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"Homo- and Hetero-Bimetallic $\mu(\eta^1\text{-O}:\eta^1\text{-O'})$ Formate Complexes $(\text{M-OCHO-M'})^+PF_6^-$ $[\text{M,M'}=(\eta^5\text{-}C_5H_5)(CO)(NO)Re,\ (\eta^5\text{-}C_5H_5)(CO)_3W,\text{and}\ (\eta^5\text{-}C_5H_5)(CO)_2Fe]$: Their Synthesis, Solution Lability, and Reactivity Towards Hydride Donors"

by

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The rhenium and tungsten ($\eta^1$-O) formates Cp(NO)(CO)Re-OC(O)H and $Cp(CO)_3W$-OC(O)H are available through protonolysis ($HBF_4$-$HCO_2H$) of their methyl complexes. These formates, in turn, afford homobimetallic (ReRe) and (WW) $\mu(\eta^1$-O,O') formates M-OCHO-$M^+$ upon reacting with the requisite organometallic Lewis acid [M-H/$Ph_3C^+$]. Analogous heterobimetallic $\mu$-formates (FpRe) and (FpW) [Fp=$Cp(CO)_2Fe$] also are prepared using similar reaction chemistry. The (ReRe) $\mu$-formate salt is labile in solution; its dissociative equilibrium can be intercepted with FpOC(O)H to give the mixed [FpRe] $\mu$-formate. Tungsten-containing bimetallic $\mu$-formate salts, in contrast, do not reversibly dissociate in solution. Reactions of hydride donors, including $Et_3BDLi$, with $Cp(CO)_3W$-OCHO-$W(CO)_3Cp^+$ give only the W formate and $Cp(CO)_3W$-H(D); no evidence was found for hydride (deuteride) adding to the carboxylate carbon of the formate bridge.


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# Homo- and Hetero-Bimetallic $\mu(\eta^1\text{-O}:\eta^1\text{-O}')$ Formate Complexes $(\text{M-OCHO-M}')^+PF_6^-$ [M,M'=$(\eta^5\text{-}C_5H_5)$(CO)(NO)Re, $(\eta^5\text{-}C_5H_5)(CO)_3W$, and $(\eta^5\text{-}C_5H_5)(CO)_2Fe$]: their Synthesis, Solution Lability, and Reactivity Towards Hydride Donors



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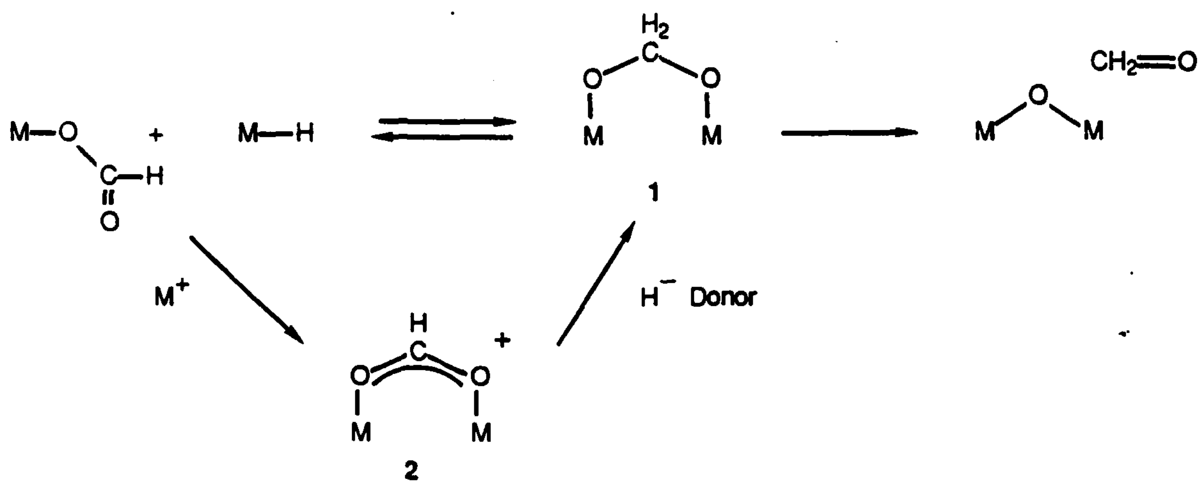
## Abstract

The rhenium and tungsten $(\eta^1\text{-O})$ formates Cp(NO)(CO)Re-OC(O)H and $Cp(CO)_3W$-OC(O)H are available through protonolysis ($HBF_4$-$HCO_2H$) of their methyl complexes. These formates, in turn, afford homobimetallic (ReRe) and (WW) $\mu(\eta^1$-O,O') formates M-OCHO-M$^+$ upon reacting with the requisite organometallic Lewis acid [M-H/$Ph_3C^+$]. Analogous heterobimetallic μ-formates (FpRe) and (FpW) [Fp=$Cp(CO)_2Fe$] also are prepared using similar reaction chemistry. The (ReRe) μ-formate salt is labile in solution; its dissociative equilibrium can be intercepted with FpOC(O)H to give the mixed [FpRe] μ-formate. Tungsten-containing bimetallic μ-formate salts, in contrast, do not reversibly dissociate in solution. Reactions of hydride donors, including $Et_3BDLi$, with $Cp(CO)_3W$-OCHO-$W(CO)_3Cp^+$ give only the W formate and $Cp(CO)_3W$-H(D); no evidence was found for hydride (deuteride) adding to the carboxylate carbon of the formate bridge.

