

Iron and Molybdenum Methyldene Compounds (C₅H₅)(CO)₂FeCH₂⁺ and (C₅H₅)(CO)₃MoCH₂⁺PF₆⁻ as Alkylating Agents toward Vinyl, Allyl, and Acetyl Ligands. Preparation and Characterization of a Molybdenum (Methyleneoxy)ethyldene Iron Compound, (C₅H₅)(CO)(PPh₃)FeC(CH₃)OCH₂Mo(CO)₃(C₅H₅)⁺PF₆⁻

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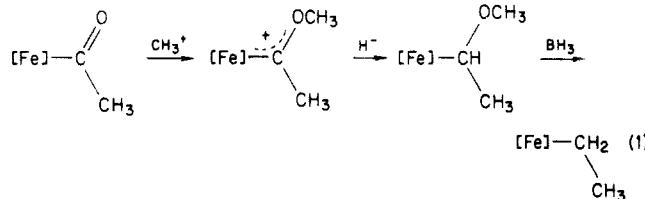
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Received July 17, 1984

The methyldene complexes Cp(CO)₂Fe=CH₂⁺ (1) and Cp(CO)₃MoCH₂⁺PF₆⁻ (2) are used as alkylating agents toward coordinated ligands. Thus, 1 adds to the uncoordinated double bonds of FpCH=CH₂ and FpCH₂CH=CH₂ (Fp = Cp(CO)₂Fe) to give the homologated Fp₂ salts [FpCH₂]₂CH⁺ and Fp[CH₂=CHCH₂CH₂Fp]⁺. The former salt arises from electrophilic attack of 1 on the vinylic β -carbon, followed by isomerization of the resulting alkylidene intermediate FpCH⁺CH₂CH₂Fp to the observed Fp₂ β -carbenium ion salt. The acetyl complex Cp(CO)(PPh₃)FeCOCH₃ (4), but not FpCOCH₃, also undergoes alkylation by 1. A partially characterized [(methyleneoxy)ethyldene]iron, Cp(CO)(PPh₃)FeC(CH₃)OCH₂Fp⁺ (16), results that readily degrades to the μ -acetyl compound Cp(CO)(PPh₃)FeC(CH₃)OFp⁺PF₆⁻ as the major product. Use of the more electrophilic 2 converts 4 to the fully characterized adduct Cp(CO)(PPh₃)-FeC(CH₃)OCH₂Mp⁺PF₆⁻ (5) (Mp = Cp(CO)₃Mo). Reactions of nucleophiles (I⁻, Cl⁻, various hydride donors) with 5 displace the starting acetyl complex 4 and leave the corresponding molybdenum methyl complex.

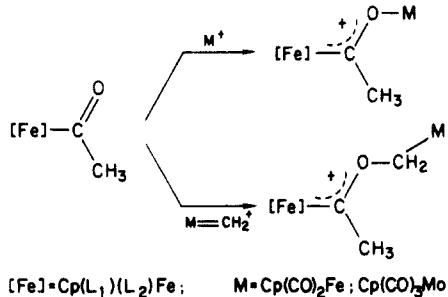
Introduction

The (η^5 -C₅H₅)(CO)₂Fe (or Fp) organometallic system and its phosphine-substituted derivatives have proved extremely useful in synthetic studies that involve reductive and other transformations of acyl ligands.¹ A variety of electrophilic alkylating agents accordingly transform the acetyl group to its α -methoxy- or ethoxyalkylidene (i.e., alkoxycarbene)^{1b,2} derivative (eq 1), which subsequently



[Fe]-Cp(L₁)(L₂)Fe:L₁, L₂=CO; L₁=CO; L₂=PPh₃; L₁, L₂=Ph₂PCH₂CH₂PPh₂
reduces (using borohydride^{2a,b,f,g} or transition-metal hy-

Scheme I. Electrophilic Activation of Acetyl Ligands



(1) Full papers are in preparation concerning the selective conversion of two carbonyls, starting with (η^5 -C₅H₅)Fe(CO)₃⁺, to the C₂ organic molecules acetaldehyde, acetic acid ester, and glycolaldehyde ether. Activated acyl ligands are used in generating the formylmethyl, (α -alkoxyformyl)methyl, and carboalkoxymethyl C₂ ligand templates that dominate much of this chemistry. For preliminary accounts: (a) Bodnar, T.; Coman, G.; LaCroce, S. J.; Lambert, C.; Menard, K.; Cutler, A. *J. Am. Chem. Soc.* 1981, 103, 2471. (b) Cutler, A.; Bodnar, T.; Coman, G.; LaCroce, S.; Lambert, C.; Menard, K. In "Catalytic Activation of Carbon Monoxide"; Ford, P., Ed.; American Chemical Society: Washington, DC, 1981; *ACS Symp. Series No.* 152, Chapter 19. (c) Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* 1982, 21, 1275. (d) Crawford, E. J.; Lambert, C.; Menard, K. P.; Cutler, A. R. *J. Am. Chem. Soc.* 1985, 107, 3130.

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dride^{2e} reagents) to an α -alkoxyalkyl ligand. Continued reduction using an electrophilic reducing agent (e.g., BH₃)^{1b,6b} or treatment of the starting acetyl group with excess B₂H₆³ produces the fully reduced alkyl functional group. Overall, activation of the acetyl ligand (as its alkoxycarbene or metal carboxonium cation) toward nucleophilic addition to the α -carbon or carbenoid carbon is required, since nucleophilic hydride donors preferentially react with ancillary carbonyls.⁴

We are interested in using electrophiles of organometallic origin to activate acyl ligands toward hydride addition at the α -carbon. These acyl-activating functionalities would prove especially interesting if their preparative chemistry could be juxtaposed with (or perhaps involved in) obtaining the acyl complexes. Projected use of two such electrophiles, the organometallic Lewis acids Cp(CO)_xM⁺ (M = Mo, x = 3, Mp⁺; M = Fe, x = 2, Fp⁺) and their methyldene compounds, in activating the acetyl complex [Fe]COCH₃ as cationic oxycarbene species is illustrated in Scheme I. Beck's group⁵ and we⁶ have

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reported a number of the former, bimetallic μ -(η^1 -*c,o*)-acetyl compounds, and in a future paper we will further elaborate their reductive chemistry.⁷ No examples, however, have been published where electrophilic methylidene compounds add onto acyl or other coordinated ligands.⁸

In this paper we report that electrophilic methylidene compounds $\text{Fp}=\text{CH}_2^+$ (1) and $\text{Mp}=\text{CH}_2^+$ (2),^{9,10} reacting analogous to organic carbocation reagents, alkylate organoiron acetyl, vinyl, and η^1 -allyl complexes. In particular, reactions of both 1 and 2 with acetyl complexes FpCOCH_3 (3) and $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCOCH}_3$ (4) (Scheme I), full characterization of a resulting Mo (methyleneoxy)-ethylidene Fe complex, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mp}^+\text{PF}_6^-$ (5), and its reactions with nucleophiles—including hydride donors—are detailed.

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere using standard syringe/septum and Schlenk-type bench-top techniques for handling moderately air-sensitive organometallics.¹¹ Infrared spectra were taken of CH_2Cl_2 solutions (0.10 mmol/1.5 mL) in a NaCl amalgam-spaced (0.10 mm) solution cell and were recorded on a Perkin-Elmer Model 297 spectrophotometer. Varian models EM-360 and XL-200 NMR spectrometers supplied the NMR spectra, which were reported as δ values in ppm downfield from internal Me_4Si . Combustion microanalyses were performed by Baron Consulting Co., Orange, CT.

