a Carbonyl Ligand in $[Re(CO)_6]^+$ by Ethylene Glycol

Mark A. Andrews* and Willie L. Myles[1]

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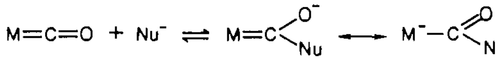
Simple nucleophilic addition reactions of metal carbonyls (eq 1) are well-known. Grubbs et al. have suggested that these



$$M{=}C{=}O + Nu^- \rightleftharpoons M{=}C(O^-)(Nu) \longleftrightarrow M^-{-}C({=}O)(Nu) \quad (1)$$

reactions could be used as a new way to activate carbon monoxide toward hydrogenation.[2] We envisioned an alternative approach based on ketone-like metal carbonyl derivatization reactions, exemplified by eq 2–4. Such reactions would convert a metal

$$M{=}C{=}O + H_2S \rightleftharpoons M{=}C{=}S + H_2O \quad (2)$$

$$M{=}C{=}O + RNH_2 \rightleftharpoons M{=}C{=}NR + H_2O \quad (3)$$

$$M{=}C{=}O + 2ROH \rightleftharpoons M{=}C(OR)_2 + H_2O \quad (4)$$

carbonyl complex into other common ligand systems such as thiocarbonyls, isocyanides, and carbenes, all of which are reported to be more susceptible to hydrogenation.[3] Evaluation of our idea, however, was hampered by the lack of detailed studies regarding the equilibria represented by eq 2–4. Literature reports provide circumstantial evidence that equilibria 2 and 3 may be unfavorable.[4] We report here our observations regarding equilibrium 4, for which no previous data appear to exist.

Results

Metal carbonyls normally react with alcohols only in the presence of a base, leading then to the production of metal alkoxides[5] or metalloesters.[6] Not surprisingly, therefore, attempts to ketalize simple metal carbonyls such as $W(CO)_6$ and $Fe(CO)_5$ with alcohols under typical neutral or acidic conditions were unsuccessful.

In order to test whether this was a kinetic or a thermodynamic problem, the reaction was then approached from the reverse direction. One of the few dialkoxycarbene complexes known at the time this work was begun was $Fe(CO)_4(\overline{COCMe_2CMe_2O})$,[7] formally derived from iron pentacarbonyl and pinacol. This carbene complex could not be hydrolyzed in wet tetrahydrofuran under neutral, basic (Et_3N), or acidic (*p*-toluenesulfonic acid) conditions.

We then shifted our attention to cationic complexes, for which both the forward and reverse reaction kinetics were expected to

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(1) Participant in the Brookhaven National Laboratory Semester Student Program for undergraduates.

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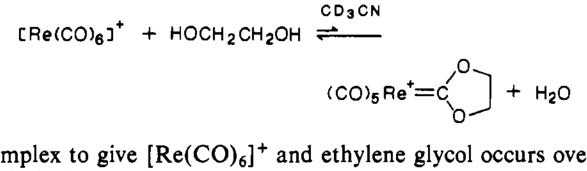
be much more favorable.[6] The manganese hexacarbonyl cation and the corresponding cyclic dialkoxycarbene $[Mn(CO)_5(\overline{COCH_2CH_2O})]^+$ were both known, but $[Mn(CO)_6]^+$ decomposes in water.[8] In contrast, $[Re(CO)_6]^+$ is stable in water and furthermore is known to undergo facile ^{18}O exchange with labeled water,[9] presumably by a ketone-like carbonyl addition–elimination mechanism.[9,10] We therefore prepared a cyclic dialkoxycarbene complex of Re by the same method previously used for the Mn complex.[8,11] (eq 5 and 6). Synthesis of the intermediate 2-chloroethyl metalloester (eq 5) also led to ca. 20% coformation of the *ethyl* ester. The formal hydride source in this surprising reductive side reaction is unknown. No attempt was made to separate the two metalloesters since the presence of the ethyl ester did not interfere with the following silver-induced cyclization to give the carbene complex. Spectral data for the carbene complex are comparable to those of $Re(CO)_4Cl(\overline{COCH_2CH_2O})$.[11e]

$$[Re(CO)_5]^- + ClC({=}O)OCH_2CH_2Cl \rightarrow Re(CO)_5C({=}O)OCH_2CH_2Cl\ (+Re(CO)_5C({=}O)OC_2H_5) \quad (5)$$

$$Re(CO)_5C({=}O)OCH_2CH_2Cl + Ag^+ \rightarrow [Re(CO)_5(\overline{COCH_2CH_2O})]^+ \quad (6)$$

