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BIMETALLIC ACTIVATION OF COORDINATED LIGANDS. REACTIONS OF THE LEWIS ACID $(\eta\text{-}C_5H_5)(CO)_3Mo^+ PF_6^-$ WITH ORGANO-IRON AND -MOLYBDENUM η^1-METHOXYMETHYL AND ETHYL COMPLEXES

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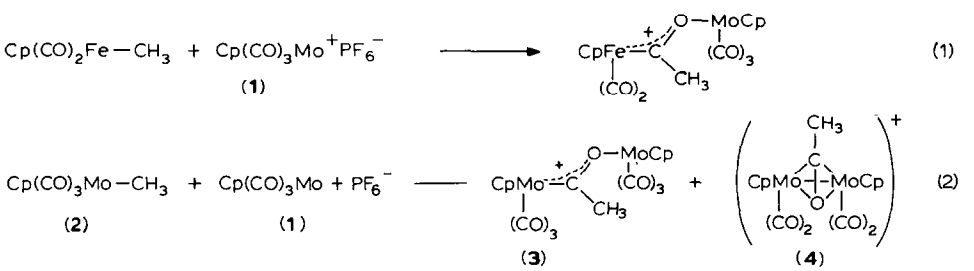
Summary

The organometallic Lewis acid $Cp(CO)_3Mo^+ PF_6^-$ reacts with organo-iron and -molybdenum methoxymethyl and ethyl complexes via methoxide and/or hydride abstraction. Thus, $Cp(CO)_3MoCH_2OCH_3$ and $Cp(CO)(L)FeCH_2OCH_3$ ($L = CO$, PPh_3) produce the corresponding methoxymethylidene salts Mo or $Fe{=}CHOCH_3$ and Mo or Fe methyl complexes as primary products, the latter resulting from hydride transfer to methylidene intermediates Mo or $Fe{=}CH_2^+$. Analogous ethyl complexes afford the μ-[η^2-*C*,*O*]propionyl compound $[Cp(CO)_2Mo]_2C(O)CH_2CH_3^+$ and the η^2-ethylene salt $Cp(CO)(PPh_3)Fe(CH_2CH_2)^+$ as primary products.

Introduction

The organometallic Lewis acid $(\eta\text{-}C_5H_5)(CO)_3Mo^+ PF_6^-$ (**1**) [1] promotes CO insertion on methyl compounds and forms bimetallic μ-(η^1-*C*,*O*) and -(η^2-*C*,*O*)



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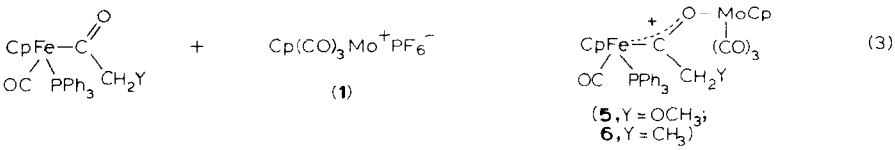


acetyl compounds (eqs. 1 and 2) [2,3]. We are interested in synthesizing other bimetallic acyl complexes that are derived from alkyl compounds other than methyl. In particular, two bimetallic acyl complexes, μ-(η^1-*C*,*O*)-methoxyacetyl (**5**) and -propionyl (**6**), had been prepared from their requisite acyl compounds (eq. 3) and had been characterized as unexceptional bimetallic complexes [4]. We now report, however, that organo-iron and -molybdenum methoxymethyl and ethyl compounds, upon reacting with **1**, produce complex mixtures of organometallic products that also entail formal hydride and methoxide abstraction from these alkyl ligands.

Experimental

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 [5]. Solvents for synthetic work and for recording spectral data were deoxygenated by bubbling nitrogen through for ~ 20 min. Camag alumina (neutral, activity 3) was used in column chromatography.

Most reactions in this study afforded mixtures of products that were only partially resolved. All products, therefore, were quantified by a combination of IR and ^{1}H NMR spectral procedures. Infrared spectra were taken of CH_2Cl_2 solutions (0.10 mmol/1.5–3.0 ml) in a NaCl amalgam-spaced (0.10 mm) solution cell and were recorded on a Perkin–Elmer Model 297 spectrophotometer. The ν(CO) frequencies (2200–1600 cm^{-1}) were calibrated against the polystyrene 1601 cm^{-1} absorption; they are accurate to ± 2 below and ± 5 cm^{-1} above 2000 cm^{-1}. IR spectra of the iron and molybdenum alkyl complexes and cationic salts used in this study exhibited straight-line Beer's law behavior in CH_2Cl_2 solution, which permitted their quantitation in solution. By this procedure as little as 2% of an organometallic was routinely detected, although the accuracy for its quantification typically was 5–8%. ^{1}H NMR spectra of weighed samples were recorded in concentrated $CDCl_3$ or CD_3NO_2 solutions, after centrifuging trace amounts of insoluble residues. Quantitative analysis (5% accuracy) was done by using the mean of three to five integration traces; when necessary, either Cp_2Fe or $Cp(CO)_2FeCH_3$ was included as an internal standard. Varian models T-60, EM-360, and XL-200 NMR spectrometers supplied the NMR spectra, which are reported as δ values downfield from internal $(CH_3)_4Si$. Combustion microanalyses were provided by Baron Consulting Company, Orange, Connecticut.

Organic solvents and reagents were procured commercially and used as received. Methylene chloride was distilled from P_4O_{10}, and CH_3NO_2 was dried by storing (under nitrogen) over freshly activated molecular sieves (4 Å). The anhydrous ether used was taken from a freshly opened can, or it was distilled from sodium benzophenone ketyl. $AgPF_6$ was used as received (as a free-flowing white powder)

from Ozark-Mahoning, but being very hygroscopic, it was stored under nitrogen. Further vacuum drying (10^{-3} mmHg) of $AgPF_6$ at 120°C did not improve the yields in the subsequent synthetic chemistry. A modification of Dauben's procedure was used to prepare $Ph_3C^+ PF_6^-$ [6]. Although stored under nitrogen at +5°C, trityl salts slowly decompose [7] (as indicated by appearance of white fumes), which necessitated periodic reprecipitation from CH_2Cl_2/ethyl acetate and vacuum drying.