Organic reagents were procured commercially and used as received. Methylene chloride was distilled under nitrogen off of P_2O_5 , and CH_3NO_2 was dried by storing (under nitrogen) over freshly activated molecular sieves, 4 Å. The *anhydrous* ether used either was taken from a freshly opened can or was distilled under nitrogen from sodium benzophenone ketyl. Silver salts AgPF_6 and AgBF_4 were used as received (as free-flowing white powders) from Ozark-Mahoning, but being very hygroscopic, they must be stored under nitrogen. Further vacuum drying of these salts at 100 °C did not lead to improved yields in the subsequent synthetic chemistry. Metal carbonyl complexes $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{OCH}_3$ and $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{Cl}$,^{1c,9a} $\text{Cp}(\text{CO})_2\text{FeCH}=\text{CH}_2$,¹² $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}=\text{CH}_2$,¹³ $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}_2\text{CH}=\text{CH}_2$,¹⁴ $\text{Cp}(\text{CO})_2\text{FeCOCH}_3$,¹⁵ $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCOCH}_3$,¹⁶ Cp

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$(\text{CO})_3\text{MoCH}_2\text{OCH}_3$ and $\text{Cp}(\text{CO})_3\text{MoCl}$,^{9a} and $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}^+$ ¹⁷ were prepared by literature procedures and judged pure by IR and NMR spectroscopy. Authentic samples of $\text{Cp}(\text{CO})_2\text{FeI}$,¹⁸ $\text{Cp}(\text{CO})_2\text{FeCH}_3$,¹⁹ $\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CH}_2)^+\text{PF}_6^-$ (6),²⁰ $\text{Cp}(\text{CO})_3\text{Fe}^+\text{PF}_6^-$,^{1c} $\text{Cp}(\text{CO})_3\text{Fe}(\text{CH}_2=\text{CHCH}_3)^+\text{PF}_6^-$ (10),¹³ $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{S}(\text{CH}_3)_2^+\text{PF}_6^-$ (9),^{21a,b} $\text{Cp}(\text{CO})_2\text{FeS}(\text{CH}_3)_2^+\text{PF}_6^-$,^{21a,c} $[\text{Cp}(\text{CO})_2\text{FeCH}_2]_2\text{CH}^+\text{PF}_6^-$ (11),²² $\text{Cp}(\text{CO})\text{Fe}(\eta^3\text{-CH}_2\text{CHCH}_2)$,^{13a} and $\text{Cp}(\text{CO})_3\text{MoCH}_3$ ²³ were available from previous studies for direct spectroscopic comparison.

Trapping of $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}_2^+\text{PF}_6^-$ (1) with Dimethyl Sulfide. In a flame-dried flask a clear CH_2Cl_2 solution (10 mL) of AgPF_6 (260 mg, 1.03 mmol) was cooled to -80 °C, and while being magnetically stirred, it was treated with $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{Cl}$ (226 mg, 1.00 mmol). This immediately produced a deep burgundy mixture, although precipitate formation was not discerned due to the dark color. This mixture, containing 1.00 mmol of $\text{Cp}(\text{CO})_2\text{FeCH}_2^+\text{PF}_6^-$ (1), was treated with excess $(\text{CH}_3)_2\text{S}$ (5 mL) over 3 min. The resulting light orange suspension, after being stirred 10 min at -78 °C, was warmed to room temperature (with no further physical changes apparent). It was dumped into excess ether (100 mL); the resulting light yellow precipitate was filtered, extracted with CH_2Cl_2 (until a gray AgCl precipitate and colorless filtrates obtained), and reprecipitated by adding to excess ether. The remaining yellow powder was vacuum dried and spectroscopically identified as the dimethyl sulfide adduct $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{S}(\text{CH}_3)_2^+\text{PF}_6^-$ (9)^{21a,c} (211 mg, 53%).

Reaction of $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}_2^+\text{PF}_6^-$ (1) with $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}=\text{CH}_2$. Excess $\text{Cp}(\text{CO})_2\text{FeCH}=\text{CH}_2$ (306 mg, 1.50 mmol) was added to a cold (-78 °C) CH_2Cl_2 solution (15 mL) containing 1.00 mmol $\text{Cp}(\text{CO})_2\text{FeCH}_2^+$. No color changes occurred over 10 min at low temperature, but on warming to 20 °C the stirred solution turned orange and gave with a yellow precipitate. This precipitate was filtered on Celite and washed with degassed acetone (2 × 15 mL). Removal of solvent (25 mL, 20 °C) from the combined acetone and CH_2Cl_2 filtrates left an orange solid; extraction with ether (5 × 20 mL) and evaporation recovered $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}=\text{CH}_2$ (168 mg, 0.82 mmol).

The remaining ether insoluble residue was dissolved in 10 mL of acetone, and the resulting brown solution was filtered slowly into excess ether (70 mL). A dark orange precipitate formed almost immediately; it was collected, washed with ether (2 × 15 mL), and dried under vacuum (10⁻² mm, 2 h). The resulting orange solid (394 mg) corresponded to a mixture of the β -metallocarbonium ion salt $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}_2]_2\text{CH}^+\text{PF}_6^-$ (11)²² (57%), $(\text{C}_5\text{H}_5)(\text{CO})\text{Fe}(\text{CH}_2=\text{CH}_2)^+\text{PF}_6^-$ (6) (yield, 8%), and $(\text{C}_5\text{H}_5)(\text{CO})_3\text{Fe}^+\text{PF}_6^-$ (8%).

Reaction of $\text{Cp}(\text{CO})_2\text{Fe}=\text{CH}_2^+$ (1) with $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}=\text{CH}_2$. $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{Cl}$ (149 mg, 0.66 mmol) was combined with AgPF_6 (167 mg, 0.66 mmol) in 8 mL of dry, degassed CH_2Cl_2 at -78 °C. A room-temperature solution of $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}=\text{CH}_2$ (192 mg, 0.66 mmol) in 2 mL of CH_2Cl_2 was then added immediately (but over 2 min) to the stirred mixture. The reaction solution remained deep red after 1 min at -78 °C, but it turned back orange (with a light yellow precipitate evident) on warming to room temperature.

The CH_2Cl_2 -insoluble material was separated on Celite pad in a Schlenk filter and was washed with acetone. These filtrates were evaporated to give light orange crystals (143 mg), which were identified by NMR spectroscopy as a mixture of $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CH}_2)^+\text{PF}_6^-$ (6) (yield 16%), $(\text{C}_5\text{H}_5)(\text{CO})_3\text{Fe}^+\text{PF}_6^-$ (19%), and $(\text{C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{CH}_2=\text{CHCH}_3)^+\text{PF}_6^-$ (10) (11%).

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The filtered reaction solution was concentrated to 5 mL on a rotary evaporator (25 mm, 20 °C) and then was added dropwise to degassed Et₂O (100 mL). A yellow solid that precipitated almost immediately was collected in a Schlenk filter, washed with Et₂O (2 × 20 mL), and then dried under a stream of nitrogen. IR and ¹H NMR spectra of this yellow powder were consistent with a mixture of (C₅H₅)(CO)₂Fe(CH₂=CHCH₃)⁺PF₆⁻ (10) (7% yield) and the bimetallic salt (C₅H₅)(CO)₂Fe[CH₂=CHCH₂CH₂Fe(CO)₂(C₅H₅)]⁺PF₆⁻ (12) (41%). An analytically pure sample of this bimetallic salt, but with the BP₄⁻ counterion, was independently prepared.

Solvent removal from the combined Et₂O filtrates and washings left a dark yellow oil (35 mg), which by ¹H NMR spectroscopy consisted of a mixture of the dimer [Cp(CO)₂Fe]₂, Cp(CO)₂FeCH₃, unreacted Cp(CO)₂FeCH₂CH=CH₂, and the η^5 -allyl complex (exo isomer only) η^5 -Cp(CO)Fe(CH₂CHCH₂) (relative intensities of π -Cp signals in NMR ca. 0.5:1.0:1.0:1.0, respectively). Bands arising from the individual components were not resolved in the IR spectrum, which showed only two strong absorbances in the terminal carbonyl region at 2004 and 1945 cm⁻¹.

Preparation of (C₅H₅)(CO)₂Fe[CH₂=CHCH₂CH₂Fe(CO)₂(C₅H₅)]⁺BF₄⁻ (12). A CH₂Cl₂ solution (150 mL) containing only (C₅H₅)(CO)₂FeFBF₃ was prepared according to Graham et al.,²⁴ from (C₅H₅)(CO)₂FeI (1.67 g, 5.50 mmol) and AgBF₄ (1.14 g, 5.86 mmol). After transfer (-80 °C) via a double-ended needle (fitted with a sintered-glass frit) to another flask, the solution was judged to contain only (C₅H₅)(CO)₂FeFBF₃ by IR spectroscopy. After adding (at 22 °C) (C₅H₅)(CO)₂FeCH₂CH₂CH=CH₂ (1.28 g, 5.50 mmol), the resulting dark orange solution did not change over 48 h.