Equilibrium 7 was then examined by NMR and IR spectroscopy from both directions. The reverse reaction was slow but readily observable. Essentially complete hydrolysis of the carbene complex to give $[Re(CO)_6]^+$ and ethylene glycol occurs over a period of months at room temperature or over a period of days at 57 °C. In contrast, no evidence for the forward reaction, ketalization of $[Re(CO)_6]^+$ by ethylene glycol, could be obtained, even after 14 days at 57 °C. Instead, gradual substitution of the hexacarbonyl cation by acetonitrile occurred to give $[Re(CO)_3(CH_3CN)_3]^+$. While it was therefore not possible to quantitatively determine an equilibrium constant for reaction 7, it is clear that the equilibrium must lie well toward the left.



(7)

Conclusions

The slow kinetics and unfavorable equilibrium constant observed here for ketalization of a metal carbonyl, even in the case of a reactive cationic carbonyl complex and an entropically favorable 1,2-diol, suggest that it will be difficult to achieve practical carbon monoxide activation by this type of approach. Although we do not currently contemplate further work in this area, reactions similar to eq 2–4 may offer interesting possibilities for the synthesis of certain ligand systems such as thiocarbonyls[12,13] and alkoxy isocyanide (fulminate ester)[14] complexes.

Experimental Section

$[Re(CO)_6]^+[BF_4]^-$ [10] and $Fe(CO)_4(\overline{COCMe_2CMe_2O})$[7] were prepared by literature methods. 2-Chloroethyl chloroformate was used as received from Tridom Chemical. NMR spectra were obtained on a JEOL MH-100 NMR spectrometer or a Bruker AM-300 FT-NMR spectrometer and IR spectra on a Nicolet MX-1 FT-IR spectrophotometer. Unless otherwise indicated, all reactions were carried out under nitrogen.

Attempted Hydrolysis of $Fe(CO)_4(\overline{COCMe_2CMe_2O})$. A. Neutral Conditions. A solution of the iron carbene complex (47 mg, 170 μmol) in tetrahydrofuran (10 mL) was treated with water (0.5 mL, 28 mmol) and heated at reflux for 18 h. A small amount of iron metal formed, but an IR spectrum showed very little of the carbene complex had decomposed.

B. Basic Conditions. The reaction was conducted the same as in (A) except that triethylamine (24.6 μL, 176 μmol) was added. The results were essentially identical.

C. Acidic Conditions. *p*-Toluenesulfonic acid (9 mg, 52 μmol) was added to the reaction mixture in (A). The solution turned light yellow, and the iron metal dissolved. An IR spectrum taken after 16.5 h at room temperature followed by 6.5 h at reflux showed that no significant reaction had occurred. Adding more *p*-toluenesulfonic acid (65 mg) and refluxing for 7.5 h led to substantial decomposition of the carbene complex to non-carbonyl-containing compounds.