Metal carbonyl complexes $Cp(CO)_3MoH$ [8], $Cp(CO)_3MoCH_2OCH_3$ (**7**), $Cp(CO)_3MoCH_2Cl$ [9], $Cp(CO)_3MoCH_2CH_3$ (**14**) [10], $Cp(CO)_2FeCH_2OCH_3$ (**11a**) [9,21], $Cp(CO)(PPh_3)FeCH_2OCH_3$ (**11b**) [11], and $Cp(CO)(PPh_3)FeCH_2CH_3$ (**16**) [12] were prepared by literature procedures and judged pure by IR and NMR spectroscopy. Authentic samples of $Cp(CO)_3Mo(\overline{O(CH_2)_3CH_2})^+ PF_6^-$ [1,26a], $Cp(CO)_3Mo(CH_2{=}CH_2)^+ PF_6^-$ [1,10], $Cp(CO)_3MoCO^+ PF_6^-$ [1,13], $Cp(CO)_3MoHMo(CO)_3Cp^+ PF_6^-$ (**9**) [1,14], $[Cp(CO)_2Mo]_2COCH_3^+ PF_6^-$ (**4**), $Cp(CO)_3MoC(CH_3)OMo(CO)_3Cp^+ PF_6^-$ (**3**) [3], $Cp(CO)_3MoCH_3$ (**2**) [15], $[Cp(CO)_3Mo]_2$ [16], $Cp(CO)_2FeCH(OCH_3)^+ PF_6^-$ (**12a**) [12,18], $Cp(CO)(PPh_3)FeCH(OCH_3)^+ PF_6^-$ (**12b**) [17], $Cp(CO)_2FeCH_3$ (**13a**) [19], $Cp(CO)(PPh_3)FeCH_3$ (**13b**) [20], $Cp(CO)_2FeCO^+ PF_6^-$ [21], $Cp(CO)(PPh_3)FeCO^+ PF_6^-$ [22], $Cp(CO)(PPh_3)Fe(CH_2{=}CH_2)^+ PF_6^-$ (**17**) [23], and $Cp(CO)(PPh_3)FeCOCH_2CH_3$ (**18**) [24] were available from previous studies for direct spectroscopic comparison.

Reaction of $Cp(CO)_3MoCH_2OCH_3$ (7) with $Cp(CO)_3Mo^+ PF_6^-$ (1) (2/1 stoichiometry)

A yellow CH_2Cl_2 solution (30 ml) of $Ph_3C^+ PF_6^-$ (388 mg, 1.00 mmol), initially at −78°C, was treated with $Cp(CO)_3MoH$ (246 mg, 1.00 mmol) before warming to −20°C (over 10 min). This produced a burgundy solution containing $Cp(CO)_3Mo^+ PF_6^-$ (**1**) [IR 2070s, 1998vs, br cm^{-1}], which was treated with $Cp(CO)_3MoCH_2OCH_3$ (**7**) (580 mg, 2.00 mmol). The resulting burgundy suspension then was warmed to +22°C (0.5 h) and stirred for an additional 1.5 h. Filtration retained an orange solid that was washed with CH_2Cl_2 (5 ml) and vacuum dried, 241 mg. This solid assayed (quantitative IR and NMR spectroscopy) as $Cp(CO)_3MoCH(OCH_3)^+ PF_6^-$ (**8**) (46% yield), although it was contaminated by trace amounts (~5% yields) of $[Cp(CO)_3Mo]_2H^+ PF_6^-$ (**9**) [1,14], [IR (CH_3NO_2) 2071m, 2055m, 1990s, br cm^{-1}; ^1H NMR (CD_3NO_2) δ 5.93 (s, 10H, Cp), −20.8 (s, 1H, Mo_2H)] and $Cp(CO)_3MoCO^+ PF_6^-$ [1,13] [IR (CH_3NO_2) 2120, 2040 cm^{-1}; NMR (CD_3NO_2) δ 6.20 (Cp)].

A gray precipitate (106 mg), obtained from the combined CH_2Cl_2 filtrates after adding to excess ether (80 ml), was filtered, washed with ether, and vacuum dried. It assayed as spectroscopically pure $[Cp(CO)_2Mo]_2COCH_3^+ PF_6^-$ (**4**) [3] (17% yield, based on $Cp(CO)_3MoH$); [IR (CH_2Cl_2) 2061m, 2015s, 1920m, br cm^{-1}, ^1H NMR (CD_3NO_2) δ 5.97 (s, 10H, Cp), 3.02 (s, 3H, $COCH_3$)]. The filtrates were then evaporated to a brown residue (880 mg), which, in addition to Ph_3CH, contained starting $Cp(CO)_3MoCH_2OCH_3$ (**7**) (52% yield) and traces of $Cp(CO)_3MoCH_3$ (**2**) [15] and $[Cp(CO)_3Mo]_2$ [16].

This reaction was repeated, but the stoichiometry of $Cp(CO)_3MoCH_2OCH_3$ (**7**) to $Cp(CO)_3Mo^+ PF_6^-$ (**1**) was varied from 2/1 to 1/1 and 1/2. Significant differences in these reactions were only recorded in the yields of $Cp(CO)_3MoCH(OCH_3)^+ PF_6^-$ (**8**), 18% for 1/1 and 35% for 1/2, and of $[Cp(CO)_3Mo]_2H^+ PF_6^-$ (**9**), 11% for 1/1 and 33% for 1/2. In particular, the yields of isolated

$[Cp(CO)_2Mo]_2COCH_3^+$ PF_6^- (**4**) remained invariant (17–19%) with respect to changes in the starting stoichiometry.

*Preparation of $Cp(CO)_3MoCH(OCH_3)^+$ PF_6^- (**8**)*

To a cooled (−25°C) CH_2Cl_2 solution (4.0 ml) containing $Cp(CO)_3MoCH_2OCH_3$ (**7**) (150 mg, 0.52 mmol) was added Ph_3C^+ PF_6^- (202 mg, 0.52 mmol) in portions. The initially yellow solution immediately turned orange, and lemon yellow crystals appeared as the reaction mixture was warmed slowly (1 h) to room temperature. Results of IR spectral examination indicated quantitative consumption of starting **7**. The yellow crystals were filtered, washed with ether, and vacuum dried (1 h, 10^{-3} mmHg); 155 mg (69% yield) of analytically pure $Cp(CO)_3MoCH(OCH_3)^+$ PF_6^- (**8**) was collected: IR (CH_3NO_2) 2081s, 1990s, br) cm^{-1}; NMR (CD_3NO_2) δ 6.10 (s, 5H, Cp), 4.81 (s, 3H, OCH_3), 13.44 (s, 1H, Mo=CH).