The reaction mixture afforded an orange solid by concentrating (60 mL) under reduced pressure, filtering into excess ether (250 mL), collecting the orange precipitate, and washing it with ether (3 × 20 mL). Examination of this precipitate by ¹H NMR spectroscopy in acetone-*d*₆ indicated the presence of a second unidentified material having a Cp resonance at δ 5.32. A filtered acetone solution (20 mL) therefore was left at room temperature for 48 h to decompose this latter component to a CH₂Cl₂-insoluble material. Solvent removal from the clear solution (which had turned from orange to dark yellow) left a dark gummy residue. Its CH₂Cl₂ extracts (4 × 15 mL) upon adding dropwise into ether (200 mL) precipitated a yellow solid that was filtered, recrystallized from CH₂Cl₂-ether, and vacuum dried: 340 mg, 12% yield (based on FpI) of (C₅H₅)(CO)₂Fe[CH₂=CHCH₂CH₂Fe(CO)₂(C₅H₅)]⁺BF₄⁻ (12); IR (CH₂Cl₂) 2072, 2035 cm⁻¹ (Fp⁺), 2004, 1948 cm⁻¹ (FpR); NMR (CD₃NO₂) δ 5.60 (s, 5 H, Cp:Fp⁺), 5.15 (m, 1 H, =CH₂), 4.91 (s, 5 H, Cp:FpR), 3.79 (d, *J* = 8.0 Hz, 1 H, (E)-HC=), 3.32 (d, *J* = 14.3 Hz, 1 H, (Z)-HC=), 2.45 and 1.85–0.93 (m's, 4 H, CH₂CH₂).

Anal. Calcd for C₁₈H₁₇Fe₂O₄BF₄: C, 43.60; H, 3.46. Found: C, 43.87; H, 3.70.

Reaction of (C₅H₅)(CO)₂FeCH₂⁺PF₆⁻ (1) with (C₅H₅)(CO)₂FeCOCH₃ (3). A CH₂Cl₂ solution (15 mL) containing 0.88 mmol of Cp(CO)₂FeCH₂⁺PF₆⁻ (1) at -78 °C was treated with Cp(CO)₂FeCOCH₃ (3) (194 mg, 0.88 mmol). The mixture remained deep burgundy over 25 min at low temperature, but upon warming to 20 °C it turned orange with a light precipitate evident. Filtration left a light yellow solid that was washed with CH₂Cl₂ (2 × 5 mL) and extracted with CH₃NO₂ (3 × 8 mL). These extracts were stripped (25 mm, 20 °C), and the remaining light orange crystals (132 mg after vacuum drying 10⁻² mm for 1 h) were characterized by ¹H NMR spectroscopy as a mixture of Cp(CO)₂Fe(CH₂=CH₂)⁺ (6) (32% yield) and Cp(CO)₃Fe⁺PF₆⁻ (11%).

Solvent removal from the filtered reaction solution and combined CH₂Cl₂ washings produced an orange gummy residue, which was extracted with degassed Et₂O until the extracts were colorless (4 × 20 mL). Filtration of the combined extracts and solvent evaporation left light orange crystals of unreacted Cp(CO)₂FeCOCH₃ (153 mg recovered, 79%). The ether-insoluble red solid remaining (140 mg after drying) corresponding to a mixture of Cp(CO)₂FeC(CH₃)OFe(CO)₂Cp⁺PF₆⁻ (14)⁶ (18% yield) [IR (CH₂Cl₂) 2067, 2020 cm⁻¹ (FpO), 2043, 1994 cm⁻¹ (FpC); NMR (CD₃NO₂) δ 5.42 (s, 5 H, Cp:FpO), 5.03 (s, 5 H, Cp:FpC), 2.61 (s,

3 H, CH₃)] and a second uncharacterized material [NMR (C₃NO₂) δ 5.30]. (Assuming that this second material is Cp(CO)₂Fe⁺PF₆, then its yield would be ca. 6%). After excess (n-butyl)₄N⁺I⁻ was added to this fraction, it quantitatively (by IR spectroscopy) converted to a 3:1 mixture of Cp(CO)₂FeI and Cp(CO)₂FeCOC₂H₅ (3).

Reaction of (C₅H₅)(CO)₂FeCH₂⁺PF₆⁻ (1) and (C₅H₅)(CO)(PPh₃)FeCOCH₃ (4). Cp(CO)(PPh₃)FeCOCH₃ (4) (545 mg, 1.20 mmol) was quickly added to a cold (-78 °C) CH₂Cl₂ solution (20 mL) containing (Cp(CO)₂FeCH₂⁺PF₆⁻ (1) (1.20 mmol), and the stirred mixture was brought to room temperature. An IR spectrum of the light orange supernatant, after the resulting yellow precipitate had settled, was consistent with Cp(CO)(PPh₃)FeC(CH₃)OCH₂Fe(CO)₂Cp⁺PF₆⁻ (16) [IR 2022, 1967 cm⁻¹ (Fp), 1980 cm⁻¹ (CpFe(CO)PPh₃)] as the major product (50%), although Cp(CO)₂FeCH₃ (25%) and unreacted 4 (25%) were also present. When an aliquot was treated with excess (n-butyl)₄N⁺I⁻, no significant color changes occurred, but an IR scan after 10 min established conversion of the carbenoid complex to a mixture of 4 and Cp(CO)₂FeCH₂I (ν (CO) 2021, 1966 cm⁻¹). (IR spectral assignments for Cp(CO)₂FeCH₂I are by comparison with Cp(CO)₂FeCH₂Cl.)

The original reaction mixture was filtered, and the remaining precipitate was washed with CH₂Cl₂ (10 mL) and then extracted with acetone (2 × 15 mL). These acetone extracts, after evaporating off solvent, left a yellow crystalline solid (115 mg) that assayed by IR and NMR spectroscopy as a mixture of Cp(CO)₂Fe(CH₂=CH₂)⁺ (6) (17% yield) and Cp(CO)₃Fe⁺PF₆⁻ (11%).

Combined CH₂Cl₂ filtrates from the reaction were concentrated to 10 mL and added to excess ether (150 mL). A light brown precipitate, which had formed almost immediately, was collected, recrystallized from CH₂Cl₂-ether (15–100 mL), and vacuum dried. The brown solid so obtained (359 mg) was deduced by IR spectroscopy to be a mixture of two bimetallic salts: Cp(CO)(PPh₃)FeC(CH₃)OCH₂Fe(CO)₂Cp⁺PF₆⁻ (16) (23% yield) and Cp(CO)(PPh₃)FeC(CH₃)OFe(CO)₂Cp⁺PF₆⁻ (17)⁶ (15%) [IR (CH₂Cl₂) 2062, 2006 cm⁻¹ (FpO), 1942 cm⁻¹ (Cp(CO)(PPh₃)Fe)]. Treatment of an aliquot with (n-butyl)₄N⁺I⁻ gave 4 and both Cp(CO)₂FeCH₂I and Cp(CO)₂FeI as the only detectable products. Numerous attempts at recording NMR spectra of this material in acetone-*d*₆ or CD₃NO₂, however, resulted in paramagnetic broadening and/or sample decomposition. For example, NMR spectra of acetone-*d*₆ solutions (which remained homogeneous) indicated only a mixture (1:1) of [Cp(CO)₂Fe]₂ and Cp(CO)(PPh₃)FeC(CH₃)OFe(CO)₂Cp⁺ (17)⁶ [NMR (acetone-*d*₆) δ 7.42 (m, 15 H, PPh₃), 5.29 (s, 5 H, CpFe), 4.60 (d, *J* = 1.5 Hz, 5 H, CpFe), 2.63 (s, 3 H, CH₃)]. Subsequent solvent evaporation and IR spectral examination of the residue confirmed both the absence of Cp(CO)(PPh₃)FeC(CH₃)OCH₂Fe(CO)₂Cp⁺ (16) and the presence of [Cp(CO)₂Fe]₂ and 17.

Et₂O filtrates and washings obtained during isolation of the above brown solid were combined, and solvent was carefully removed (25 mm, 20 °C) to leave a dark brown gummy residue. This was extracted with degassed ether (5 × 20 mL) until the extracts were colorless. Solvent removal from the filtered Et₂O washings left a dark yellow oil (267 mg) which was identified (IR and ¹H NMR spectroscopy) as a mixture of Cp(CO)₂FeCH₃ (yield 23%) and Cp(CO)(PPh₃)FeC(CH₃)OCH₂Fe(CO)₂Cp⁺ (39%).