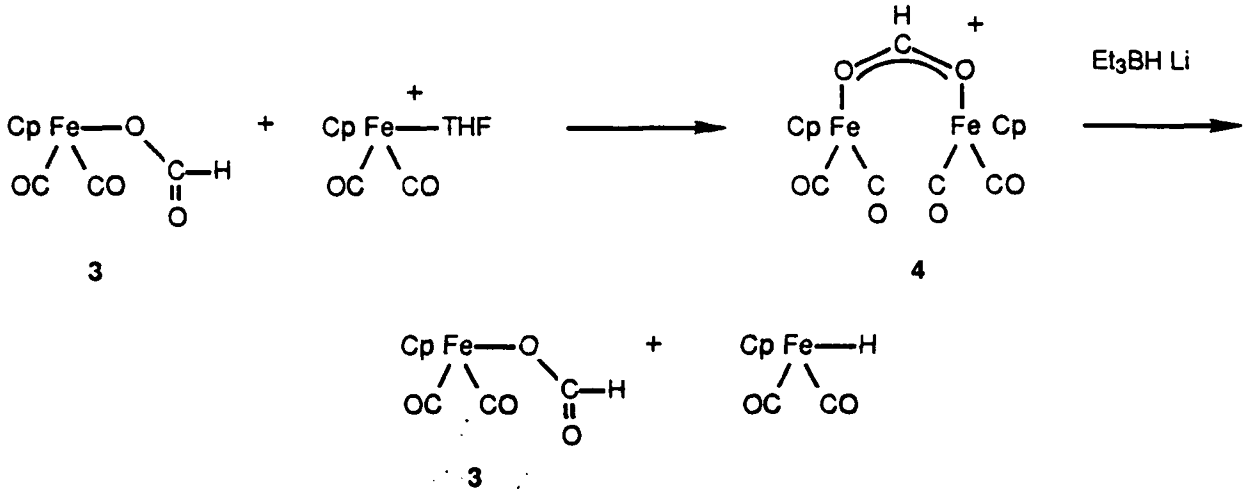
## Introduction

Many examples of organometallic hydrido compounds that incorporate $CO_2$ to give $\eta^1$-O formate complexes are known, but few of these formates undergo further reduction to formaldehyde and methanol.[1] One mechanism envisaged for homogeneous reduction of $CO_2$ nevertheless entails a formate complex M-OC(O)H adding an additional equivalent of metal hydrido compound M-H; the resulting gem-diolate M-$OCH_2O$-M (**1**) subsequently extrudes formaldehyde (eq.1).[2] Reduction of bimetallic $\mu(\eta^1$-O,$\eta^1$-O') formates M-OCHO-$M^+$ (**2**) also potentially provides another synthetic route to examples of **1** (eq.1). Our goal is to develop this latter route and synthesize homo- and heterobimetallic gem-diolate compounds **1**. Once available, their degradative reactions via formaldehyde extrusion or β-elimination of metal hydride to regenerate a formate complex[3] can be examined




(1)

We previously reported the synthesis of the bis-iron $\mu(\eta^1$–O,$\eta^1$–O') formate complex **4** by coordinating FpOC(O)H (**3**) with the Lewis and $Fp^+$ (eq.2).[4] A noteworthy observation concerning this bimetallic formate **4** is that nucleophilic hydride donors react with it by an apparent dissociative interchange ($I_D$) process[5] at an iron center to release **3** plus FpH. Alternative processes entailing either predissociation of **4** (the reverse of eq 2) and trapping of $Fp^+$ by the hydride donor or β-elimination of FpH from a gem-diolate intermediate **1** (M=Fp) are ruled out. Ionization of **4** is precluded because its solutions in acetonitrite do not give the substitution-inert $Fp(CH_3CN)^+$. Intermediacy of **1** is inconsistent with the results of a labeling



(2)

experiment: use of $LiDBEt_3$ as the hydride donor to 4 does not give FpOC(O)D, an anticipated β-elimination product of the alkoxide FpOCHDOFp.[4]

We now report syntheses of the formate complexes $Cp(CO)_3W$-OC(O)H (5) and Cp(NO)(CO)Re-OC(O)H (6), the homobimetallic $\mu(\eta^1$-O,$\eta^1$-O') formate compounds **7** [**2**: M= $W(CO)_3Cp$] and **8** [**2**: M=Re(CO)(NO)Cp], and the heterobimetallic analogs **9** [**2**: $M_2$=$W(CO)_3Cp$ and $Fe(CO)_2Cp$] and **10** [**2**: $M_2$=Re(NO)(CO)Cp and $Fe(CO)_2Cp$]. The reactions of nucleophiles, including hydride donors, with the bimetallic formates **7-10** received considerable emphasis. Since these third-row tungsten and rhenium centers potentially impart higher stability-lower reactivity to their complexes, we were particularly interested in generating examples of gem-diolate complexes **1** from **7** and **8**. The Re(CO)(NO)Cp system has found extensive applications in stabilizing $C_1$ ligands[6]; the phosphine-substituted analog also affords examples of stable alkoxide compounds $Cp(NO)(PPh_3)Re$-$OCH_2R$.[7] The tungsten system gives a surprisingly stable μ-1,2-ethanediyl compound $Cp(CO)_3W$-$CH_2CH_2$-$W(CO)_3Cp$ that does not readily eliminate ethylene.[8] Bergman and coworkers recently reported a stable tungsten-containing bimetallic alkoxide $Cp(CO)_3W$-$CH_2CH_2O$-$Zr(Cl)Cp_2$, which upon heating or photolysing extrudes ethylene and leaves the μ-oxo compound $Cp(CO)_3W$-O-$Zr(Cl)Cp_2$.[9]