Anal. Found: C, 27.51; H, 2.25. $C_{10}H_9O_4MoPF_6$ calcd.: C, 27.67; H, 2.09%.

Nitromethane solutions of **8**, stable at room temperature, react quantitatively with $(n\text{-butyl})_4N^+$ I^- and generate a 1:1 mixture of $Cp(CO)_3MoCH_2OCH_3$ (**7**) plus $(Cp(CO)_3MoCO^+$ PF_6^-, as expected [17].

*Reaction of $Cp(CO)_3MoCH_2^+$ PF_6^- (**10**) and $Cp(CO)_3MoH$*

A yellowish-green suspension containing $Cp(CO)_3MoCH_2^+$ PF_6^- (**10**) [9a,25] (0.79 mmol) in CH_2Cl_2 (15 ml) was generated by adding $Cp(CO)_3MoCH_2Cl$ (233 mg, 0.79 mmol) to a cold (−78°C) CH_2Cl_2 solution of $AgPF_6$ (200 mg, 0.79 mmol). This suspension then was injected with a CH_2Cl_2 solution (5 ml) of $Cp(CO)_3MoH$ (194 mg, 0.79 mmol), and the reaction was warmed to room temperature (1 h). After stirring for an additional 2 h at room temperature, the resulting reddish-brown suspension was centrifuged, and the combined supernatant and CH_2Cl_2 washings (3 × 8 ml) were reduced in volume (to 15 ml) and added to 75 ml of ether. A pink precipitate settled that was filtered, washed with ether, and dried (299 mg); it was identified as a 3/1 mixture of spectroscopically pure $[Cp(CO)_2Mo]COCH_3^+$ PF_6^- (**4**) and $Cp(CO)_3MoC(CH_3)OMo(CO)_3Cp^+$ PF_6^- (**3**) [3], in an overall 46% yield.

The remaining ether-soluble fraction was evaporated to a brown solid (104 mg) that contained predominantly $Cp(CO)_3MoCH_3$ (**2**) (43% yield), the remaining 16 mg being partially accounted for by trace amounts of two unidentified Cp-containing organometallics. The initial CH_2Cl_2-insoluble centrifugate was slurried with THF (2 ml), agitated for 2 min, and centrifuged. The combined red THF and CH_2Cl_2 extractants (20 ml), leaving behind a gray AgCl residue, were added to 100 ml ether to afford a pink precipitate $Cp(CO)_3Mo(\overbrace{O(CH_2)_3CH_2})^+$ PF_6^- [1] in 24% yield (88 mg).

*Reaction of $Cp(CO)_3MoCH_2^+$ PF_6^- (**10**) and $Cp(CO)_3MoCH_2OCH_3$ (**7**)*

$Cp(CO)_3MoCH_2Cl$ (295 mg, 1.00 mmol) was combined with $AgPF_6$ (253 mg, 1.00 mmol) in 12 ml of CH_2Cl_2 at −78°C. A solution of $Cp(CO)_3MoCH_2CH_3$ (**7**) (290 mg, 1.00 mmol) in 5 ml of CH_2Cl_2 then was added immediately to the stirred orange slurry, which was warmed to room temperature (0.5 h) and was stirred for another 1.0 h. The resulting red-brown suspension was centrifuged, successively washed with two 4 ml portions of CH_2Cl_2, and extracted by CH_3NO_2 (3 × 4 ml). The combined nitromethane extractants precipitated $Cp(CO)_3MoCH(OCH_3)^+$ PF_6^- (**8**) from excess ether (75 ml): the precipitate (252 mg), after it was collected and vacuum dried,

corresponded to **8** (in 57% yield) that was contaminated by small amounts of $Cp(CO)_3MoCO^+ PF_6^-$ ($\leqslant 8\%$).

The CH_2Cl_2-soluble fractions were combined, reduced in volume to 5 ml, and chromatographed (activity 3 alumina/benzene). Extensive decomposition was evident on the column; nevertheless, a yellow band containing $Cp(CO)_3MoCH_3$ (**2**) was eluted cleanly, 164 mg (63% yield). No starting **7** was detected using NMR spectral examination of the crude CH_2Cl_2-soluble fractions.

Reaction between $Cp(CO)_3Mo^+ PF_6^-$ (1) and $Cp(CO)_2FeCH_2OCH_3$ (11a)

To a cold (−20°C), burgundy CH_2Cl_2 solution (15 ml) of $Cp(CO)_3Mo^+ PF_6^-$ (**1**) (1.00 mmol, generated at −78°C) was added $Cp(CO)_2FeCH_2OCH_3$ (**11a**) (220 mg, 1.00 mmol), and the red mixture was warmed to +22°C (1 h) with stirring. The red precipitate then was filtered, washed with 5 ml CH_2Cl_2, and dried under vacuum: 213 mg of $Cp(CO)_2FeCH(OCH_3)^+ PF_6^-$ (**12a**) [17,18] (58% yield) [IR (CH_3NO_2) 2080s, 2031s cm^{-1}; NMR (CD_3NO_2) δ 13.32 (s, 1H, Fe=CH), 5.55 (s, 5H, Cp), 4.76 (s, 3H, OCH_3)] and a trace of $Cp(CO)_2FeCO^+ PF_6^-$ [21].

The combined CH_2Cl_2-soluble fractions were reduced in volume and added to excess ether (50 ml). A light reddish-violet precipitate accordingly was collected and vacuum dried, 44 mg; it contain $Cp(CO)_3FeCO^+ PF_6^-$ (total yield 10%) and a trace of **12a**. The ether-soluble fraction after evaporation (416 mg) was chromatographically separated (using benzene/CH_2Cl_2) into Ph_3CH, $[Cp(CO)_3Mo]_2$ (167 mg, 68% yield), and a third fraction containing small amounts (4–8%) each of $Cp(CO)_2FeCH_3$ (**13a**) [19], $Cp(CO)_3MoCH_2OCH_3$ (**7**), and $Cp(CO)_3MoCH_3$ (**2**).