Reaction of (C₅H₅)(CO)₃MoCH₂⁺PF₆⁻ (2) and (C₅H₅)(CO)₂FeCOCH₃ (3). To a cold (-78 °C) CH₂Cl₂ solution (15 mL) of AgPF₆ (202 mg, 0.80 mmol) was added Cp(CO)₃MoCH₂Cl (236 mg, 0.80 mmol). The vigorously stirred mixture was maintained at -78 °C for 5 min, after which Cp(CO)₂FeCOCH₃ (3) (176 mg, 0.80 mmol) was added and the resulting yellow suspension was stirred (-78 °C) for another 25 min. No color changes occurred, but while being warmed to room temperature the reaction turned dark yellow-green with a gray precipitate evident. This solid after isolation contained no CH₃NO₂-soluble metal carbonyl species.

The filtered reaction solution when added slowly to degassed Et₂O (150 mL) resulted in a beige precipitate. This was collected, washed with Et₂O (2 × 20 mL), and then dried under a stream of nitrogen (130 mg). Its IR spectrum (CH₂Cl₂) indicated a mixture (ca. 4:5) of unidentified Cp(CO)₃Mo(solvate)⁺ and Cp(CO)₂FeC(CH₃)OMo(CO)₃Cp⁺PF₆⁻ (15)⁶ [IR (CH₂Cl₂) 2068, 1975 cm⁻¹ (Cp(CO)₃Mo), 2044, 1933 cm⁻¹ (Fp); NMR (CD₃NO₂) δ 6.08 (s, 5 H, CpMo), 5.06 (s, 5 H, CpFe), 2.61 (s, 3 H, CH₃)]. Treating

the IR sample with excess $(n\text{-butyl})_4\text{N}^+\text{I}^-$ converted it to a mixture of $\text{Cp}(\text{CO})_3\text{MoI}$ and **3**. Evaporation of solvent from the combined Et_2O filtrates (25 mm, 20 °C) left a dark orange, oily residue; it was identified by IR spectroscopy as $\text{Cp}(\text{CO})_2\text{FeCOCH}_3$ (**3**) (recovered 134 mg, 76%).

Preparation of $(\text{C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)^+\text{PF}_6^-$ (5). To a stirred solution of AgPF_6 (1.51 g, 5.97 mmol) in dry, degassed CH_2Cl_2 (90 mL) at -78 °C was added 1 equiv of $\text{Cp}(\text{CO})_3\text{MoCH}_2\text{Cl}$ (1.76 g, 5.97 mmol). $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{O})\text{CH}_3$ (**4**) (2.71 g, 5.97 mmol) was then quickly added, and the orange mixture (containing undissolved $\text{Cp}(\text{CO})_3\text{MoCH}_2\text{Cl}$) was brought to room temperature. During this operation the $\text{Cp}(\text{CO})_3\text{MoCH}_2\text{Cl}$ dissolved and a flocculent gray solid precipitated. The dark yellow mixture was then filtered and concentrated (25 mm, 20 °C) to 30 mL on a rotary evaporator. (Nitromethane washing of the gray precipitate removed no soluble metal carbonyl-containing material.) Dropwise addition of the concentrated filtrate into ether (200 mL) precipitated a golden yellow solid, which was filtered, washed with ether, recrystallized from CH_2Cl_2 -ether, and vacuum dried. The resulting yellow powder (3.45 g, 68%) of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mo}(\text{CO})_3\text{Cp}^+\text{PF}_6$ (**5**) was analytically pure: IR (CH_2Cl_2) 1979 cm^{-1} [$\text{CpFe}(\text{CO})(\text{PPh}_3)$], 2036, 1955 br cm^{-1} [$\text{CpMo}(\text{CO})_3$]; NMR (acetone-*d*₆) δ 7.51 (br s, 15 H, PPh_3), 5.56 (s, 5 H, MoCp), 5.01 (d, *J* = 1.5 Hz, 5 H, CpFe), 4.82 (br s, 2 H, OCH_2), 2.68 (s, 3 H, CH_3); ¹³C{¹H} NMR (CH_2Cl_2) δ 237.28 (Mo-CO cis), 228.08 (Mo-CO trans), 133-129 (PPh_3), 94.00 (CpMo), 87.76 (CpFe), 72.48 (CH_2), 45.04 (CH_3). The latter two assignments were confirmed by gated decoupling study.

Anal. Calcd for $\text{C}_{35}\text{H}_{30}\text{FeMoO}_5\text{P}_2\text{F}_6$: C, 48.98; H, 3.52. Found: C, 48.90; H, 3.78.

Although stable as a solid, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mo}(\text{CO})_3\text{Cp}^+$ (**5**) proved unstable in solution under all conditions examined. In acetone solutions (NMR spectral studies) it degraded to several diamagnetic materials of unknown composition (ca. 30% within 1 h), whereas in nitromethane it provided the bimetallic acetyl $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OMo}(\text{CO})_3\text{Cp}^+$ (**18**)⁶ as the major product. Even CH_2Cl_2 solutions are unstable.

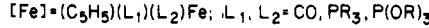
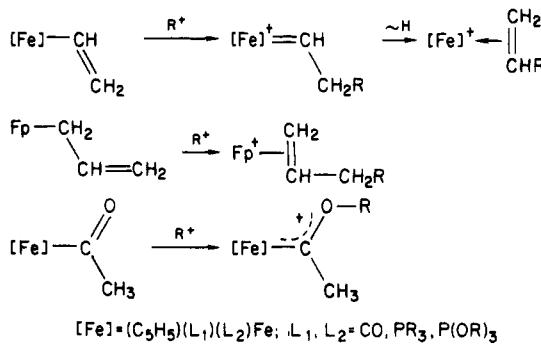
A clear yellow CH_2Cl_2 solution (4 mL) of **5** (172 mg, 0.20 mmol) upon sitting 20 h (20 °C) under nitrogen turned clear orange. Its IR spectrum indicated the absence of starting material. Dropwise addition of the reaction solution into degassed Et_2O (50 mL) precipitated a red solid that was filtered, recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, and dried under a stream of nitrogen. The resulting red powder was the bimetallic acetyl complex $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OMo}(\text{CO})_3\text{Cp}^+\text{PF}_6^-$ (**18**)⁷ (yield 66 mg, 39%): IR (CH_2Cl_2) 2060, 1972 cm^{-1} (br); NMR (acetone-*d*₆) δ 7.44 (m, 15 H, PPh_3), 6.13 (s, 5 H, CpMo), 4.75 (d, *J* = 1.5 Hz, 5 H, CpFe), 2.41 (s, 3 H, CH_3). Accordingly, a CH_2Cl_2 solution of this fraction upon treatment with excess $(n\text{-butyl})_4\text{N}^+\text{I}^-$ rapidly and quantitatively converts to an equimolar mixture of $\text{Cp}(\text{CO})_3\text{MoI}$ and $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCOCH}_3$ (**4**).

The initial ether/ CH_2Cl_2 filtrates were combined and evaporated, leaving an orange oily residue; this was extracted with degassed Et_2O (5 × 10 mL) until the extracts were colorless. (The small amount of an orange, Et_2O -insoluble solid remaining assayed by IR spectroscopy as **18**.) The Et_2O washings after filtering, evaporating solvent, and vacuum drying left an orange gummy residue (63 mg), which corresponding to a 1:1 mixture of **4** and $\text{Cp}(\text{CO})_3\text{MoCH}_3$ (yields 44% each).

Reaction of $(\text{C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mo}(\text{CO})_3(\text{C}_5\text{H}_5)^+\text{PF}_6^-$ (5) with $\text{PhCH}_2\text{NEt}_3^+\text{Cl}^-$. $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mo}(\text{CO})_3\text{Cp}^+\text{PF}_6^-$ (**5**) (343 mg, 0.40 mmol) and $\text{PhCH}_2\text{NEt}_3^+\text{Cl}^-$ (137 mg, 0.60 mmol) were combined in dry, degassed CH_2Cl_2 (6 mL). The resulting dark yellow solution remained clear but lightened over 2 h. Solvent was then removed, and the residue was extracted with degassed Et_2O (7 × 10 mL) until the filtrates were colorless. Evaporation of solvent left a yellow oil (292 mg after vacuum drying), which by ¹H NMR spectroscopy assayed as a mixture of $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCOCH}_3$ (**4**) and $\text{Cp}(\text{CO})_3\text{MoCH}_2\text{Cl}$ (97% yields).

