

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

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Registry No. $\text{Zn}[\text{Fe}(\text{CO})_2\text{Cp}]_2$, 82246-68-2; $[\text{Fe}(\text{CO})_2\text{Cp}]_2$, 12154-95-9; $\text{Zn}[\text{Co}(\text{CO})_4]_2$, 16985-99-2; $[\text{CH}_3\text{OZnCo}(\text{CO})_4]_2$, 38999-00-7; $\text{HCo}(\text{CO})_4$, 16842-03-8; $[\text{HOZnCo}(\text{CO})_4]_2$, 82246-70-6; $\text{HFe}(\text{CO})_2\text{Cp}$,

35913-82-7; $[\text{CH}_3\text{OZnFe}(\text{CO})_2\text{Cp}]_4$, 37328-46-4; $[\text{C}_2\text{H}_5\text{OZnFe}(\text{CO})_2\text{Cp}]_4$, 37328-48-6; $[\text{HOZnFe}(\text{CO})_2\text{Cp}]_2$, 82246-72-8; $[\text{C}_6\text{H}_5\text{OZnFe}(\text{CO})\text{Cp}]_2$, 82246-74-0; $\text{Zn}[\text{Mn}(\text{CO})_5]_2$, 21686-75-9; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; $\text{Zn}[\text{Re}(\text{CO})_5]_2$, 33728-44-8; $\text{Re}_2(\text{CO})_{10}$, 14285-68-8; $\text{Hg}[\text{Re}(\text{CO})_5]_2$, 33728-46-0; $[\text{CH}_3\text{OZnMn}(\text{CO})_5]_4$, 38999-01-8; $[\text{C}_2\text{H}_5\text{OZnMn}(\text{CO})_5]_4$, 38999-02-9; $\text{HMn}(\text{CO})_5$, 16972-33-1; $\text{Zn}[\text{Mo}(\text{CO})_3\text{Cp}]_2$, 54244-98-3; $[\text{Mo}(\text{CO})_3\text{Cp}]_2$, 12091-64-4; $[\text{CH}_3\text{OZnMn}(\text{CO})_3\text{Cp}]_2$, 82246-76-2; $[\text{C}_2\text{H}_5\text{OZnMo}(\text{CO})_3\text{Cp}]_2$, 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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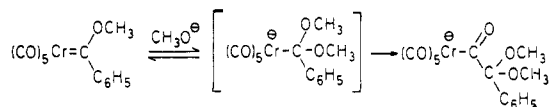
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Addition of NaOCH_3 to $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}(\text{OCH}_3)^+\text{PF}_6^-$, **4**, and to $(\text{C}_5\text{H}_5)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{Fe}=\text{CH}(\text{OCH}_3)^+\text{PF}_6^-$, **6** led to the isolation of the stable acetals $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}(\text{OCH}_3)_2$, **5**, and $(\text{C}_5\text{H}_5)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{FeCH}(\text{OCH}_3)_2$, **7**. Similarly addition of NaOCH_3 to $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{C}(\text{OCH}_3)\text{C}_6\text{H}_5^+\text{BF}_4^-$, **8**, led to the isolation of the stable ketal $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeC}(\text{OCH}_3)_2\text{C}_6\text{H}_5$, **9**.

Introduction

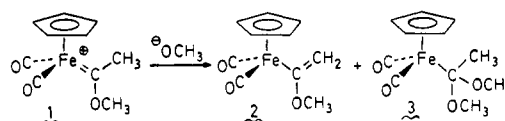
Anionic ketal derivatives of metal acyl compounds have previously been suggested as unstable intermediates in the exchange of alkoxy groups of alkylalkoxycarbene complexes¹⁻³ and in the conversion of alkylalkoxycarbene complexes into (2,2-dialkoxyacyl)metal complexes.^{2,3} Here we report the synthesis and isolation of stable neutral acetal and ketal derivatives related to metal formyl and metal acyl complexes. A dithioacetal complex, $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}[\text{C}(\text{H})\text{S}(\text{CH}_2)_3\text{S}]$, and ortho ester complexes such as $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeC}(\text{SCH}_3)_3$ have recently been reported.⁴



Results and Discussion

In the course of studying the reactions of $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{C}(\text{OCH}_3)\text{CH}_3]^+\text{BF}_4^-$, **1**, with methyl organometallic reagents, we found that deprotonation to give the vinyl ether $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{C}(\text{OCH}_3)=\text{CH}_2$, **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** with NaOCH_3 in CH_2Cl_2 at -78

$^\circ\text{C}$. In addition to vinyl ether **2**, this reaction also produced $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCOCH}_3$ and the dimethyl ketal $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeC}(\text{OCH}_3)_2\text{CH}_3$, **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 $(\text{C}_5\text{H}_5)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{Fe}=\text{C}(\text{OCH}_2\text{CH}_3)\text{CH}_3^+$ to $(\text{C}_5\text{H}_5)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{FeC}(\text{OC}_2\text{H}_5)_2=\text{CH}_2$ 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 $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}(\text{OCH}_3)^+\text{PF}_6^-$ (**4**).¹⁰ The acetal complex $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}(\text{OCH}_3)_2$ (**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 $(\text{C}_5\text{H}_5)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{Fe}=\text{CH}(\text{OCH}_3)^+\text{PF}_6^-$ (**6**)¹⁰ gave the acetal complex $(\text{C}_5\text{H}_5)(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{FeCH}(\text{OCH}_3)_2$ (**7**) in 99% yield as a yellow solid. In the ^1H and ^{13}C NMR

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(6) The PF_6^- and CF_3SO_3^- salts related to **1** have been reported previously.