Reaction of $Cp(CO)_3Mo^+ PF_6^-$ (1) and $Cp(CO)(PPh_3)FeCH_2OCH_3$ (11b)

$Cp(CO)(PPh_3)FeCH_2OCH_3$ (**11b**) (457 mg, 1.00 mmol) was added to CH_2Cl_2 solution (15 ml) containing $Cp(CO)_3Mo^+ PF_6^-$ (**1**) (1.00 mmol) at −20°C. The resulting dark violet solution was warmed to room temperature (1 h), before it was added to 300 ml of ether with scraping. A grayish-tan precipitate settled that was filtered, washed with ether, and dried (356 mg). This proved to be a 1/1 mixture of $Cp(CO)(PPh_3)FeCH(OCH_3)^+ PF_6^-$ (**12**) [17] (29%) [IR (CH_2Cl_2) 1995 cm^{-1}; NMR (CD_3NO_2) δ 13.25 (s, 1H, Fe=CH), 7.55 (br s, 15H, PPh_3), 5.15 (s, 5H, Cp), 4.02 (s, 3H, OCH_3)] and $Cp(CO)(PPh_3)FeCO^+ PF_6^-$ [22] (28%), with only a trace of $[Cp(CO)_3Mo]_2H^+ PF_6^-$ (**9**) evident. The combined ether filtrates were evaporated and chromatographed with CH_2Cl_2. In addition to extensive decomposition on the column, a broad red band eluted that afforded a dark red gum (504 mg) after drying. This fraction contained, in addition to Ph_3CH, a mixture of $Cp(CO)_3MoCH_3$ (**2**) (18% yield), $[Cp(CO_3Mo]_2$ (4%), $Cp(CO)(PPh_3)FeCH_2OCH_3$ (**11b**) (12%), and $Cp(CO)(PPh_3)FeCH_3$ (**13b**) [20] (9%). Similar results obtained when $Cp(CO)(PPh_3)FeCH_2OCH_2CH_3$ was used in place of the methyl ether analog **11b**.

Reaction of $Cp(CO)_3Mo^+ PF_6^-$ (1) and $Cp(CO)_3MoCH_2CH_3$ (14)

A burgundy CH_2Cl_2 solution (15 ml) containing $Cp(CO)_3Mo^+ PF_6^-$ (**1**), generated from $Cp(CO)_3MoH$ (246 mg, 1.00 mmol) and $Ph_3C^+ PF_6^-$ (388 mg, 1.00 mmol) at −78°C, was warmed to −20°C (0.5 h) and was treated with $Cp(CO)_3MoCH_2CH_3$ (**14**) (274 mg, 1.00 mmol). A reddish-orange supernatant/red precipitate formed after bringing the mixture to room temperature (0.5 h) and stirring for an additional

1.5 h. It was filtered, and the CH_2Cl_2 filtrates were added to 75 ml of ether, in order to deposit an orange precipitate. After vacuum drying, this solid proved to be analytically pure $[Cp(CO)_2Mo]_2COCH_2CH_3^+ PF_6^-$ (**15**) (327 mg, 51%): IR (CH_2Cl_2) 2062m, 2017s, 1915s, br cm^{-1}; NMR [$(CD_3)_2CO$] δ 6.18 (s, 10H, Cp), 3.20 (quart, *J* 8 Hz, 2H, CH_2), 1.48 (t, *J* 8 Hz, 3H, CH_3).

Anal. Found: C, 31.96; H, 2.58. $C_{17}H_{15}O_5Mo_2PF_6$ calcd. C, 32.10; H, 2.40%.

It was quantitatively converted by one equivalent of $(n\text{-butyl})_4N^+ I^-$ in CH_2Cl_2 or CH_3NO_2 solution (0.5 h) into a 1/1 mixture $Cp(CO)_3MoCH_2CH_3/Cp(CO)_3MoI$, as expected [3].

The CH_2Cl_2-insoluble precipitate (78 mg) assayed as a 2.3/2.0/1.0 mixture of $[Cp(CO)_3Mo]_2H^+ PF_6^-$ (**9**)/$Cp(CO)_3MoCO^+ PF_6^-$/$Cp(CO)_3Mo(CH_2{=}CH_2)^+ PF_6^-$ [10]. The combined ether-soluble residues, after evaporating, afforded 512 mg of a reddish-purple solid that contained (in addition to Ph_3CH) $Cp(CO)_3MoCH_2CH_3$ (**14**) (23% recovered) and 8% $[Cp(CO)_3Mo]_2$.

Reaction between $Cp(CO)_3Mo^+ PF_6^-$ (1) and $Cp(CO)(PPh_3)FeCH_2CH_3$ (16)

$Cp(CO)_3Mo^+ PF_6^-$ (**1**) (0.78 mmol) was generated by treating a CH_2Cl_2 solution (15 ml) of $Ph_3C^+ PF_6^-$ (303 mg, 0.78 mmol) with $Cp(CO)_3MoH$ (192 mg, 0.78 mmol) at $-78°C$, and warming to $-20°C$. This burgundy solution was treated with $Cp(CO)(PPh_3)FeCH_2CH_3$ (**16**) (345 mg, 0.78 mmol), and the resulting reddish-yellow solution was warmed to room temperature. After stirring for another hour, the reaction was added slowly to ether (120 ml) (with stirring) to produce a brown precipitate. This was collected, washed with ether, and dried as a tan powder (284 mg), which consisted of a 3/1 mixture of $Cp(CO)(PPh_3)Fe(CH_2CH_2)^+ PF_6^-$ (**17**) [23] (47% yield) and of $Cp(CO)(PPh_3)FeCO^+ PF_6^-$ (15% yield), plus a trace of $Cp(CO)_3MoCO^+ PF_6^-$.

The ether filtrates were evaporated to a reddish residue; this was chromatographed with pentane/CH_2Cl_2. Pentane eluted $[Cp(CO)_3Mo]_2$ (28% yield); 1/1 CH_2Cl_2/pentane removed $[Cp(CO)_2Mo]_2$ (10%) as a pink band; and CH_2Cl_2 brought down a yellow band containing $Cp(CO)(PPh_3)FeCOCH_2CH_3$ (**18**) [24] (14% yield) plus a trace of $Cp(CO)_3MoCH_3$ (**2**). The column remained dark green.