## Experimental Section

Synthetic manipulations were performed under a nitrogen atmosphere using standard syringe-septum and Schlenk techniques.[10] Infrared spectra were taken of $CH_2Cl_2$ solutions or of KBr pressed disks and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The ν(CO) frequencies (2200-1500 $cm^{-1}$) were calibrated against the polystyrene 1601 $cm^{-1}$ absorption; they are accurate to ±2 $cm^{-1}$ below and ±5 $cm^{-1}$ above 2000 $cm^{-1}$. NMR spectral data were obtained on a Varian Model XL-200 spectrometer; chemical shifts ( δ) are referenced to internal $(CH_3)_4Si$. Combustion microanalysis were done by MicAnal, Tuison, AZ.

Organic reagents were obtained commercially and used as received. Dichloromethane was distilled under nitrogen from $P_2O_5$; anhydrous diethyl ether was taken from a freshly opened can, or it was distilled from sodium benzophenone ketyl. $Ph_3C^+PF_6^-$ was prepared according to Dauben's procedure[11]; it was reprecipitated from dichloromethane-ethyl acetate, vacuum dried, and stored in an inert atmosphere at-10°C. Organometallic starting materials FpOC(O)H (3), $Fp_2(O_2CH)^+PF_6^-$(4)[4], $Cp(CO)_3WH$[12], $Cp(CO)_3WCH_3$[13], $Fp(THF)^+PF_6^-$[14], Cp(NO)(CO)ReH[6b,d], and $Cp(NO)(CO)ReCH_3$[6b,c], were prepared by literature procedures and judged pure by IR and $^1H$ NMR spectroscopy. Authentic samples and spectral data of FpH[15], FpI, $Fp_2$[16], $(Cp(CO)_3W)_2$[17], $Cp(CO)_3WI$[18], and Cp(NO)(CO)ReI[19] were available from previous studies for direct comparison.

### Preparation of $(\eta^5\text{-}C_5H_5)(CO)_3W\text{-}OC(O)H$ (5)

To a yellow dichloromethane solution (40mL) of $Cp(CO)_3W\text{-}CH_3$ (2.06g, 5.77 mmol) was added first 88% formic acid (0.45 mL, 8.6 mmol) and then with efficient stirring $HBF_4.OEt_2$ (1.1mL, 8.6 mmol). Vigorous gas evolution ensued as the tetrafluoroboric acid was added dropwise. An IR spectrum of the red solution after 5 min. indicated quantitative formation of a new complex that was tentatively formulated as $Cp(CO)_3W(O{=}CHOH)^+BF_4^-$: 2060,1960(br), 1612 $cm^{-1}$ [ν(CO)]. Anhydrous potassium carbonate (6.00g, 40 mmol) was added with stirring; the mixture was filtered; and all color was extracted from the potassium carbonate with dichloromethane. IR spectra of the combined red filtrates indicated that only one organometallic species was present: 2052,1958(br) [ν(CO)], 1635 $cm^{-1}$ [$\nu(CO_2)$]. This solution was diluted with heptane before concentrating under reduced pressure. Recrystallization from dichloromethane-heptane offered a red crystalline solid (1.351g) that was identified as $Cp(CO)_3W$-OC(O)H (**5**) (62% yield). IR (KBr) 2045,1955(br),1925(sh) [ν(CO)], 1628 [$\nu_{asym}(CO_2)$], 1285 $cm^{-1}$ [$\nu_{sym}(CO_2)$]; $^1H$ NMR ($CDCl_3$) δ 7.37 (s, OCHO), 5.79 (s, Cp); $\{^1H\}^{13}C$ NMR ($CDCl_3$) δ 233.5 (*trans*-CO), 220.4 (*cis*-CO), 169.0 (OCHO, $^1J_{C-H}$=207.9 Hz: gated decoupling), 93.8 (Cp).

Anal. Ca1cd for $C_9H_6O_5W$: C,28.58; H,1.59. Found: C,28.11; H,1.60.