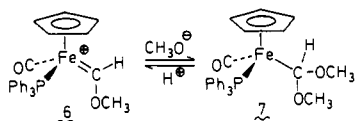
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spectra of 7, separate signals were observed for the diastereotopic methoxy groups. When NaOCD₃ (prepared from 8 mg of Na, 0.348 mmol, in 0.45 mL of CD₃OD) was added to 6 (110 mg, 0.182 mmol) in 15 mL of CH₂Cl₂ at -78 °C, a 9:1 mixture of the diastereomers of (C₅H₅)(C-O)[P(C₆H₅)₃]FeCH(OCH₃)(OCD₃) 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 Gladysz¹¹ in deuteride addition to (C₅H₅)(NO)[P(C₆H₅)₃]Re=CHC₆H₅⁺.



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 HBF₄ (0.16 mmol) at -10 °C led to loss of methoxide and precipitation of 6 (40 mg, 84% yield). Similarly, demethoxylation of 7 was accomplished by treatment with (C₆H₅)₃C⁺PF₆⁻.

Attempts to add NaOCH₃ to the diposphine adduct C₅H₅[(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂]Fe=CH(OCH₃)⁺PF₆⁻ 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 (C₅H₅)(CO)₂Fe=C(OCH₃)C₆H₅⁺BF₄⁻ (8)⁷ led to the formation of the ketal (C₅H₅)(CO)₂FeC(OCH₃)₂C₆H₅ (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 Bruker 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.

(C₅H₅)(CO)₂FeC(OCH₃)=CH₂ (2). A suspension of NaOCH₃ (108 mg, 2.0 mmol) in 2 mL of THF was added to a solution of 1 (644 mg, 2.0 mmol)^{6,8} in 15 mL of CH₂Cl₂ 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%), (C₅H₅)(CO)₂FeC(OC-

H₃)₂CH₃ (3, 39%), and (C₅H₅)(CO)₂FeCOCH₃ (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 CH₂Cl₂ 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 (CDCl₃, 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); ¹³C NMR (C₆D₆, 15 MHz) δ 216.2 (CO), 176.6 (CH=CH₂), 97.3 (CH=CH₂), 85.6 (C₅H₅), 56.3 (OCH₃); IR (CH₂Cl₂) 2018, 1969 cm⁻¹; exact mass 233.9979, calcd for C₁₀H₁₀O₃Fe 233.9979.

(C₅H₅)(CO)₂FeCH(OCH₃)₂ (5). Sodium methoxide (54 mg, 1.00 mmol) in 3 mL of methanol was added to a suspension of (C₅H₅)(CO)₂Fe=CH(OCH₃)⁺PF₆⁻ (4) (269 mg, 0.82 mmol), in 10 mL of CH₂Cl₂ 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 (C₆D₆, 100 MHz) δ 6.58 (s, 1 H, FeCH), 4.39 (s, 5 H, C₅H₅), 3.38 (s, 6 H, OCH₃); ¹³C NMR (C₆D₆, off resonance decoupled, 15 MHz) δ 217.1 (s, CO), 116.2 (d, FeCH), 86.0 (d, C₅H₅), 54.9 (q, OCH₃); IR (CH₂Cl₂) 2002, 1952 cm⁻¹.

(C₅H₅)(CO)[P(C₆H₅)₃]FeCH(OCH₃)₂ (7). Sodium methoxide (25 mg, 0.46 mmol) in 2.5 mL of methanol was added to a solution of 6¹⁰ (215 mg, 0.36 mmol) in CH₂Cl₂ 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 (CDCl₃, 100 MHz) 7.3 (m, 15 H, C₆H₅), 4.69 (d, *J*_{PH} = 6 Hz, 1 H, FeCH), 4.42 (d, *J*_{PH} = 1 Hz, 5 H, C₅H₅), 3.12 (s, 3 H, diastereotopic OCH₃), 2.83 (s, 3 H, diastereotopic OCH₃); ¹³C NMR (CD₂Cl₂, 0.02 M Cr(acac)₃, 15 MHz) 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 (C₅H₅), 58.7 and 55.0 (diastereotopic OCH₃); IR (CH₂Cl₂) 1904 cm⁻¹. Anal. Calcd for C₂₇H₂₇FeO₃P: C, 66.68; H, 5.59. Found: C, 67.11; H, 5.74.

(C₅H₅)(CO)₂FeC(OCH₃)₂C₆H₅ (9). A methanol solution of NaOCH₃ (45 mg, 0.83 mmol in 2 mL) was added to a solution of (C₅H₅)(CO)₂Fe=C(OCH₃)C₆H₅⁺BF₄⁻ (8⁷) (250 mg, 0.65 mmol), in 10 mL of CH₂Cl₂ 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 (CDCl₃, 100 MHz) δ 7.4 (m, 5 H, C₆H₅), 4.40 (s, 5 H, C₅H₅), 3.20 (s, 6 H, OCH₃); ¹³C NMR (CD₂Cl₂, 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 (C₅H₅), 51.3 (OCH₃); IR (CH₂Cl₂) 2000, 1955 cm⁻¹. Anal. Calcd for C₁₆H₁₆FeO₄: C, 58.56; H, 4.91. Found: C, 58.71; H, 5.22.

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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; (C₅H₅)(CO)₂FeCOCH₃, 12108-22-4.

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