This reaction was repeated, but using 2/1 stoichiometry for $Cp(CO)_3Mo^+ PF_6^-$ (**1**) and $Cp(CO)(PPh_3)FeCH_2CH_3$ (**16**). Accordingly, a CH_2Cl_2 solution (20 ml) containing $Cp(CO)_3Mo^+ PF_6^-$ (**1**) (2.00 mmol) at $-20°C$ was treated with $Cp(CO)(PPh_3)FeCH_2CH_3$ (**16**) (440 mg, 1.00 mmol) and the red reaction mixture was stirred for 1 h, as it warmed to room temperature. The maroon precipitate that formed was filtered, washed with CH_2Cl_2 (12 ml), and dried (484 mg). It corresponded to $[Cp(CO)_3Mo]_2H^+ PF_6^-$ (**9**) (0.76 mmol) plus a trace of $[Cp(CO)_3Mo]_2$.

The CH_2Cl_2 filtrates produced a brown precipitate with ether (300 ml), which as an orange-brown solid (446 mg) it consisted of more $[Cp(CO)_3Mo]_2H^+ PF_6^-$ (**9**) (0.09 mmol, total yield 85%) plus $Cp(CO)(PPh_3)Fe(CH_2{=}CH_2)^+ PF_6^-$ (**17**) (48% yield) and $Cp(CO)(PPh_3)FeCO^+ PF_6^-$ (23%).

Results and discussion

Beck and Schloter first characterized $(Cp(CO)_3Mo^+ PF_6^-$ (**1**), obtained by abstracting hydride from $Cp(CO)_3MoH$ in the non-coordinating solvent CH_2Cl_2

(eq. 4) [1], as an organometallic Lewis acid bearing an accessible or latent coordination site. A large variety of two-electron donating Lewis bases (e.g., L = THF or acetone) accordingly form stable, coordinatively saturated compounds $Cp(CO)_3MoL^+$ (eq. 5). Indeed, $Cp(CO)_3Mo^+$ is sufficiently electrophilic that even the BF_4^- counterion coordinates and affords the covalent molecule $Cp(CO)_3MoFBF_3$, in contrast to the ionic $Cp(CO)_3Mo^+ PF_6^-$ (**1**) [26,27]. In the absence of a stabilizing Lewis base L, **1** evidently disproportionates (eq. 6) above −20°C to the stable tetracarbonyl salt $Cp(CO)_3MoCO^+$ and insoluble Mo residues. In our experience, **1** is best generated by mixing $Cp(CO)_3MoH$ and purified $Ph_3C^+ PF_6^-$ in CH_2Cl_2 at −78°C, warming slowly to −20°C (with a color change of the CH_2Cl_2 solution from reddish-yellow to reddish-purple evident at ca. −26°C), and then adding the reactant substrate before warming slowly to room temperature [28].

$$\underset{\underset{(CO)_3}{|}}{CpMo{-}H} + Ph_3C^+ PF_6^- \rightarrow \underset{\underset{(CO)_3}{|}}{CpMo^+} PF_6^- + Ph_3C{-}H \qquad (4)$$

(**1**)

$$\underset{\underset{(CO)_3}{|}}{CpMo^+} PF_6^- + L \rightarrow \underset{\underset{(CO)_3}{|}}{CpMo{-}L^+} \qquad (5)$$

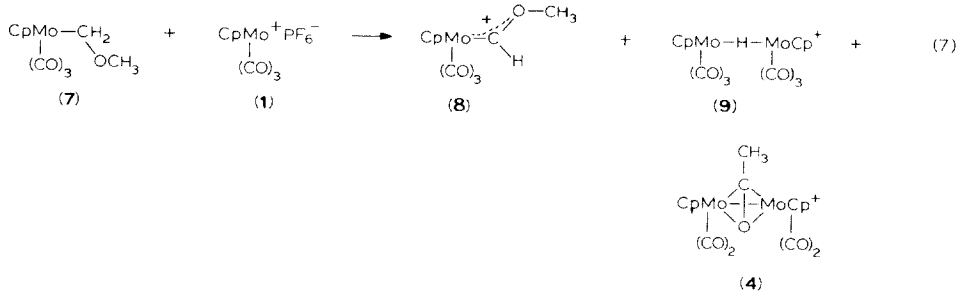
$$\underset{\underset{(CO)_3}{|}}{CpMo^+} PF_6^- \rightarrow \tfrac{3}{4}\underset{\underset{(CO)_3}{|}}{CpMo{-}CO^+} + \text{Mo residues} \qquad (6)$$

(**1**)

Reactions between the Lewis acid $Cp(CO)_3Mo^+ PF_6^-$ (**1**) in CH_2Cl_2 and organo-iron and -molybdenum complexes bearing η^1-methoxymethyl or ethyl ligands typically produced an array of organometallic products. These were worked up as (1) CH_3NO_2-soluble/CH_2Cl_2-insoluble, (2) CH_2Cl_2-soluble/ether-insoluble, and (3) ether-soluble fractions. The cationic organometallics thus separated cleanly as CH_2Cl_2-insoluble (1) and CH_2Cl_2-soluble ether-insoluble (2) fractions; whereas neutral complexes remained in the ether-soluble (3) fraction. IR and NMR spectral data then were used to identify all organometallic products (by comparing their data with that of authentic samples) and to quantify these components.

Reactions of methoxymethyl complexes with $Cp(CO)_3Mo^+ PF_6^-$ (1)

Treatment of a burgundy CH_2Cl_2 solution of **1** at −20°C with (η-C_5H_5)$(CO)_3MoCH_2OCH_3$ (**7**) (1/1) and warming to room temperature affords two major products derived from the methoxymethyl ligand (eq. 7). The CH_3NO_2-soluble/CH_2Cl_2-insoluble fraction thus contains the methoxymethylidene salt $Cp(CO)_3MoCH(OCH_3)^+ PF_6^-$ (**8**) (18%), along with variable yields of $[Cp(CO)_3Mo]_2H^+$ (**9**) [1,14] (11%) and $Cp(CO)_3MoCO^+ PF_6^-$. The other major product, surprisingly, is the μ-(η^2-C,O) acetyl compound **4** [2,3] (17% yield), which precipitates from the CH_2Cl_2-soluble fraction with ether. (Remaining ether-soluble components, in addition to Ph_3CH, are $Cp(CO)_3MoCH_3$ (**2**) (5%) and variable amounts of **7** and $[Cp(CO)_3Mo]_2$ (ca. 3%)).