$Re(CO)_5CO_2CH_2CH_2Cl$. A solution of $[Re(CO)_5]^-$ was prepared by stirring $Re_2(CO)_{10}$ (3.26 g, 5.00 mmol) and sodium amalgam (0.70 g (30 mmol) of Na, 7.5 mL of Hg) in 75 mL of dry tetrahydrofuran (THF) under nitrogen for 1.5 h. The resulting red-orange solution was slowly added at −78 °C to a stirred, precooled solution of 2-chloroethyl chloroformate (2.0 mL, 19.3 mmol) in 25 mL of THF. The reaction mixture was allowed to gradually warm to room temperature and was then stirred for an additional 4 h. The THF was evaporated with an aspirator and the resulting solid extracted with hexane until IR spectra of the extracts were essentially blank. Evaporation of the hexane extracts yielded 3.8 g of yellow-orange solid that was contaminated with $Re_2(CO)_{10}$. The crude product was recrystallized in air from 100 mL of hot hexane containing charcoal. Cooling to −20 °C gave 2.27 g (52%) of mixed metalloesters as pale yellow crystals. IR (cyclohexane, ν_{CO}): 2143 (vw), 2032 (s), 2006 (m), 1652 (w) cm^{-1} (cf. $Re(CO)_5CO_2C_2H_5$ (cyclohexane): 2141 (w), 2030 (s), 2003 (m), 1646 (w) cm^{-1}). ^1H NMR ($CDCl_3$) showed the product to be an 80:20 mixture of $Re(CO)_5CO_2CH_2CH_2Cl$ (δ 4.18 (2 H, t, $J = 5.6$ Hz), 3.63 (2 H, t, $J = 5.6$ Hz)) and $Re(CO)_5CO_2C_2H_5$ (δ 3.98 (2 H, q, $J = 7.3$ Hz), 1.20 (3 H, t, $J = 7.3$ Hz)). The latter component was identified by the excellent correspondence of its ^1H NMR and IR spectra with that of an authentic sample.[15] The starting 2-chloroethyl chloroformate was shown by ^1H NMR to contain no significant impurities.

$[Re(CO)_5(\overline{COCH_2CH_2O})]^+[BF_4]$–. A solution of 2.17 g of the 80:20 mixture of $Re(CO)_5CO_2CH_2CH_2Cl$ and $Re(CO)_5CO_2C_2H_5$ (4.09 mmol of the chloro ester) dissolved in 25 mL of acetone was added to a solution of $AgBF_4$ (0.856 g, 4.66 mmol) in 15 mL of acetone in air. The mixture turned black. After 1.5 h, the reaction was filtered to give a pale green solution, which was concentrated to 30 mL. Ether (80 mL) was added and the resulting grayish precipitate collected by filtration, washed with ether, and dried (1.51 g). The crude product (1.47 g) was placed in a fritted funnel and extracted with dichloromethane (8 × 20 mL). Evaporation of the extracts yielded 0.67 g (35% based on the starting chloro ester) of the carbene complex as a white powder. Extraction of the dichloromethane-insoluble material with acetone yielded 0.72 g (40%) of $[Re(CO)_6]^+[BF_4]^-$. The carbene complex can be recrystallized from acetonitrile/ether. IR (CH_3CN, ν_{CO}): 2163 (w), 2098 (w, sh), 2053 (s) cm^{-1}. ^1H NMR (CD_3CN): δ 4.79 (4 H, s). ^{13}C NMR (CD_3CN, [Re] = 0.2 M, $[Cr(acac)_3]$ = 0.06 M): δ 217.33 (carbene C), 180.33 (trans CO), 178.97 (cis $(CO)_4$), 74.51 ($-CH_2CH_2-$). Anal. Calcd for $C_8H_4BF_4O_7Re$: C, 19.81; H, 0.83. Found: C, 19.89; H, 0.97.

Attempted Ketalization of $[Re(CO)_6]^+[BF_4]^-$. A mixture of ethylene glycol (1.11 mL, dried over 3A molecular sieves) and CD_3CN (3.9 mL, dried over 3A molecular sieves) was dried twice more over 3A molecular sieves in oven-dried glassware in a glovebox. $[Re(CO)_6]^+[BF_4]^-$ (46 mg,

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100 μmol) was added to 0.75 mL of the 4 M glycol solution and transferred to screw-capped NMR tubes under nitrogen and heated to 57 °C. After 20 h, IR analysis showed $[Re(CO)_6]^+[BF_4]^-$ (ca. 0.09 M) and weak absorbances at 2013 and 1953 cm^{-1}. No trace of the carbene complex could be detected in the ^1H NMR spectrum at δ 4.79, even after heating at 57 °C for 14 days. At that time IR spectra showed that nearly all of the hexacarbonyl had been consumed by side reactions, the primary species present being $[Re(CO)_3(CH_3CN)_3]^+$ (2053 and 1951 cm^{-1}), identified by comparison with a literature spectrum in the same solvent.[16] The carbene detectability limit was estimated at better than 1 part of carbene in 10^4 parts of ethylene glycol on the basis of NMR spectra of calibrated mixtures in CD_3CN.

