$CH_3OH_2^+$ and $Co(CO)_4^-$, and effectively inhibit formation of significant amounts of alkoxide.

Acknowledgment. We are grateful to the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Sloan Foundation for support of this work. G.E.W. acknowledges a research assistantship sponsored by the Materials Science Center which also provided support for the structure determination.

Registry No. $Zn[Fe(CO)_2Cp]_2$, 82246-68-2; $[Fe(CO)_2Cp]_2$, 12154-95-9; $Zn[Co(CO)_4]_2$, 16985-99-2; $[CH_3OZnCo(CO)_4]_4$, 38999-00-7; $HCo(CO)_4$, 16842-03-8; $[HOZnCo(CO)_4]_x$, 82246-70-6; $HFe(CO)_2Cp$, 35913-82-7; $[CH_3OZnFe(CO)_2Cp]_4$, 37328-46-4; $[C_2H_5OZnFe(CO)_2Cp]_4$, 37328-48-6; $[HOZnFe(CO)_2Cp]_x$, 82246-72-8; $[C_6H_5OZnFe(CO)Cp]_x$, 82246-74-0; $Zn[Mn(CO)_5]_2$, 21686-75-9; $Mn_2(CO)_{10}$, 10170-69-1; $Zn[Re(CO)_5]_2$, 33728-44-8; $Re_2(CO)_{10}$, 14285-68-8; $Hg[Re(CO)_5]_2$, 33728-46-0; $[CH_3OZnMn(CO)_5]_4$, 38999-01-8; $[C_2H_5OZnMn(CO)_5]_4$, 38999-02-9; $HMn(CO)_5$, 16972-33-1; $Zn[Mo(CO)_3Cp]_2$, 54244-98-3; $[Mo(CO)_3Cp]_2$, 12091-64-4; $[CH_3OZnMn(CO)_3Cp]_x$, 82246-76-2; $[C_2H_5OZnMo(CO)_3Cp]_x$, 82264-85-5.

Supplementary Material Available: Table VII (calculated planes), Table VIII (thermal parameters), Table XI (calculated H atom positions), and a listing of structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

Acetal and Ketal Derivatives Related to Metal Formyl and Metal Acyl Complexes

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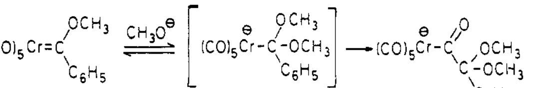
Received February 8, 1982

Addition of $NaOCH_3$ to $(C_5H_5)(CO)_2Fe{=}CH(OCH_3)^+PF_6^-$, **4**, and to $(C_5H_5)(CO)[P(C_6H_5)_3]Fe{=}CH(OCH_3)^+PF_6^-$, **6** led to the isolation of the stable acetals $(C_5H_5)(CO)_2FeCH(OCH_3)_2$, **5**, and $(C_5H_5)(CO)[P(C_6H_5)_3]FeCH(OCH_3)_2$, **7**. Similarly addition of $NaOCH_3$ to $(C_5H_5)(CO)_2Fe{=}C(OCH_3)C_6H_5^+BF_4^-$, **8**, led to the isolation of the stable ketal $(C_5H_5)(CO)_2FeC(OCH_3)_2C_6H_5$, **9**.

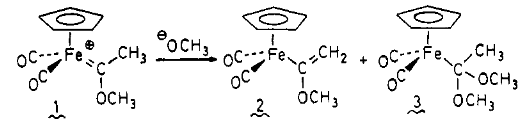
Introduction

Anionic ketal derivatives of metal acyl compounds have previously been suggested as unstable intermediates in the exchange of alkoxy groups of alkylalkoxycarbene complexes[1-3] and in the conversion of alkylalkoxycarbene complexes into (2,2-dialkoxyacyl)metal complexes.[2,3] Here we report the synthesis and isolation of stable neutral acetal and ketal derivatives related to metal formyl and metal acyl complexes. A dithioacetal complex, $(C_5H_5)(CO)_2Fe[\overline{C(H)S(CH_2)_3S}]$, and ortho ester complexes such as $(C_5H_5)(CO)_2FeC(SCH_3)_3$ have recently been reported.[4]