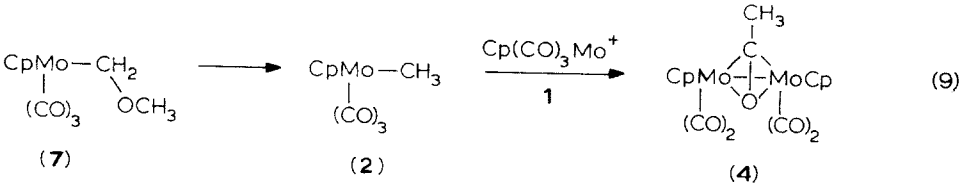
(7) (1) (8) (9) (4)

The methoxymethylidene salt **8** originates via a formal hydride abstraction from the starting methoxymethyl complex **7**. Accordingly, **8** was synthesized independently by reacting trityl hexafluorophosphate with **7** (eq. 8). This hydride removal proceeds quantitatively, as ascertained by IR spectral monitoring, and **8** crystallizes from the reaction medium in 69% yield. We [17] and others [18,29,30] have previously documented similar preparation of other alkoxymethylidene salts, although it is worth noting that Kegley et al. have observed that Ph_3C^+ preferentially extracts alkoxide from $Cp(CO)_2(PPh_3)MoCH_2OR$ [30].

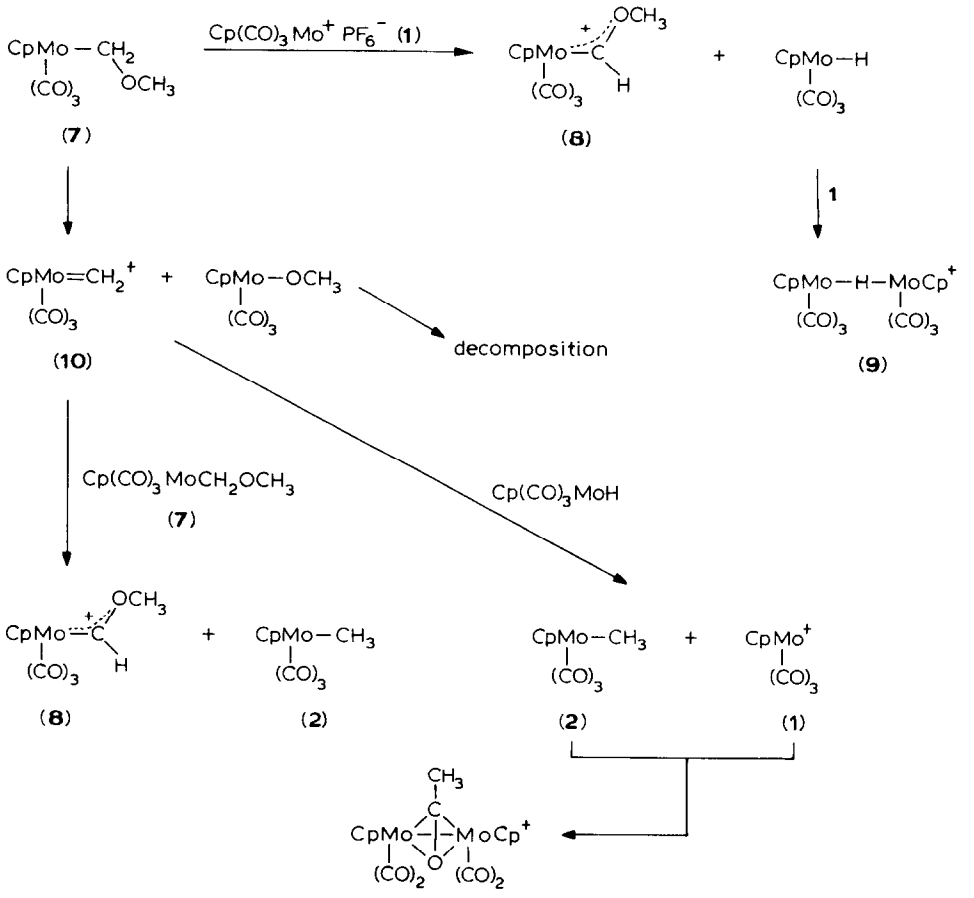
(7) (8) (8)

In the chemistry represented by eq. 7, $Cp(CO)_3Mo^+$ (**1**) functions as the hydride abstractor towards **7**. The μ-hydride compound **9** then originates in **1** competitively trapping $Cp(CO)_3MoH$, itself a by-product of **1** removing hydride from **7** (see Scheme 1). ($Cp(CO)_3MoH$ otherwise decomposes autocatalytically to $(Cp(CO)_3Mo)_2$ and insoluble materials in the presence of the reaction residues, as established independently.) Accordingly, the yield of **9** increased to 35% (as did that of **8**) when the starting stoichiometry (eq. 7 was 1/2 in favor of **1**. Inverting the stoichiometry (2/1), however, lowered the yield of **9** to 5%, while that of **8** increased to 46%. Clearly, an excess of $Cp(CO)_3Mo^+$ (**1**) in this reaction (eq. 7) favors the μ-hydride compound **9**, whereas excess methoxymethyl **7** favors the methoxymethylidene salt **8**. In all three experiments of differing stoichiometry between **1** and **7**, the isolated yield of the μ-acetyl compound **4** remained invariant, 17–19%. (All yields are normalized to 1 equivalent of **7**).

The bimetallic acetyl **4** produced in eq. 7 entails net reduction of methoxymethyl **7** to methyl **2**, followed by reaction of **1** and **2** (eq. 9). We envision two independent pathways for so obtaining the methyl complex **2**: in both, **1** abstracts methoxide from **7** and gives the unstable methylidene compound $Cp(CO)_3Mo{=}CH_2^+$ (**10**) [9a] (Scheme 1). Certainly precedent abounds for acid converting methoxymethyl complexes, including **7** [9a], to their reactive electrophilic methylidene salts [31].