### Preparation of $(\eta^5\text{-}C_5H_5)(CO)_3W\text{-}OCHO\text{-}W(CO)_3(\eta^5\text{-}C_5H_5)^+PF_6^-$ (7)

A bright yellow dichloromethane solution (20mL) containing $Ph_3C^+PF_6^-$ (0.412g, 1.06 mmol) was cooled (-78°C) and was treated with $Cp(CO)_3WH$ (0.355g, 1.06mmol) in dichloromethane solution (10mL). To the resulting dark red solution (5 min) was added $Cp(CO)_3W$-OC(O)H (**5**) (0.401g, *1.06 mmol), and* the solution was warmed to room temperature (1.5h). IR spectral monitoring of the resulting red solution established the presence of one formate species: 2052,1965(br) [ν(CO)], 1572 $cm^{-1}$ [$\nu(CO_2)$]. The solution then was filtered through a celite pad, concentrated under reduced pressure (20mL), and added dropwise to 100mL of diethyl ether. This precipitated $[Cp(CO)_3W]_2(OCHO)^+PF_6^-$(7) as a reddish-brown microcrystalline solid that was filtered, washed with ether, and vacuum dried: 0.537g (59% yield); IR (KBr) 2055,1945(br),1918(sh) [ν(CO)], 1575 $cm^{-1}$ [$\nu_{asym}(CO_2)$]; $^1H$ NMR ($CD_3NO_2$) δ 7.21 (s, OCHO), 6.09 (s,Cp); $\{^1H\}^{13}C$ NMR ($CH_2C1_2$) δ 240.4 (*trans*-CO), 234.6 (**cis**-CO), 195.6 (OCHO;$^1J_{CH}$=219.3Hz: gated decoupling), 108.2 (Cp).

Anal. Calcd for $C_{17}H_{11}O_8W_2PF_6$: C, 23.84; H,1.29. Found: C, 23.62; H,1.31.

To a dichloromethane solution (5.0mL) of $[Cp(CO)_3W]_2(OCHO)^+PF_6^-$(7) (81 mg, 0.10 mmol) was added $(n\text{-}Bu)_4N^+I^-$(37mg, 0.10mmol). IR spectral monitoring of the red solution (0.5h) established quantitative conversion to $Cp(CO)_3W$-I (2039,1960(br) $cm^{-1}$) and $Cp(CO)_3W$-OC(O)H (5).

### Preparation of $(\eta^5\text{-}C_5H_5)(CO)_3W\text{-}OCHO\text{-}Fe(CO)_2(\eta^5\text{-}C_5H_5)^+PF_6^-$(9)

$Cp(CO)_3WOC(O)H$ (5) (0.421g, 1.11mmol) and $Cp(CO)_2Fe(THF)^+PF_6^-$ (0.438g, 1.11mmol) were dissolved in 25mL of dichloromethane. After 5h, IR spectral monitoring of the red solution indicated complete conversion to $Cp(CO)_3W\text{-}OCHO\text{-}Fe(CO)_2Cp^+PF_6^-$ (9): ν(CO) 2068,2025 [ν(CO)] [$Cp(CO)_2Fe$], 2063,1958(br) [ν(CO)] [$Cp(CO)_3W$]; 1577 $cm^{-1}$ [ν($CO_2$)]. This solution was filtered through celite, and the combined filtrates were concentrated to 10mL before adding dropwise to excess ether (50mL). The resulting red-orange precipitate was filtered and was reprecipitated from dichloromethane-ether(15-60 mL). Yield 0.561g (72%) of 9 as a red-orange powder: IR (KBr) 2075,2056,2024,1978(sh),1940(br) [ν(CO)], 1573$cm^{-1}$ [$\nu_{asym}(CO_2)$]; $^1H$ NMR ($CD_3NO_2$) δ 7.15 (s, OCHO), 6.05 (s, CpW), 5.33 (s, CpFe).

Anal. Calcd for $C_{16}H_{11}O_7FeWPF_6$: C,27.44; H,1.57. Found: C,27.01; H,1.68.

$(n\text{-}Bu)_4N^+I^-$ (37mg, 0.10mmol) was added to a dichloromethane solution (2.5mL) containing $Cp(CO)_3W\text{-}OCHO\text{-}Fe(CO)_2Cp^+ PF_6^-$ (9) (70mg, 0.10mmol). Results of IR spectral monitoring (0.5h) were consistent with quantitative cleavage of 9 to $Cp(CO)_3WOC(O)H$ (5) and $Cp(CO)_2Fe\text{-}I$ [2058,2002 $cm^{-1}$]. The presence of at least 8% of the alternative products, $Cp(CO)_2FeOC(O)H$ (3) [2005,2049,1617 $cm^{-1}$] and $Cp(CO)_3WI$, would have been detected.

**NMR Spectral Observations: Attempted Exchange Reactions to Prepare $(\eta^5\text{-}C_5H_5)(CO)_3W\text{-}OCHO\text{-}Fe(CO)_2(\eta^5\text{-}C_5H_5)^+PF_6^-$ (9).**

A solution of $[Cp(CO)_3W]_2(OCHO)^+PF_6^-$ (7) (32mg, 0.037mmol) and $Cp(CO)_2FeOC(O)H$ (3) (8.3mg, 0.037mmol) in $CD_3NO_2$ (0.4mL) was prepared in a NMR tube. $^1H$ NMR spectral monitoring of the red solution over 24 hours was consistent with only starting materials being present. In particular, absorptions for $Cp(CO)_3WOCHOFe(CO)_2Cp^+PF_6^-$ (9) were not detected. $^1H$ NMR spectral monitoring of a $CD_3NO_2$ solution (0.4mL) of $[Cp(CO)_2Fe]_2(OCHO)^+PF_6^-$ (4) (24mg, 0.044mmol) and $Cp(CO)_3WOC(O)H$ (5) (17mg, 0.044mmol) afforded similar results (10h). *Prominent absorptions for* 4, δ 7.03 (OCHO) and 5.36 (Cp), *remained; and those for* 9 *and* 3, δ 8.12 (OCHO) and 5.19 (Cp), were not evident.