Results and Discussion

In the course of studying the reactions of $[(C_5H_5)(CO)_2Fe{=}C(OCH_3)CH_3]^+BF_4^-$, **1**, with methyl organometallic reagents, we found that deprotonation to give the vinyl ether $(C_5H_5)(CO)_2Fe{-}C(OCH_3){=}CH_2$, **2**, was a major product of the reaction with methyllithium.[5] In an attempt to prepare a pure sample of vinyl ether **2**, we examined the reaction of **1**[6] with $NaOCH_3$ in CH_2Cl_2 at −78 °C. In addition to vinyl ether **2**, this reaction also produced $(C_5H_5)(CO)_2FeCOCH_3$ and the dimethyl ketal $(C_5H_5)(CO)_2FeC(OCH_3)_2CH_3$, **3**, in a 55:6:39 ratio. Dimethyl ketal **3** was tentatively identified by the ^1H NMR ($CDCl_3$) spectrum of the mixture which had resonances at δ 4.84, 3.20, and 1.80 in an area ratio of 5:6:3 in addition to peaks due to **2**. Attempted purification of **3** by both vacuum sublimation and alumina chromatography failed. Similar treatment of **1** with the more hindered base potassium *tert*-butoxide led to the isolation of vinyl ether **2** in 87% yield. The related conversion of $(C_5H_5)(CO)[P(C_6H_5)_3]Fe{=}C(OCH_2CH_3)CH_3^+$ to $(C_5H_5)(CO)[P(C_6H_5)_3]FeC(OCH_2CH_3){=}CH_2$ has been reported by Davison and Reger.[9]



This observation of a mixture of compounds containing a stable ketal of a metal acyl complex led us to attempt the synthesis of pure compounds containing this new functional group by studying the reactions of methoxide with cationic iron methoxycarbene complexes which cannot be deprotonated to vinyl ether complexes.

The preparation of an acetal complex related to a metal formyl complex was achieved by addition of methoxide to $(C_5H_5)(CO)_2Fe{=}CH(OCH_3)^+PF_6^-$ (**4**).[10] The acetal complex $(C_5H_5)(CO)_2FeCH(OCH_3)_2$ (**5**) was isolated as a yellow oil in 77% yield and was characterized by ^1H and ^{13}C NMR and by IR spectroscopy. Similarly, addition of methoxide to $(C_5H_5)(CO)[P(C_6H_5)_3]Fe{=}CH(OCH_3)^+PF_6^-$ (**6**)[10] gave the acetal complex $(C_5H_5)(CO)[P(C_6H_5)_3]FeCH(OCH_3)_2$ (**7**) in 99% yield as a yellow solid. In the ^1H and ^{13}C NMR

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[1] Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390.

[2] Fischer, E. O.; Schubert, U.; Kalbfus, W.; Kreiter, C. G. *Z. Anorg. Allg. Chem.* **1975**, *416*, 135.

[3] Schubert, U.; Fischer, E. O. *Justus Liebigs Ann. Chem.* **1975**, 393.

[4] McCormick, F. B.; Angelici, R. J.; Pickering, R. A.; Wagner, R. E.; Jacobson, R. A. *Inorg. Chem.* **1981**, *20*, 4108.

[5] Casey, C. P.; Miles, W. M.; Tukada, H.; O'Conner, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761.

[6] The PF_6^-[7] and $CF_3SO_3^-$[8] salts related to **1** have been reported previously.

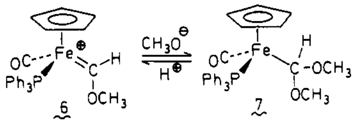
[7] Bodner, T.; LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 3292.

[8] Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979.

[9] Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237.

[10] Cutler, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 604.

spectra of **7**, separate signals were observed for the diastereotopic methoxy groups. When $NaOCD_3$ (prepared from 8 mg of Na, 0.348 mmol, in 0.45 mL of CD_3OD) was added to **6** (110 mg, 0.182 mmol) in 15 mL of CH_2Cl_2 at −78 °C, a 9:1 mixture of the diastereomers of $(C_5H_5)(CO)[P(C_6H_5)_3]FeCH(OCH_3)(OCD_3)$ was obtained. The ^1H NMR indicated that the major diastereomer had a methoxy resonance at δ 2.83 and the minor diastereomer had a methoxy resonance at δ 3.12. High stereospecificity was also observed by Gladysz[11] in deuteride addition to $(C_5H_5)(NO)[P(C_6H_5)_3]Re{=}CHC_6H_5^+$.