(7) (2) (4)

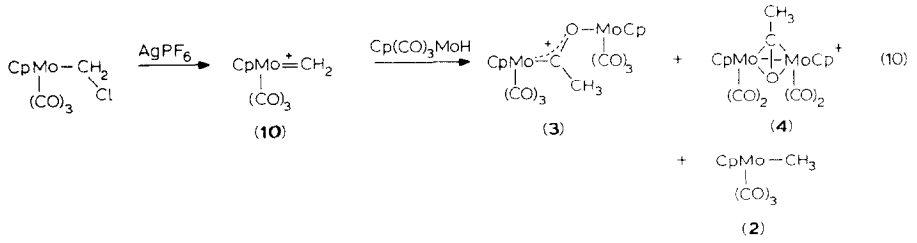


SCHEME 1

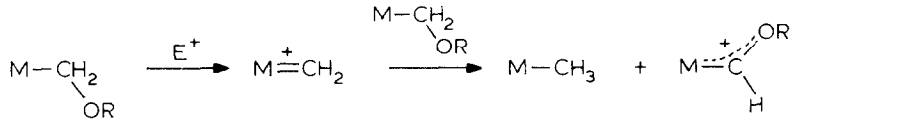
The methylidene salt **10**, once generated from **7**, extracts hydride from $Cp(CO)_3MoH$ and/or $Cp(CO)_3MoCH_2OCH_3$ (**8**) – the two pathways for converting **8** to the methyl complex **2** (Scheme 1). In the latter pathway, the methoxymethylidene **8** would be the anticipated by-product, and in the former $Cp(CO)_3Mo^+$ (**1**) also would be produced. Once generated, $Cp(CO)_3MoCH_3$ readily reacts with the **1** present and gives the μ-acetyl **4**. That **10**, however, could react with the above organometallic hydride donors was independently verified.

The methylidene salt **10** was generated in situ ($-80°C$) from $Cp(CO)_3MoCH_2Cl$ and $AgPF_6$ in CH_2Cl_2 [9a]; it was then warmed to room temperature in the presence of one equivalent of the hydride donors **7** or $Cp(CO)_3MoH$. Complex **7** was quantitatively consumed, with approximately equal quantities of **8** (57%) and **2** (63%) produced as the major organometallic components (Scheme 1). The reaction of **10** with $Cp(CO)_3MoH$ gave a 1/3 mixture of bimetallic acetyl salts **3** and **4** (in 46% yield) as the CH_2Cl_2-soluble/ether-insoluble fraction, and $Cp(CO)_3MoCH_3$ (**2**) (in 43% yield) after chromatography of the ether-soluble fraction (eq. 10). Reduction of the methylidene salt **10** to $Cp(CO)_3MoCH_3$ (**2**) using $Cp(CO)_3MoCH_2OCH_3$ (**7**)

and $Cp(CO)_3MoH$ as hydride donors must be extremely facile since $Cp(CO)_3Mo(CH_2{=}CH_2)$ [10], the disproportionation product of **10**, was not detected.



Methoxymethyl ligands are established hydride donors to methylidene ligands with at least three organometallic systems (eq. 11). The reaction chemistry depicted in eq. 11 (using acid, methyl fluorosulfonate, or trimethylsilyltriflate as the electrophile reagents) accordingly resembles that exhibited by $Cp(CO)_3Mo^+ PF_6^-$ (**1**) with $Cp(CO)_3MoCH_2OCH_3$ (**7**). In other studies we had established that the electrophilic methylidene compounds $Cp(CO)_2Fe{=}CH_2^+$ and $Cp(CO)_3Mo{=}CH_2^+$ (**10**) (also reacting as transient, metal-stabilized α-carbocationic intermediates) actively alkylate and/or abstract hydride or alkoxide from a variety of coordinated acetyl and alkyl ligands [25].



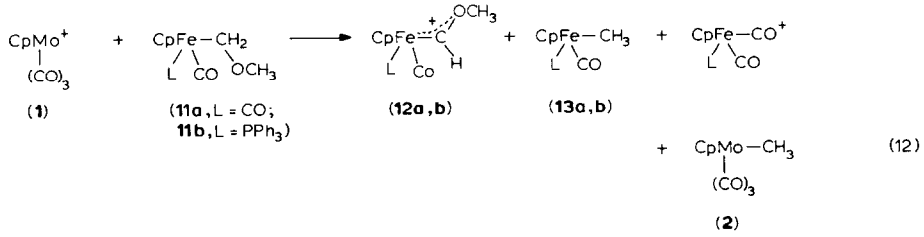
M = Cp(NO)(PPh$_3$)Re[29], Cp(CO)$_2$(PPh$_3$)Mo[30], Cp(CO)$_2$Fe[32]
E = electrophilic reagent

Although $Cp(CO)_3MoH$ is regarded as a weak acid [33], it clearly reduces $Cp(CO)_3MoCH_2^+$ (**10**) to its methyl complex (eq. 10). Such hydride transfer reactions had been previously noted between other more electron rich Cp metal hydrido complexes (e.g., $Cp(CO)(PPh_3)FeH$) and cationic alkoxycarbene complexes [34]. With $Cp(CO)_3MoH$, however, we found no reaction occurring at room temperature with $Cp(CO)_3MoCH(OCH_3)^+$ (**8**), with $Cp(CO)_3MoCO^+$, or even with $Cp(CO)_3Mo(CH_2{=}CH_2)^+$. This hydride in perhaps related chemistry, however, reductively eliminates aldehydes upon reacting with the requisite alkyl complexes $Cp(CO)_3MoR$ [35].

Two features of the reaction chemistry in Scheme 1 remain puzzling. First, we cannot explain why the reaction between $Cp(CO)_3MoH$ and $Cp(CO)_3Mo{=}CH_2^+$ (**10**) ultimately affords both μ-acetyl compounds **3** and **4** (eq. 10), whereas only **4** results from interacting **1** with **7**. Insertion reactions promoted by **1**, however, are extremely sensitive to reaction conditions: relative yields of **3** and **4** derived from $Cp(CO)_3MoCH_3$ plus **1** depend on the precise reaction conditions [3,28]. The same reaction using $Cp(CO)_3MoFBF_3$ in place of **1** converts $Cp(CO)_3MoCH_3$ exclusively to **4**, for example [2,27]. Second, we were unable to detect $Cp(CO)_3MoOCH_3$, the anticipated by-product of methoxide extraction from **7** by **1**, or even to generate it from **1** plus methoxide. Intractable reaction residues resulted instead in the latter

studies, one plausible decomposition pathway involving β-deinsertion of formaldehyde from $Cp(CO)_3MoOCH_3$ [36].