**Reaction of $[(\eta^5\text{-}C_5H_5)(CO)_3W]_2(OCHO)^+PF_6^-$ (7) and $LiDBEt_3$**

$[Cp(CO)_3W]_2(OCHO)^+PF_6^-$ (7) (76mg, 0.089mmol) was dissolved in 6.0 mL of dichloromethane and was cooled to -78°C. A tetrahydrofuran solution of $LiDBEt_3$ (0.09mL, 0.09mmol) was added dropwise, and the unchanged red solution was maintained at -78°C (0.5h). After warming to room temperature (over 1.0h), solvent was removed under reduced pressure (30mm, 1h), 0.8mL of $CDCl_3$ (purified by passing through activity 1 alumina) was added, and the solution was filtered through a bed of alumina (1/8 X 1/8" diameter) to remove a trace of suspended material. $^1H$ NMR spectral measurements were recorded. In addition to residual THF and $CH_2Cl_2$, absorptions for $Cp(CO)_3WOC(O)H$ (5), $Cp(CO)_3WH$ / $Cp(CO)_3WD$ [$\delta$ 5.50 (Cp), -7.30 (W-H)], and $[Cp(CO)_3W]_2$ ($\delta$ 5.39) were observed: molar ratio 3.2: 1.0: 1.3 based on intensities of Cp singlets. Relative integration values of absorptions for 5 (0.9: 5.0) and for $Cp(CO)_3WH$ (5.0: 0.48) was calculated.

### Preparation of $(\eta^5\text{-}C_5H_5)(NO)(CO)Re\text{-}OC(O)H$ (6)

A dichloromethane solution (25 mL) of $Cp(NO)(CO)ReCH_3$ (0.200g, 0.617mmol) was treated with 88% formic acid (0.04mL, 0.93mmol) and then $HBF_4.OEt_2$ (0.12mL, 0.87mmol) with vigorous stirring. Immediate gas evolution (presumably methane) concurrent with the initially red solution turning brown was observed. IR spectral monitoring (5 min) established that the starting methyl complex had transformed quantitatively to a new species, presumably $Cp(NO)(CO)Re(O{=}CHOH)^+BF_4^-$: 1999 [$\nu$(CO)],1725(br) $cm^{-1}$ [$\nu$(NO)]. Anhydrous potassium carbonate (0.5g, 3.3mmol) was added, and the resulting red supernatant liquid was filtered through celite. The combined filtrates afforded $Cp(NO)(CO)ReOC(O)H$ (6) as a red crystalline solid (0.158g, 73% yield) after crystallization from dichloromethane-heptane. IR ($CH_2Cl_2$) 1992 [$\nu$(CO)], 1727 [$\nu$(NO)], 1641 $cm^{-1}$ [$\nu(CO_2)$]; IR (KBr) 1987,1961(sh) [$\nu$(CO)], 1732(sh),1700 [$\nu$(NO)], 1638 [$\nu_{asymn}(CO_2)$], 1255 $cm^{-1}$[$\nu_{sym}(CO_2)$]. $^1H$ NMR ($CDCl_3$) $\delta$ 7.46 (s, OCHO), 5.86 (s,Cp); $\{^1H\}^{13}C$ NMR ($CDCl_3$) $\delta$ 199.6 (CO), 170.1 (OCHO, $^1J_{C\text{-}H}$=208.2 Hz: gated decompling), 93.2 (Cp).

Anal. Calcd for $C_7H_6NO_4Re$: C,23.71; H,1.69. Found: C,23.79;H,1.80.

**Preparation of $(\eta^5\text{-}C_5H_5)(NO)(CO)Re\text{-}OCHO\text{-}Re(CO)(NO)(\eta^5\text{-}C_5H_5)^+$ $PF_6^-$ (8)**

To a dichloromethane solution (20mL) of $Ph_3C^+PF_6^-$ (0.168, 0.433mmol), which was kept at -78°C, was added dropwise a dichlomethane solution (6mL) of Cp(NO)(CO)ReH (0.134g, 0.432mmol). The initially red-orange solution formed a yellow-orange suspension (0.75h) to which Cp(NO)(CO)ReOC(O)H (**6**) (0.153g, 0.432mmol) was added with vigorous stirring. The suspension was warmed to room temperature (1h), by then a yellow-orange solution was evident. This was filtered throught celite, concentrated to 10mL, and added slowly to 60mL of diethly ether to give a yellow-brown precipitate. Reprecipitation afforded $[Cp(NO)(CO)Re]_2(OCHO)^+PF_6^-$ (**8**) (0.276g, 79% yield). IR ($CH_2Cl_2$) 2012 [v(CO)], 1749 [v(NO)], 1561 $cm^{-1}$ [$v(CO_2)$]; IR (KBr) 1982 [v(CO)], 1720 (br) [v(NO)], 1560 [$v_{asym}(CO_2)$], 1315 $cm^{-1}$ [$v_{sym}(CO_2)$]; $^1H$ NMR ($CD_3NO_2$) $\delta$ 7.72 (s, OCHO), 6.13 (s, Cp); $\{^1H\}^{13}C$ NMR ($CH_2Cl_2$) $\delta$ 209.72,209.64 (CO), 198.96,198.66 (OCHO; $^1J_{C-H}$=220.4 and 220.7 Hz: gated decoupling), 107.4(Cp).