Hydrolysis of $[Re(CO)_5(\overline{COCH_2CH_2O})]^+[BF_4]^-$. The carbene complex (98 mg, 202 μmol) was dissolved under nitrogen in 2.0 mL of a reaction solvent prepared by adding water (270 μL, 15 mmol) to 2.7 mL of CD_3CN (dried over molecular sieves) to give a solution that was 0.1 M in carbene complex and 5 M in water. An aliquot heated in a screw-capped NMR tube at 57 °C showed a 43:57 ratio of carbene (δ 4.79) to ethylene glycol (δ 3.50) after 19 h, a 4:96 ratio after 67 h, a ca. 1:1200 ratio after 116 h, and no detectable carbene after 236 h. (A trace peak at δ 4.78 remained unchanged throughout the experiment.) An aliquot monitored by ^1H NMR at room temperature showed a 97:3 carbene to glycol ratio after 20 h, an 83:17 ratio after 4 days, a 14:86 ratio after 48 days, and a 0.5:99.5 ratio after 103 days. Infrared monitoring of the same sample showed disappearance of the carbene complex and the formation of $[Re(CO)_6]^+$ with partial, gradual formation of $[Re(CO)_5(CH_3CN)]^+$ (ν_{CO} = 2170 (w), 2060 (s), 2030 (m) cm^{-1}).[17] Complete disappearance of the carbene complex in the infrared spectrum could not be ascertained due to a near-coincidence between a ^{13}C IR band of $[Re(CO)_6]^+$ at 1953 cm^{-1} and the major bands of both $[Re(CO)_5(CH_3CN)]^+$ and the carbene complex. Another room-temperature reaction that was 0.17 M in carbene and 1.1 M in H_2O showed a 97:3 carbene to glycol ratio after 13 days and an 87:13 ratio after 39 days, indicating that the rate of carbene hydrolysis is roughly proportional to $[carbene][H_2O]^2$ with a third-order rate constant of approximately 10^{-8} M^{-2} s^{-1} at room temperature.

Acknowledgment. We thank Drs. Kevin Kelly and Morris Bullock for helpful discussions. This work was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the United States Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Registry No. $Fe(CO)_4(\overline{COCMe_2CMe_2O})$, 54854-43-2; $Re(CO)_5CO_2CH_2CH_2Cl$, 112816-21-4; $Re_2(CO)_{10}$, 14285-68-8; $Re(CO)_5CO_2C_2H_5$, 15692-05-4; $[Re(CO)_5(\overline{COCH_2CH_2O})]^+[BF_4]^-$, 112816-23-6; $[Re(CO)_6]^+[BF_4]^-$, 63750-84-5; $[Re(CO)_3(CH_3CN)_3]^+[BF_4]^-$, 75576-70-4; $[Re(CO)_5(CH_3CN)]^+$, 29421-17-8; $ClC(=O)OCH_2CH_2Cl$, 627-11-2; ethylene glycol, 107-21-1.

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Additions and Corrections

1987, Volume 26

Graham A. Bowmaker, Peter D. W. Boyd,* Richard J. Sorrenson, Christopher A. Reed,* and John W. McDonald: Magnetic and Theoretical Studies of the Electronic Structure and Spin State of the Bis(tetrathiomolybdato)iron Trianion, $[Fe(MoS_4)_2]^{3-}$.

Page 5. The horizontal axis of Figure 3 should read $1/T$ (K^{-1}), not H/T (kg K^{-1}).—Christopher A. Reed