Attempted Reduction of $(\text{C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5^+\text{PF}_6^-$ (5) with $\text{Ph}_3\text{PMe}^+\text{BH}_3\text{CN}^-$. $\text{Ph}_3\text{PMe}^+\text{BH}_3\text{CN}^-$ (95 mg, 0.30 mmol) was added to a dark yellow CH_2Cl_2 solution (5 mL) of **5** (257 mg, 0.30 mmol). After 60 min at room temperature, the reaction solution had lightened and its'

Scheme II. Alkylation of Vinyl, η^1 -Allyl, and Acetyl Ligands



IR spectrum indicated the absence of starting material. This solution then was diluted with 5 mL of CH_2Cl_2 and was added to degassed pentane (100 mL). A brown oil separated immediately; after the mixture was cooled to -78 °C, the supernatant (light orange) was decanted. (An IR spectrum of the petrol immiscible oil showed no bands in the terminal carbonyl region.) Evaporation of solvent from the petrol/ CH_2Cl_2 solution (25 mm, 20 °C) left a yellow-orange gum that was extracted with degassed petrol until the extracts were colorless (5 × 20 mL). (A brown solid which remained also contained no metal carbonyl-containing organometallics, as demonstrated by IR spectroscopy.) Solvent removal from the filtered petrol extracts left an orange residue (180 mg), which was identified as a 1:1 mixture of $\text{Cp}(\text{CO})_3\text{MoCH}_3$ and the acetyl complex $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCOCH}_3$ (**4**) (84% yields).

Similar reactions between $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mo}(\text{CO})_3\text{Cp}^+\text{PF}_6^-$ (**5**) and $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$ (20 °C, 4 h) or a THF solution of $\text{LiHB}(\text{CH}_2\text{CH}_3)_3$ (-78 °C, fast) afforded essentially the same results: quantitative conversion to $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCOCH}_3$ (**4**) and $\text{Cp}(\text{CO})_3\text{MoCH}_3$. In contrast, a THF solution of $\text{BH}_3\text{-THF}$ does not react with **5** over 3 h (20 °C).

Results and Discussion

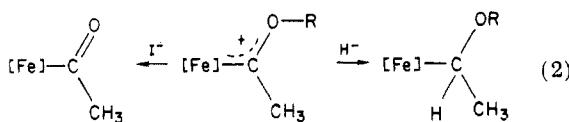
General Aspects. This study had two objectives. First, the use of methylene complexes **1** and **2** as alkylating agents toward organoiron vinyl, allyl, and acetyl complexes was investigated. These reactions parallel those depicted in Scheme I, $\text{R} = \text{CH}_2\text{Fp}$ and CH_2Mp . Second, the potential of acetyl complexes so alkylated as [(metallo-methylene)oxy]alkylidene compounds to add hydride at the acyl carbon was evaluated.

Neutral vinyl, η^1 -allyl, and acetyl complexes are particularly susceptible to electrophilic attack at the ligand unsaturation. Scheme II summarizes reactions observed when carbocationic alkylating agents add to these ligands coordinated as Cp organoiron complexes. The alkylidene-to-alkene isomerization (subsequent to electrophilic attack at the vinylic β -carbon) has precedent.^{28-1,25} With Fp- η^1 -allyl complexes, many electrophiles, including carbocationic alkylating agents, add at the allylic γ -carbon and directly produce the indicated η^5 -alkene compounds.^{13b} The alkoxyalkylidene compounds that result from alkylating an acetyl ligand typically are stable thermodynamically and do not isomerize to their η^2 -vinyl ether compounds.²⁶

Nucleophiles react with the alkoxyalkylidene complexes by two independent pathways (eq 2). Reactions with

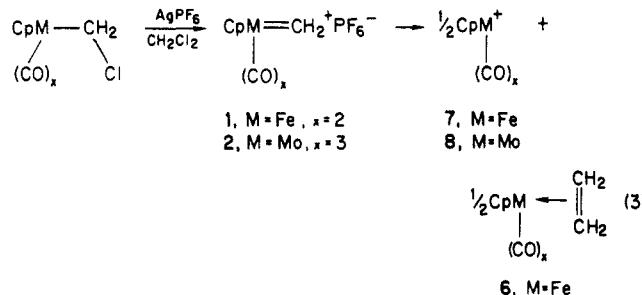
(25) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* 1972, 94, 4354. Klemarczyk, P.; Rosenblum, M. *J. Org. Chem.* 1978, 43, 3488. Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* 1980, 102, 2455. Marten, D. C. *J. Chem. Soc., Chem. Commun.* 1980, 341; *J. Org. Chem.* 1981, 46, 5422. Bates, D. J.; Rosenblum, M.; Samuels, S. B. *J. Organomet. Chem.* 1981, 209, C55.

(26) An exception should be noted. α, β -Dialkoxyethylidene salts $\text{Fp}-\text{CH}(\text{OR})\text{CH}_2\text{OR}^+$ irreversibly rearrange at room temperature to their corresponding η^2 -*cis*- α, β -dialkoxyethylene compounds $\text{Fp}[\text{CH}(\text{OR})=\text{CH}(\text{OR})]^+$. Bodnar, T.; Crawford, E.; Cutler, A., manuscript submitted for publication.



iodide and with borohydride reagents thus illustrate de-alkylation to the starting acyl functionality vs. nucleophilic addition at the α -carbon, respectively.^{2a,b,27} This dual reactivity previously has been rationalized by Davison,^{2b} using the delocalized carboxonium structure illustrated for these carbene compounds.

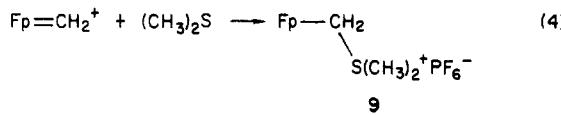
Both FpCH_2^+ (1) and MpCH_2^+ (2) methylidene salts used in this study are conveniently generated in CH_2Cl_2 solution by halide abstraction from their chloromethyl complexes at -80°C (eq 3).^{9a} Even at -80°C , 1 and 2 are



best regarded as transient intermediates, each disproportionating into its η^2 -ethylene salt plus organometallic Lewis acid Fp^+ or Mp^+ .^{9a,b,28} A plausible mechanism for this disproportionation reaction has been advanced.²⁹

The methylidene salt 1 nevertheless readily reacts with alkenes and with carbon monoxide. Building upon Pettit's early observations with 1,^{9a} the Brookhart,^{2f} Helquist,^{2i,21b} and Casey^{2h} research groups have been especially successful in transferring alkylidene groups from these organoiron alkylidene salts to a wide variety of olefins. The mechanism favored for this cyclopropanation reaction entails electrophilic attack of 1 on the alkene followed by ring closure and ejection of Fp^+ (7).³⁰ We also reported that 1 adds exogenous CO (as opposed to ligated CO via a ligand migration reaction) to the methylidene ligand and gives the stable $\eta^2\text{-C,C-ketene}$ compound $\text{Fp}(\text{CH}_2=\text{C=O})^+\text{PF}_6^-$.³¹ Such reactivity toward alkenes and CO is in keeping with the description of 1 (and related electrophilic alkylidene complexes) as metal-stabilized α -carbenium ions⁸ and hence potential carbocationic alkylating agents.

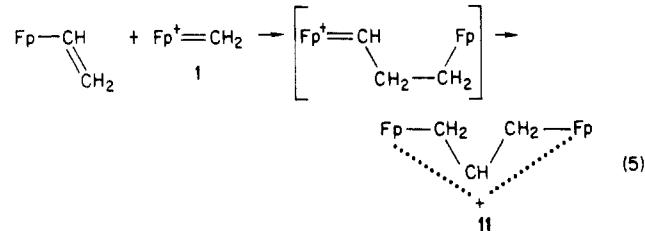
We established that $\text{Fp}=\text{CH}_2^+ \text{PF}_6^-$ (1) is trapped as its dimethyl sulfide adduct 9 (eq 4) in over 50% yield—it



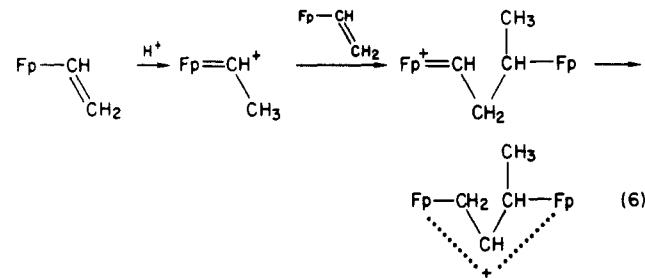
made no difference whether the Me_2S was present before

or after 1 was generated. The sulfonium salt complex 9 was prepared previously by methylating $\text{FpCH}_2\text{SCH}_3$.^{21b} Under our conditions for trapping 1 as 9, none of the known FpSMe_2^+ salt was detected.^{21a,c} This salt, which would have resulted from trapping the disproportionation product Fp^+ 7, was independently prepared by displacing tetrahydrofuran from $\text{Fp}(\text{THF})^+\text{PF}_6^-$.^{21a} Although we cannot account for the disappointing conversion of 1 to 9, clearly 1 can be trapped as another organometallic complex before it disproportionates.