Anal. Calcd for $C_{13}H_{11}N_2O_6Re_2PF_6$: C,19.30; H1.36. Found C,19.59; H,1.45.

Treating a dichloromethane solution of **8** (3.0mL, 0.10mmol) with excess $n\text{-}Bu_4N^+I^-$ immediately afforded a red-brown solution, 2000(br) [v(CO)], 1730(br) [v(NO)], 1641 $cm^{-1}$ [$v(CO)_2$)].

**Preparation of $(\eta^5\text{-}C_5H_5)(NO)(CO)Re\text{-}OCHO\text{-}Fe(CO)_2(\eta^5\text{-}C_5H_5)^+PF_6^-$ (10).**

A mixture of Cp(NO)(CO)ReOC(O)H (**6**) (0.112g, 0.316mmol) and $Cp(CO)_2Fe(THF)^+$ $PF_6^-$ (0.125g, 0.316mmol) was reacted as a dark red dichloromethane solution (6.0mL). After 4h, IR spectral monitoring confirmed quantitative conversion to Cp(NO)(CO)Re-OCHO-$Fe(CO)_2Cp^+PF_6^-$ (**10**): 2070,2020 [v(CO)], 1751 [v(NO)], 1572 $cm^{-1}$[$v(CO_2)$]. The solution was filtered through celite, and the red product was isolated by precipitating in excess ether (50mL) and reprecipitating from dichloromethane-ether. Yield 0.168g (78%) **10**: IR (KBr) 2070,2015(br) [v(CO)], 1748(br) [v(NO)], 1575 [$v_{asym}(CO_2)$], 1348 $cm^{-1}$ [$v_{sym}(CO_2)$]; $^1H$ NMR ($CD_3NO_2$) $\delta$ 7.37 (OCHO), 6.09 (s, CpRe), 5.36 (s, CpFe).

Anal. calcd for $C_{14}H_{11}NO_6FeRePF_6$: C,27.44; H,1.57. Found C,26.98; H, 1.68.

A dichloromethane solution (3.0mL) containing $Cp(NO)(CO)ReOCHOFe(CO)_2Cp^+PF_6^-$ (**10**) (67mg,0.10mmol) was treated with $n\text{-}Bu_4N^+I^-$ (37mg,0.10mmol). IR spectral analysis of the red solution (0.5h) established quantitative cleavage of **10** to Cp(NO)(CO)ReI and $Cp(CO)_2FeOC(O)H$ (**3**): 2058,2000(br) [ν(CO)], 1735 [ν(NO)], 1617 $cm^{-1}$[ν($CO_2$)]. The presence in this mixture of at least 5% Cp(NO)(CO)ReOC(O)H (**6**) would have been detected by its formate absorption (1635$cm^{-1}$).

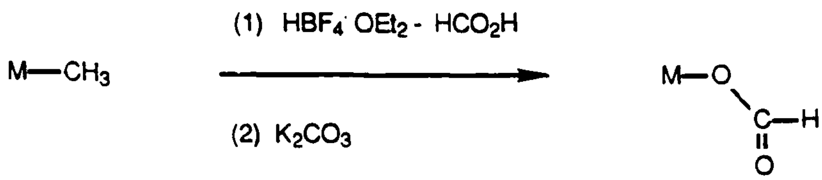
### NMR Spectral Observations: Exchange Reaction between [$\eta^5$-$C_5H_5$)(NO)(CO)Re]$_2$(OCHO)$^+PF_6^-$ (8) and ($\eta^5$-$C_5H_5$)(CO)$_2$FeOC(O)H (3)

A $CD_3NO_2$ solution (0.4mL, predried by passage through alumina) of $[Cp(NO)(CO)Re]_2(OCHO)^+ PF_6^-$ (**8**) (28mg, 0.035mmol) and $Cp(CO)_2FeOC(O)H$ (**3**) (8mg, 0.035mmol) was examined by $^1H$ NMR spectroscopy. After 1h, a 1.0: 1.0: 1.76: 1.76 ratio of Cp(NO)(CO)ReOC(O)H (**6**): $Cp(NO)(CO)Re\ OCHOFe(CO)_2Cp^+$ (**10**): $Cp(CO)_2FeOC(O)H$ (**3**): $[Cp(NO)(CO)Re]_2(OCHO)^+$ (**8**) was quantified by integration of Cp and of formate absorptions. No other organametallic species were detected. After 10h, this ratio had changed to 6.15 **6**: 6.15 **10**: 1.0 **3**: 1.0 **8**, with no other detectable compounds in the dark red solution.