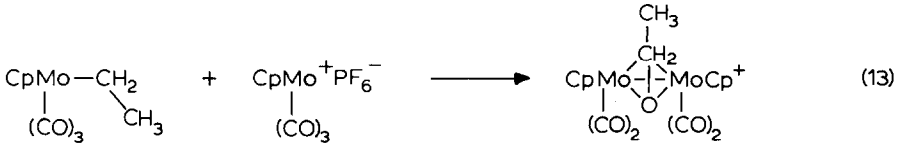
Organoiron methoxymethyl complexes $Cp(L)(CO)FeCH_2OCH_3$ (**11a**, L = CO; **11b**, L = PPh_3), reacting analogous to $Cp(CO)_3MoCH_2OCH_3$ (7), also serve as hydride and methoxide donors to **1**, eq. 12. Thus both **11a,b** and **1** give methoxymethylidene **12a** (46%) and **12b** (29%) [17] and carbonyl salts $Cp(L)(CO)_2Fe^+ PF_6^-$ (L = CO, 9%; L = PPh_3, 28%) as the cationic products. No bimetallic acyl compounds, e.g., **5**, were detected.



Iron methyl complexes **13a** (3%) and **13b** (9%), $Cp(CO)_3MoCH_3$ (**2**) (< 5% from **11a**; 18% with **11b**), and variable amounts of $[Cp(CO)_3Mo]_2$, resulting from subsequent decomposition of $Cp(CO)_3MoH$ under the reaction conditions, are the other products. Identical yields of methyl complexes **13b** and **2** are realized when $Cp(PPh_3)(CO)FeCH_2OCH_2CH_3$ was substituted for **11b**. The net reduction of the methoxymethyl ligand on **11a,b**, upon reacting with **1**, to the corresponding methyl group on **13a,b** presumably entails a mechanism analogous to that advanced in Scheme 1. The molybdenum methyl complex **2** can be accounted for by an established methyl transfer [3] from **13a,b** to **1**, with subsequent decomposition of $Cp(L)(CO)Fe^+$ to the observed carbonyl salts $Cp(L)(CO)FeCO^+$.

Reactions of ethyl complexes with $Cp(CO)_3Mo^+ PF_6^+$ (1)

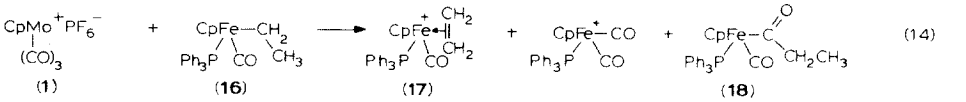
The molybdenum ethyl complex $Cp(CO)_3MoCH_2CH_3$ (**14**) reacts with **1** predominately via CO insertion to give the μ-(η^2-*C,O*)propionyl salt **15** as an orange powder (53%, from CH_2Cl_2-soluble/ether-insoluble fraction) (eq. 13). Minor amounts (3–8%) of $Cp(CO)_4Mo^+$, $Cp(CO)_3Mo(CH_2{=}CH_2)^+$, and **9** were also recovered in the CH_2Cl_2-insoluble residue.



Chemical and physical properties of **15**, analogous to those of **4**, are consistent with its symmetric (η^2-*C,O*) structure depicted. (A single crystal X-ray diffraction study by Beck and coworkers [2] has established the structure of **4**).

A rather different reaction ensues when the more electon rich iron ethyl complex $Cp(CO)(PPh_3)FeCH_2CH_3$ (**16**) reacts with **1** (eq. 14). A mixture of the η^2-ethylene salt $Cp(CO)_2(PPh_3)Fe(CH_2{=}CH_2)^+$ (**17**) [23] (47%) and $Cp(CO)_2(PPh_3)Fe^+$ (15%) precipitate from CH_2Cl_2/ether, leaving varying amounts of $Cp(CO)_3MoH$/$[Cp(CO)_3Mo]_2$ (28%) and $Cp(CO)(PPh_3)FeCOCH_2CH_3$ (**18**) [24] (14% after column

chromatography) in solution. Use of 2 equivalents of **1** in this reaction produces the μ-hydride salt **9** (85%) in addition to undiminished yields of **17** and **18**. Evidently, **1**, like Ph_3C^+ [23], efficiently abstracts hydride from the ethyl complex **16** to produce the ethylene compound **17**.



(1) (16) (17) (18) (14)

Conclusions

Overall, the chemical reactivity of $Cp(CO)_3Mo^+ PF_6^-$ (**1**) resembles that of H^+ or of Ph_3C^+ in its initial reactions with the organoiron and -molybdenum methoxymethyl and ethyl complexes. Thus, **1** also abstracts hydride and methoxide from these coordinated ligands to give methoxymethylidene or ethylene and methylidene salts, respectively, as primary intermediates. The latter intermediate then engages in subsequent coordinated ligand transformations, as outlined in Scheme 1. In addition, **1** also promotes alkyl-CO insertion to give primarily bimetallic propionyl and acetyl complexes, the latter being derived from starting methoxymethyl complexes. Indeed, we have been unsuccessful in generating bimetallic μ-methoxyacetyl compounds from the requisite methoxymethyl complexes.

The coordinated ligand transformations delineated in this synthetic study entail a vacant coordination site on one metal center removing hydride (or methoxide), in an intermolecular reaction, from a ligand on another metal center. Usefulness of this chemistry remains to be tested, although we note that converting a carbonyl-hydrido complex plus an electrophilic carbonylmethylidene directly to a bimetallic μ-acetyl complex, the results of a control reaction (eq. 10), uniquely generates the acetyl ligand from C_1 fragments.

Rather less is known regarding the mechanism(s) extant as **1** removes hydride from the methoxymethyl and ethyl complexes reported herein. Both (1) direct hydride extraction by **1**, and (2) prior one-electron oxidation of the substrate alkyl complexes by **1**, followed by hydrogen atom removal by the seventeen-electron radical species $Cp(CO)_3Mo$, will account for the observed reaction chemistry. Precedent indeed exists for both pathways of formal hydride abstraction using Ph_3C^+ in place of **1** [38]. A consequence of the oxidation pathway is that the cation-radical alkyl complex intermediate is now prone towards alkyl-CO insertion [39]; this migration, coupled with scavenging of CO within the system and a radical chain transfer process [39], would produce an acyl complex. This CO insertion mechanism, therefore, could account for **1** converting the iron ethyl complex **16** into the propionyl **18** by-product. Moreover, we recently found that **1** reacts with the iron methyl complexes **13a,b** via separate pathways involving Lewis acid assistance and one-electron oxidative enhancement of the methyl-CO migratory insertion, before forming the μ-acetyl compounds [37]. Work is continuing in order to extend these synthetic studies towards understanding that mechanism(s) of interaction of organometallic Lewis acids with alkyl complexes.

Acknowledgment

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