Alkylation of Fp Vinyl and Fp Allyl with $\text{FpCH}_2\text{PF}_6^-$ (1). Reaction between Fp vinyl and $\text{FpCH}_2^+\text{PF}_6^-$ (1) produces the $\text{Fp}_2\beta$ -carbonium ion 11 (57% yield), which also contains small amounts (in 8% yields) of $\text{Fp}(\text{CH}_2=\text{CH}_2)^+$ (6) and FpCO^+ in the ether-insoluble fraction. Bimetallic 11 previously has been prepared either by abstracting hydride from $\text{FpCH}_2\text{CH}_2\text{CH}_2\text{Fp}^{22a}$ or by adding Fp^+ (7) (generated thermally from its η^2 -isobutylene complex) to Fp η^1 -allyl.^{22b} In the current study, 11 derives from electrophilic attacking of 1 at the vinylic β -carbon and rearrangement of the resulting γ -Fp-propylidene-Fp $^+$ intermediates (eq 5).

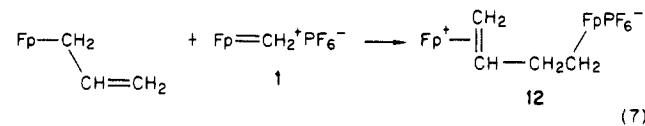


A pathway analogous to that in eq 5 was postulated for the reaction of Fp vinyl with 0.5 equiv of acid.^{2g} The Fp(ethylidene)⁺ derived from protonating Fp vinyl (eq 6)



alkylates Fp vinyl at the β -carbon, and the resulting Fp_2 alkylidene salt rearranges to the observed metallo- β -carbonium ion. Related examples of $\text{Fp}(\text{alkylidene})^+$ -to- $\text{Fp}(\text{alkene})^+$ ligand isomerization likewise have been documented.²⁵

Fp methylidene 1 also alkylates the uncoordinated double bond on **Fp** η^1 -allyl and gives the **Fp**₂ butene salt 12 (eq 7) in 41% yield. No 11, the anticipated product of



of adding just Fp^+ to the allylic double bond, was detected. Complex 12 is new, although its next higher homologue $\text{Fp}-\eta^2-(\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{Fp})^+$ was previously characterized.^{22b} Since it was not feasible to completely separate 12 from the propene salt 10 (resulting from protonation of Fp allyl), 12 was independently prepared. Thus, FpFBF_3^{24} metalated $\text{FpCH}_2\text{CH}_2\text{CH}=\text{CH}_2^{14}$ and produced analytically pure 12 as its BF_4^- salt. The reason for the low yield of 12 from the reaction is uncertain, but it is worth noting that more traditional procedures for coor-

(27) Cutler, A. R. *J. Am. Chem. Soc.* 1979, 101, 604.

(28) Ancillary phosphine substituents help in stabilizing these and related alkylidene compounds. For example, the corresponding methylidene salts $\text{Cp}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Fe}=\text{CH}_2^+ \text{PF}_6^{-28a}$ and $\text{Cp}(\text{CO})_2(\text{PPh}_3)\text{Mo}=\text{CH}_2^+ \text{AsF}_6^{-28b}$ have been spectroscopically characterized. The disproportionation reaction of the latter was also described. (a) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* 1980, 102, 1203. (b) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* 1982, 1, 760.

(29) Patton, A. T.; Strouse, C. E.; Knobler, C. B.; Gladysz, J. A. *J. Am. Chem. Soc.* 1983, 105, 5804.

(30) Brookhart, M.; Kegley, S. E.; Husk, G. R. *Organometallics* 1984, 3, 650.

(31) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* 1983, 105, 5926.

Table I. Selected Spectral Data (C_5H_5)(CO)(PPh₃)FeC(CH₃)OCH₂Mo(CO)₃(C₅H₅)⁺PF₆⁻ (5) and Related Complexes

compound	IR(CH ₂ Cl ₂) ν (CO), cm ⁻¹		¹ H NMR δ		
	FeCO	Mo(CO) ₃	CpFe	CpMo	COCH ₃
$CpFe(C(CH_3)OCH_2Mp^+)_2$	1979	2033 1955 (br)	4.96	5.57	2.85 ^a
$CpFe(C(CH_3)_2OCH_2CH_3)^+PF_6^-$	1986		4.89		2.79 ^b
$CpFe(C(CH_3)_2OMp^+PF_6^-)_2$	1972	2051 1972	4.66	5.88	2.40 ^a
$CpFe(C(CH_3)_2=O)_2$	1916		4.43		2.32 ^c
$CpMo(CH_2OCH_3)_2$		2020 1931 (br)		5.33	c
$CpMo(THF)^+PF_6^-$		2070 1985 (br)		6.10	a

^a Recorded in CD₃NO₂. ^b Recorded in CF₃CO₂H. ^c Recorded in CDCl₃.

dinating alkenes to Fp⁺ (using labile isobutylene^{13b} or (THF)Fp⁺³² intermediates) invariably transformed FpCH₂CH₂CH=CH₂ into intractable reaction residues.

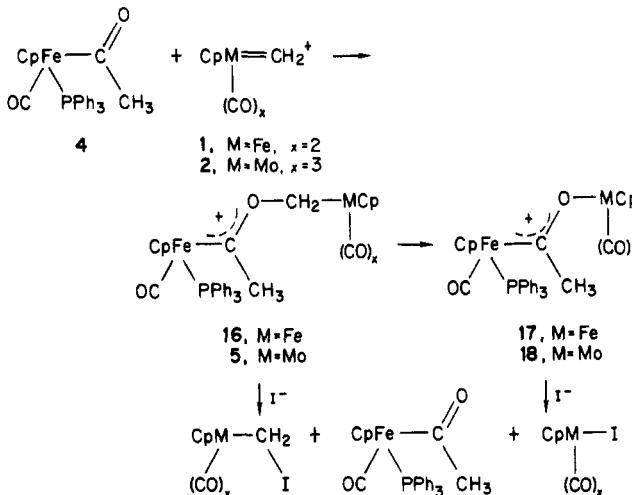
The structure of 12 represents a superposition of non-interacting Fp(η^2 -1-butene)⁺ and Fp- η^1 -alkyl centers on one molecule. Compound 12 differs from 11 in that distinct Fp centers, analogous to those of Fp ethyl and on Fp(1-butene)⁺, are easily identified. The chemical shifts and especially the splitting pattern of the geminal vinylic hydrogens on 12, furthermore, closely match those on Fp(1-butene)⁺ or on the propene salt 10.^{12b} In contrast, IR and ¹H NMR spectral values for 11, a delocalized Fp₂ β -carbonium ion possessing electronically equivalent Fp centers in solution,³³ are intermediate between those of Fp-ethyl and of η^2 -1-butene compounds.

Reactions of FpCH₂⁺ (1) and MoCH₂⁺ (2) with the Acetyl Complexes Cp(CO)(L)FeCOCH₃ (L = CO and PPh₃). Both FpCH₂⁺ (1) and MoCH₂⁺ (2) were used in attempts to alkylate the acetyl complexes FpCOCH₃ (3) and Cp(CO)(PPh₃)FeCOCH₃ (4). The molybdenum compound 2 supplied a more electrophilic methylidene center and perhaps a more reactive alkylating agent. This expectation agrees with numerous observations from synthetic studies employing Fp⁺ (7) and Mp⁺ (8) Lewis acids, in which 8 proved to be more reactive than 7 (under comparable reaction conditions).⁶

Neither methylidene salt, however, formed a stable adduct with FpCOCH₃ (3). In both reactions nearly 80% of 3 was recovered, with the remaining 3 largely bound as its bimetallic μ -(η^1 -c,o)-acetyl compounds Cp(CO)₂FeC(CH₃)OFp⁺ (14) and Cp(CO)₂FeC(CH₃)OMp⁺ (15).⁶ We cannot assign the origin of these bimetallic salts. They could derive either from the desired Fp or Mp (methylenoxy)ethylidene salt subsequently degrading (vide infra), or from the methylidene salt 1 (or 2) first decomposing to Fp⁺ (7) [or Mp⁺ (8)] and then trapping 3. Fortunately, reactions of 1 and 2 with the PPh₃-substituted acetyl complex proved more informative.