## Results and Discussion

### Preparation of Formate Complexes

We prepared the tungsten and rhenium formate complexes **5** and **6** using essentially the same procedure as that used previously in preparing FpOC(O)H (**3**).[4] Treatment of the methyl compounds $Cp(CO)_3WCH_3$[13] and $Cp(NO)(CO)ReCH_3$[6b,c] first with tetrafluoroboric acid etherate-formic acid and then with potassium carbonate affords **5** and **6** as air-stable red crystalline solids in 60-75% yields (eq.3). Characterization of these formate species as detailed in the experimental section is straightfoward.



(3)

M = W(CO)$_3$Cp 5

M = Re(NO)(CO)Cp 6

The presence of unidentate ($\eta^1$-O) formate bonding for **5** and **6** is consistent with IR spectral data. Carbonyl stretching frequencies, both the energies and the band shapes, closely resemble those of related halide complexes $Cp(CO)_3WX$ and $Cp(NO)(CO)ReX$. The intense carboxylate stretching frequencies are particularly diagnostic for covalent ($\eta^1$-O) formate species; higher energy $\nu_{asym}(CO_2)$ absorptions, for example, appear above 1600 $cm^{-1}$. A more conclusive observation is that differences in the carboxylate stretching frequencies, $\Delta\nu = \nu_{asym}(CO_2) - \nu_{sym}(CO_2)$, for **5** (343 $cm^{-1}$) and for **6** (383 $cm^{-1}$) are in the expected range for ($\eta^1$-O) formate ligands.[20]

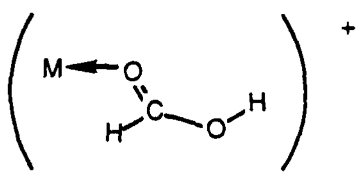
The corresponding tungsten acetate $Cp(CO)_3W\text{-}OC(O)CH_3$ has been reported by two research groups.[9,21] Werner and coworkers[21] recently prepared it by protonating $Cp(CO)_3WCH_3$ with $HBF_4\text{-}CH_3CO_2H$; they also confirmed the ($\eta^1$-O) acetate bonding by means of its X-ray structure determination. Warming this ($\eta^1$-O) acetate drives it over to the ($\eta^2$-O,O') chelating structure $Cp(CO)_2W\text{-}OC(O)CH_3$.[21a] Reversible interconversion of ($\eta^1$-O) and ($\eta^2$-O,O') carboxylate ligands (including both formate and acetate) recently has been reported for *trans*-$(PPh_3)_2(CO)_2(NO)W\text{-}OC(O)R$ / $(PPh_3)_2(CO)(NO)W\text{-}OC(O)R$ and for the Mo(II) systems $(PR'_3)_2(CO)_2[RC(O)O]Mo\text{-}OC(O)R$: R'=Et,Ph.[23] Under the conditions of our experiements, we did not observe any transformation of the ($\eta^1$-O) formate compexes **5** and **6** (and **3**) to analogous chelating ($\eta^2$-O,O') formate structures.

Two observations on the preparative route used in obtaining formate complexes **5** and **6** are worth nothing. First, protolytic cleavage of transition-metal methyl compounds with strong acid (e.g.,$HBF_4$) generally affords labile organometallic Lewis Acids.[24] We previously reported that treating $FpCH_3$ with $HBF_4 \cdot OR_2$ gives first the covalent fluoroborate complex $FpFBF_3$ and then the labile etherates $Fp{\cdot}OR_2^+\ BF_4^-$ (R=Me, Et).[25] Similar intermediates presumably transpire during protonation of starting tungsten and rhenium methyl compounds. Indeed, both the tungsten Lewis acid and its etherate; $Cp(CO)_3WFBF_3$ and $Cp(CO)_3W{\cdot}OEt_2^+$, are known; although Beck prepared them after abstracting hydride from $Cp(CO)_3WH$.[26]

Analogous rhenium Lewis acids and their formate derivatives also are available. Sweet and Graham[5d,27] obtained the rhenium Lewis acid $Cp(NO)(CO)Re^+$ as its labile 3,4-$\eta^2$-$C_6H_5CHPh_2$ adduct by abstracting hydride with $Ph_3C^+$ from Cp(NO)(CO)ReH. Gladysz and coworkers[28] generated $Cp(NO)(PPh_3)Re^+$ by protonating the methyl compound $Cp(NO)(PPh_3)ReCH_3$; the ($\eta^1$-O) formate derivative $Cp(NO)(PPh_3)ReOC(O)H$ is available by this route. Beck's group[29] characterized the rhenium Lewis acid $(CO)_5ReFBF_3$, which results form the reaction of $(CO)_5ReCH_3$ and $Ph_3C^+BF_4^-$, and prepared the analogous formate $(CO)_5ReOC(O)H$. The ($\eta^1$-O) formate complex ($\alpha,\alpha'$-dipyridine)$(CO)_3ReOC(O)H$ forms as the product of $CO_2$ "insertion" into the corresponding rhenium hydride.[30]

We note that the metallocarboxylic acid Cp(NO)(CO)ReC(O)OH, a tautomer of the rhenium ($\eta^1$-O) formate **6**, has been characterized. Research groups of Casey[6e] and of Graham[6d] obtained this stable metallocarboxylic acid by adding hydroxide to the carbonyl salt $Cp(NO)(CO)_2Re^+$. We recently reported using it in the synthesis of the heterobimetallic $\mu(\eta^1$-C: $\eta^2$-O,O$')$ carbon dioxide complex $Cp(NO)(CO)ReCO_2Zr(Cl)Cp_2$.[31] Distinguishing between **6** and its tautomer is straightfoward by IR and $^1H$ NMR spectral data for the formate-hydroxycarbonyl ligands; we did not observe any interconversion between these species under ambient conditions.