The acetal complex **7** can be converted back to methoxycarbene complex **6** by treatment with strong acid. For example, addition of an ether solution of **7** (43 mg, 0.088 mmol in 20 mL) to an ether solution of HBF_4 (0.16 mmol) at −10 °C led to loss of methoxide and precipation of **6** (40 mg, 84% yield). Similarly, demethoxylation of **7** was accomplished by treatment with $(C_6H_5)_3C^+PF_6^-$.

Attempts to add $NaOCH_3$ to the diphosphine adduct $C_5H_5[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe{=}CH(OCH_3)^+PF_6^-$ resulted only in the reisolation of starting material. The strongly electron-donating and bulky phosphine ligands either prevent nucleophilic attack of methoxide or make adduct formation thermodynamically unfavorable.

An example of a stable ketal complex of an iron acyl complex was also synthesized. Addition of methoxide to $(C_5H_5)(CO)_2Fe{=}C(OCH_3)C_6H_5^+BF_4^-$ (**8**)[7] led to the formation of the ketal $(C_5H_5)(CO)_2FeC(OCH_3)_2C_6H_5$ (**9**) which was isolated as yellow crystalline powder in 80% yield.

In summary, the results reported here establish that acetal and ketal derivatives of metal formyl and metal acyl complexes can be stable and readily isolated materials.

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry nitrogen by using degassed solvents. NMR spectra were recorded on JEOL MH-100, FX-60, or Brucker WH-270 spectrometers. Infrared spectra were recorded on a Beckman 4230 infrared spectrometer. Mass spectra were recorded on an AEI-MS-902 spectrometer at 70 eV.

$(C_5H_5)(CO)_2FeC(OCH_3){=}CH_2$ (2). A suspension of $NaOCH_3$ (108 mg, 2.0 mmol) in 2 mL of THF was added to a solution of **1** (644 mg, 2.0 mmol)[5,6] in 15 mL of CH_2Cl_2 at −78 °C. After evaporation of solvent under high vacuum below 0 °C, the residue was extracted with hexane to give 310 mg of a oil which was shown by ^1H NMR to be a mixture of **2** (55%), $(C_5H_5)(CO)_2FeC(OCH_3)_2CH_3$ (**3**, 39%), and $(C_5H_5)(CO)_2FeCOCH_3$ (6%). Attempted isolation of **3** either by vacuum sublimation (60 °C (10^{-5} mm)) or by chromatography on alumina led to decomposition.

A THF solution of potassium *tert*-butoxide (150 mg, 1.34 mmol) was added to a solution of **1** (409 mg, 1.27 mmol) in CH_2Cl_2 at −78 °C. Solvent was evaporated under vacuum below 0 °C, and the residue was extracted with hexane (5 × 5 mL). The hexane extract was filtered through Celite and solvent evaporated under vacuum to give pure **2** (260 mg, 87%) as a yellow oil; ^1H NMR ($CDCl_3$, 100 MHz) δ 4.80 (s, 5 H), 4.59 (d, J = 1.5 Hz, 1 H), 4.02 (d, J = 1.5 Hz, 1 H), 3.52 (s, 3 H); ^{13}C NMR (C_6D_6, 15 MHz) δ 216.2 (CO), 176.6 ($CH{=}CH_2$), 97.3 ($CH{=}CH_2$), 85.6 (C_5H_5), 56.3 (OCH_3); IR (CH_2Cl_2) 2018, 1969 cm^{-1}; exact mass 233.9979, calcd for $C_{10}H_{10}O_3Fe$ 233.9979.