Cp(CO)(PPh₃)FeCOCH₃ (4), upon mixing with FpCH₂⁺ (1), affords the desired alkylation product Cp(CO)(PPh₃)FeC(CH₃)OCH₂Fp⁺PF₆⁻ (16), although it was only partially characterized in solution (Scheme III). As elaborated in the experimental, the initial CH₂Cl₂ reaction solution contained 50% of 16; its reaction with iodide

Scheme III. Preparation and Reactions of Bimetallic (Methylenoxy)ethylidene



clearly produced the starting acetyl 4 and FpCH₂I.

Upon sitting or upon attempted workup, 16 degraded to a mixture containing the μ -acetyl compound Cp(CO)(PPh₃)FeC(CH₃)OFp⁺ (17) (which is also CH₂Cl₂-soluble, ether-insoluble). Reaction with iodide accordingly gave a mixture of FpCH₂I and FpI. (The FpI originates in the facile displacement of iron acetyl complexes from their bimetallic μ -(η^1 -C,O) derivatives with iodide.⁶) Attempts to get NMR spectra of 16 were continually thwarted by paramagnetic broadening; this and the observation that Fp₂ is the other major decomposition product of 16 suggest the presence of paramagnetic intermediates in the degradative chemistry. Furthermore, the noteworthy absence of Fp(CH₂=CH₂)⁺ (6), as a disproportionation byproduct of 1, also indicates complex decomposition pathways other than simple dissociation of 16 to starting acetyl plus 1. Therefore, we conclude that 1 indeed alkylates the acetyl complex 11, but the 1:1 adduct 16 degrades via an unknown process to its bimetallic μ -acetyl compound 17.

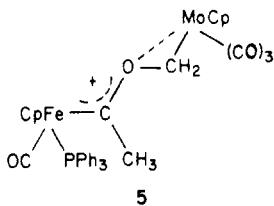
The molybdenum methylidene salt 2, on the other hand, converts the more nucleophilic² Cp(CO)(PPh₃)FeCOCH₃ (4) to its unambiguously characterized 1:1 adduct Cp(CO)(PPh₃)FeC(CH₃)OCH₂Mp⁺PF₆⁻ (5) (Scheme III). This CH₂Cl₂-soluble, ether-insoluble yellow salt was isolated in 68% yield; although stable as a solid, it slowly decomposed in solution. Identity of 5 rests on the results of an elemental analysis, of IR and ¹H and ¹³C NMR

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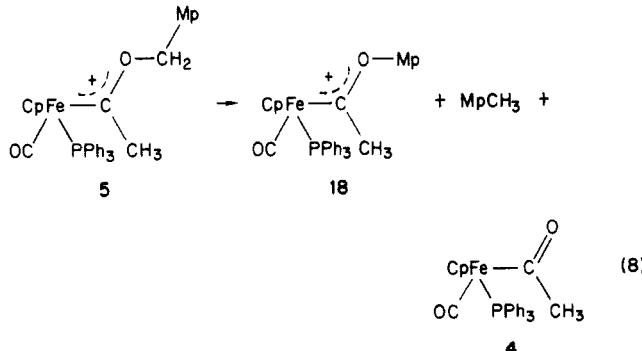
spectral examination, and of degradative studies with nucleophiles.

Solution IR and ^1H and ^{13}C NMR spectral data for 5 are in accord with charge delocalization over both Fe and Mo centers. Table I collects this data, which also includes that of the acetyl complex 4 and its ethoxy carbene $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{CH}_3^+\text{PF}_6^-$ and bimetallic acetyl 18 derivatives. Inasmuch as IR $\nu(\text{CO})$ and ^1H NMR δ (Cp) spectral data reflect the charge density on the iron centers of these complexes,³⁴ 5 also can be considered as an activated acetyl derivative. Much less of the positive charge, however, resides on the Mo center of 5 than on 18. IR $\nu(\text{CO})$ and NMR δ (Cp) spectral information on 5 nevertheless indicate a more electron-deficient Mo center than can be attributed to $\text{MpCH}_2\text{OCH}_3$ [$\nu(\text{CO})$ 2020, 1931 cm^{-1} ; NMR δ 5.33 (Cp)]. ^{13}C NMR spectral data for 5 (see Experimental Section) are as expected for this structure, with the assignments (including the 1:2:1 intensity relationship for the CO absorptions) resembling those of 18. Overall, the spectral data for 5 is consistent with partial removal of charge from molybdenum via a " β -interaction"³⁵ and the following delocalized carboxonium salt structure:

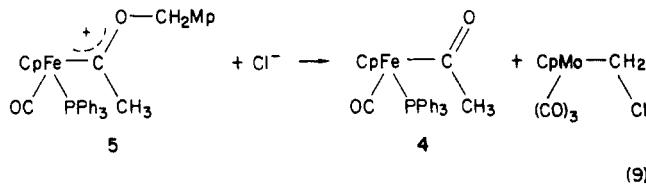


Unfortunately 5 possesses a limited lifetime in solution, although qualitatively it is much longer lived than 16. In CH_2Cl_2 , 5 degrades cleanly via unknown pathways to an approximately 1:1:1 mixture of 18,⁶ 4, and MpCH_3 (eq 8). These results resemble those for the decomposition for 16, and again we note the absence of an η^2 -ethylene compound, $\text{Mp}(\text{CH}_2=\text{CH}_2)^+$. This would have resulted from disproportionation of any $\text{Mp}=\text{CH}_2^+$ (2) that resulted from 5 dissociating. Also, degradation of 5 in polar solvents (acetone and CH_3NO_2) is both more facile and more complicated in terms of the variety of unknown materials, all in low concentrations, that are generated.

The (methyleneoxy)ethylidene salt 5, however, does react readily with nucleophiles in CH_2Cl_2 solution. A

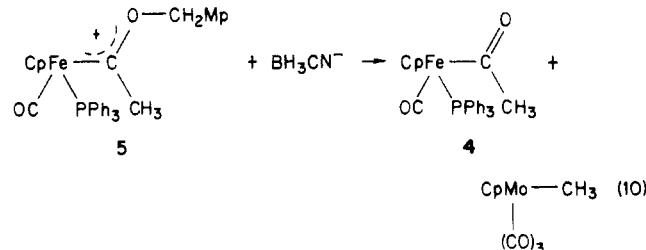


slight excess (1.5 equiv) of $\text{PhCH}_2\text{N}(\text{CH}_2\text{CH}_3)_3^+\text{Cl}^-$ thus efficiently cleaves 5 into its chloromethyl and acetyl constituents, each being obtained in 97% yield (eq 9).



Analogous results obtain using iodide, unless "aged" CH_2Cl_2 solutions of 5 are used. Such solutions after sitting have 18 present; reaction with iodide, as depicted in Scheme III, then produces mixtures of MpI and MpCH_2I .

A variety of nucleophilic hydride donors ($\text{LiHB}(\text{CH}_2\text{CH}_3)_3$, $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeH}$,³⁶ $\text{Ph}_3\text{PHC}_3^+\text{BH}_3\text{CN}^-$) readily reduce 5, but these reagents, reacting much like iodide or chloride, attack at the methylene group to displace 4 (eq 10). We found no evidence for the reduced



product $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCH}(\text{CH}_3)\text{OCH}_2\text{Mp}$ expected. If this product had formed, it should have been isolated. No obvious pathway exists for it decomposing to the observed products, and moreover the constituents $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeCH}(\text{CH}_3)\text{OR}$ and $\text{Cp}(\text{CO})_3\text{MoCH}_2\text{OR}$ certainly are handled easily. In retrospect, the facile displacement of 4 from 5 with hydride donors (and other nucleophiles) agrees with the heightened reactivity, in general, that transition organometallic methyl complexes MCH_2X , substituted with good leaving groups at the α -position, exhibit in nucleophilic displacement reactions.^{9a,b,37}

Conclusions

Methylidene complexes 1 and 2, in spite of extreme instability, function as metallo- α -carbenium ion carbocationic reagents and alkylate a variety of coordinated ligands. Fp vinyl and allyl complexes thus add 1 to their uncoordinated double bonds and generate the Fp_2 salts 11 and 12, respectively. The acetyl complex 4, but not 3, adds both methylidene reagents 1 and 2, although the bis(iron) adduct $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Fp}^+$ (16) readily decomposes. The molybdenum adduct $\text{Cp}(\text{CO})(\text{PPh}_3)\text{FeC}(\text{CH}_3)\text{OCH}_2\text{Mp}^+$ (5), on the other hand, can be isolated as a stable solid, whereas in solution (CH_2Cl_2) it slowly decomposes. Major products of both decomposition reactions (i.e., from 16 and 5) include the stable bimetallic μ -acetyl compounds 17 and 18, respectively. A variety of nucleophiles, including hydride donors, react with CH_2Cl_2 solutions of 5 and displace the starting acetyl 4.