$(C_5H_5)(CO)_2FeCH(OCH_3)_2$ (5). Sodium methoxide (54 mg, 1.00 mmol) in 3 mL of methanol was added to a suspension of $(C_5H_5)(CO)_2Fe{=}CH(OCH_3)^+PF_6^-$,[10] **4** (269 mg, 0.82 mmol), in 10 mL of CH_2Cl_2 at −78 °C. Solvent was evaporated under vacuum below 0 °C, and residue was extracted with hexane (5 × 5 mL). The hexane extract was filtered and evaporated under vacuum to give **5** (160 mg, 77%) as a yellow oil: ^1H NMR (C_6D_6, 100 MHz) δ 6.58 (s, 1 H, FeCH), 4.39 (s, 5 H, C_5H_5), 3.38 (s, 6 H, OCH_3); ^{13}C NMR (C_6D_6, off resonance decoupled, 15 MHz) δ 217.1 (s, CO), 116.2 (d, FeCH), 86.0 (d, C_5H_5), 54.9 (q, OCH_3); IR (CH_2Cl_2) 2002, 1952 cm^{-1}.

$(C_5H_5)(CO)[P(C_6H_5)_3]FeCH(OCH_3)_2$ (7). Sodium methoxide (25 mg, 0.46 mmol) in 2.5 mL of methanol was added to a solution of **6**[10] (215 mg, 0.36 mmol) in CH_2Cl_2 at −78 °C. Solvent was evaporated under high vacuum at room temperature. The residue was extracted with toluene (5 × 8 mL). The toluene extract was filtered through Celite and evaporated under vacuum to give **7** (173 mg, 99%) as a yellow crystalline powder: mp 160–162 °C dec; ^1H NMR ($CDCl_3$, 100 MHz) 7.3 (m, 15 H, C_6H_5), 4.69 (d, J_{PH} = 6 Hz, 1 H, FeCH), 4.42 (d, J_{PH} = 1 Hz, 5 H, C_5H_5), 3.12 (s, 3 H, diastereotopic OCH_3), 2.83 (s, 3 H, diastereotopic OCH_3); ^{13}C NMR (CD_2Cl_2, 0.02 M $Cr(acac)_3$, 15 HMz) δ 222.6 (d, J_{PC} = 31.3 Hz, CO) 136.6 (d, J_{PC} = 40.0 Hz, ipso), 134.0 and 128.2 (d, J_{PC} = 9.8 Hz, and d, J_{PC} = 8.8 Hz, ortho and meta), 129.6 (para), 125.6 (d, J_{PC} = 23.4 Hz, FeCH), 85.9 (C_5H_5), 58.7 and 55.0 (diastereotopic OCH_3); IR (CH_2Cl_2) 1904 cm^{-1}. Anal. Calcd for $C_{27}H_{27}FeO_3P$: C, 66.68; H, 5.59. Found: C, 67.11; H, 5.74.

$(C_5H_5)(CO)_2FeC(OCH_3)_2C_6H_5$ (9). A methanol solution of $NaOCH_3$ (45 mg, 0.83 mmol in 2 mL) was added to a solution of $(C_5H_5)(CO)_2Fe{=}C(OCH_3)C_6H_5^+BF_4^-$ (**8**[7]) (250 mg, 0.65 mmol), in 10 mL of CH_2Cl_2 at −78 °C. Solvent was evaporated under high vacuum below 0 °C, and the residue was dissolved in toluene. Evaporation of toluene gave **9** (170 mg, 80%) as a yellow crystalline powder: mp 97–98.5 °C; ^1H NMR ($CDCl_3$, 100 MHz) δ 7.4 (m, 5 H, C_6H_5), 4.40 (s, 5 H, C_5H_5), 3.20 (s, 6 H, OCH_3); ^{13}C NMR (CD_2Cl_2, 15 MHz) δ 217.3 (CO), 127.8 and 124.6 (ortho and meta), 125.9, 125.2, and 121.0 (ipso, para, and FeCH), 87.5 (C_5H_5), 51.3 (OCH_3); IR (CH_2Cl_2) 2000, 1955 cm^{-1}. Anal. Calcd for $C_{16}H_{16}FeO_4$: C, 58.56; H, 4.91. Found: C, 58.71; H, 5.22.

Acknowledgment. Research support from the National Science Foundation is gratefully acknowledged.

Registry No. 1, 81939-66-4; 2, 82246-54-6; 3, 82246-55-7; 4, 69621-12-1; 5, 82246-56-8; 6, 69621-16-5; 7, 82246-57-9; 8, 82246-58-0; 9, 82246-59-1; $(C_5H_5)(CO)_2FeCOCH_3$, 12108-22-4.

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