Acknowledgment. Continuing support from the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged.

Registry No. 1, 86846-97-1; 2, 97011-72-8; 3, 12108-22-4; 4, 12101-02-9; 5, 97011-67-1; 6, 12082-28-9; 9, 97011-60-4; 10, 12083-79-3; 11, 97011-62-6; 12- PF_6^- , 97011-64-8; 12- BF_4^- , 97011-65-9; 14, 81141-29-9; 15, 81133-01-9; 16, 97042-28-9; 17, 81132-99-2; 18,

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81133-02-0; $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{Cl}$, 12107-38-9; $(\text{C}_5\text{H}_5)(\text{CO})_3\text{Fe}^+\text{PF}_6^-$, 38834-26-3; $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{CH}=\text{CH}_2$, 38960-10-0; $[\text{Cp}(\text{CO})_2\text{Fe}]_2$, 12154-95-9; $\text{Cp}(\text{CO})_2\text{FeCH}_3$, 12080-06-7; $\eta^5\text{-Cp}(\text{CO})\text{Fe}(\text{CH}_2\text{CHCH}_2)$, 52326-25-7; $\text{Cp}(\text{CO})_2\text{FeFBF}_3$, 76391-69-0; $(\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCH}_2\text{CH}_2\text{CH}=\text{CH}_2$, 34807-88-0; $\text{Cp}(\text{CO})_2\text{Fe}^+\text{PF}_6^-$, 81141-37-9; $\text{Cp}(\text{CO})_2\text{FeI}$, 12078-28-3; $\text{Cp}(\text{CO})_3\text{MoCH}_2\text{Cl}$, 12244-

83-6; $\text{Cp}(\text{CO})_3\text{MoI}$, 12287-61-5; $\text{Cp}(\text{CO})_3\text{MoCH}_3$, 12082-25-6; $\text{Cp}(\text{CO})(\text{pph}_3)\text{FeH}$, 32660-22-3; $\text{Cp}(\text{CO})_2\text{FeCH}=\text{CH}_2$, 12152-71-5; $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{I}$, 97011-69-3; $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{CH}_3)\text{OCH}_2\text{CH}_3^+\text{PF}_6^-$, 97011-70-6; $\text{CpMo}(\text{CO})_3\text{CH}_2\text{OCH}_3$, 12244-92-7; $\text{CpMo}(\text{CO})_3(\text{THF})^+\text{PF}_6^-$, 97011-71-7; $\text{Ph}_3\text{PMe}^+\text{BH}_3\text{CN}^-$, 97011-68-2.

Iron Complexes of Phosphinine[†] Derivatives

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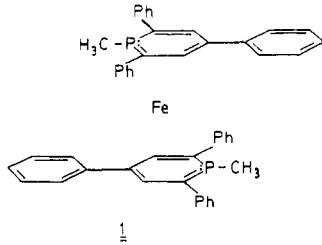
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Received December 11, 1984

New bis(1,2,4,6-tetrasubstituted phosphinine)iron complexes were synthesized according to the procedure of Märkl and Martin.¹ Contrary to former interpretations^{1,2} the compounds are very similar to the "open ferrocenes".⁸ However, the ligands are closed by a 1,5-phosphorus bridge. The phosphorus with three carbon bonds can be alkylated to give phosphonium salts. No principal change of the (η^5 -carbon)₂-Fe system occurs. A chair-like structure, phosphorus being outside of the nearly flat five-carbon unit, is claimed for the complexes (see the following paper³). Temperature-dependent ¹H and ¹³C NMR spectra agree with a rotation around the z axis, vertical to the ring planes. The activation energies of the neutral complexes are strongly influenced by the substituent in position 4. ΔG^* of 10a, 10b, and 10c are 52.3, 64.3, and 75.3 kJ/mol for R⁴ = Me, Ph, and t-Bu, respectively. The temperature-dependent NMR spectra of the bis(phosphonium)iron tetrafluoroborates 12a and 12c also have been measured. Reduction potentials of the neutral and mono- and dication complexes 10a, 11a, and 12a decrease with increasing charge at the phosphorus atom. Mössbauer spectra of the crystalline 10a, 11a, and 12a are very similar, the isomeric shifts nearly the same as those of ferrocenes and the quadrupole splittings only ca. half of ferrocene, just as those of "open ferrocenes". XPE spectroscopy of 10a, 11b, and 12c gave interesting results. The unsymmetrical mono(phosphonium)iron iodide complex 11a, which, due to the short time scale of the XPE method, shows two signals of the iron, one at the neutral and one at the cationic phosphinine ring. The bis(phosphonium)iron complexes 12a and 12c are remarkable soluble in water in spite of their hydrophobic substituents.

Introduction

Bis(1-methyl-2,4,6-triphenyl- λ^4 -phosphinine)iron, as well as its 1-phenyl derivative, was first synthesized by Märkl and Martin.¹ 2,4,6-Triphenylphosphinine was treated with methyl- (respectively phenyl-) lithium to give the phosphorus-substituted (λ^4 -phosphinine)lithium compounds⁴ which then were treated with iron(II) chloride in THF. Structure 1 of the black ferrocene-like compound was derived from the analytical data, the high-field shift in the ³¹P NMR spectrum, δ -55 (which is quite different from those of λ^5 -phosphinines (δ (³¹P)) 6-73)⁵ or the P-Fe-substituted λ^5 -phosphinine 4 (see below)), and the ¹H NMR data. A broad signal at δ 5.37 with a coupling constant, $^3J_{\text{PH}} = 8$ Hz, was assigned for the protons at C-3 and C-5, and the high-field shift of the P-CH₃ doublet at 0.04 ppm was interpreted in terms of the "anti" conformation 1, in



[†]Earlier name phosphorin: Powell, W. H. *Pure Appl. Chem.* 1983, 55, 409.

[‡]Stipendiat of the Deutscher Akademischer Austauschdienst.

[§]Synthetic and spectroscopic part.

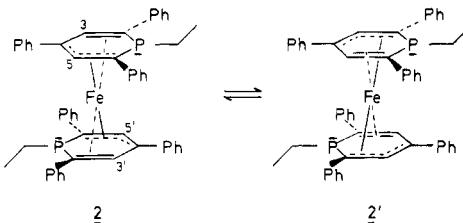
^{||}Results of temperature-dependent NMR spectra.

[¶]Results of cyclic voltammetric measurements.

[¶]Results of Mössbauer spectroscopy.

[¶]Results of X-ray photoelectrospectroscopic measurements.

which the phenyl substituent of the second phosphinine ring is situated over the P-CH₃ group. Later, Lehmkuhl et al.² measured the temperature-dependent ¹H NMR spectra of bis(1-ethyl-2,4,6-triphenylphosphinine)iron in THF-d₆. At 80 °C a sharp doublet at 5.45 ppm with a small $^3J_{\text{PH}} = 2.5$ Hz was observed, which was assigned to all four protons of the two phosphinine rings at C-3,5 and C-3',5'. At 40 °C only a broad signal at δ 5.43 is observed which at -20 °C splits into two sharp doublets at δ 5.53 ($J = 2.4$ Hz) and 5.37 ($J = 2.1$ Hz). These results were interpreted by fluxional structures 2 and 2' in which the carbon atoms 3 and 5 of each ring are differently bonded to the iron according to an allyl-ene η^2,η^3 structure. At higher temperature 2 and 2' equilibrate. From the co-



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