The second observation concerning the preparation of **5** and **6** pertains to the intermediates detected by IR spectroscopy. We tentatively assign their structures as ($\eta^1$-O) formic acid derivatives.Their deprotonation ($K_2CO_3$) affords the isolated ($\eta^1$-O) formates, which in turn react



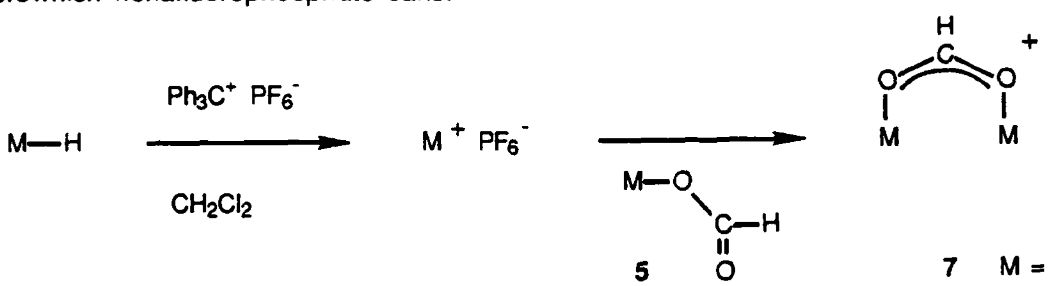

M = $W(CO)_3Cp$

M = Re(NO)(CO)Cp

with $HBF_4$ to regenerate these labile formic acid complexes. Analogous structures having the organic carbonyl functional group coordinated through the organometallic electrophile are well known.[24,32] Examples of ($\eta^1$-O) aldehyde and ketone complexes bearing $Cp(CO)_3W^{+}$[26], $Cp(NO)(CO)Re^{+}$[6d], $Cp(NO)(PPh_3)Re^{+}$[7], and $(CO)_5Re^{+}$[29b] organometallic moieties have been characterized.

**Bridging formate complexes**

Homobimetallic tungsten (**7**) and rhenium (**8**) bridging formate compounds are readily available by treating the Lewis acids $Cp(CO)_3W^+PF_6^-$[26] and $Cp(NO)(CO)Re^+PF_6^-$[27] with the requisite ($\eta^1$-O) formate complex (eq 4). These Lewis acids reagents, in turn, were generated by the standard procedure of abstracting hydride from metal hydrido complexes using $Ph_3C^+PF_6^-$. We isolated both $\mu(\eta^1\text{-O},\eta^1\text{-O}')$ formates **7** and **8** in moderate yields (60-80%) as air-stable brownish hexafluorophosphate salts.




(4)

**5**

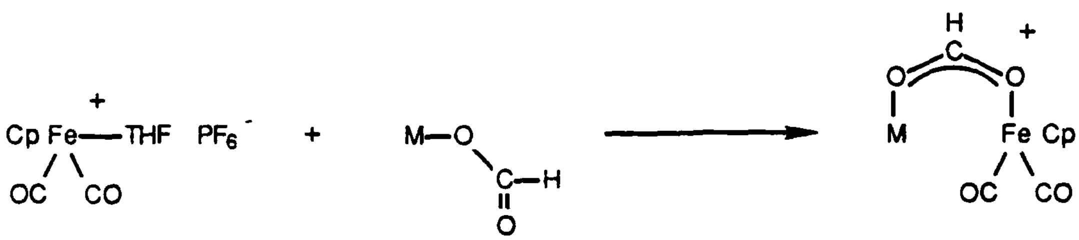
**6**

**7** M = $W(CO)_3Cp$

**8** M = $Re(NO)(CO)Cp$

A combination of IR, $^1$H and $^{13}$C NMR spectral data, and combustion microanalytical data suffice to unambiguously characterize these bridging formate complexes **7** and **8**. $^{13}$C NMR spectra of the bis-rhenium complex **8** further reveal two sets of carbonyl and formate absorptions that indicate a 1:1 mixture of diastereomers. This is consistent with the presence of two chiral rhenium centers on **8**. An analogous bis-rhenium metalloester $Cp(NO)(CO)Re\text{-}C(O)OCH_2\text{-}Re(NO)(CO)Cp$ having NMR distinguishable diastereomers has been observed by Casey.[6f] The $^{13}$C NMR spectra of both bis-tungsten bridging formate **7** and $Cp(CO)_3WOC(O)H$ (**5**) also have two carbonyl absorptions (with a 2:1 intenisty ratio), but these correspond to magnetically nonequivalent *cis*-and *trans*-carbonyls.[33]

Heterobimetallic formate complexes **9** and **10** are the products of reacting the labile tetrahydrofuranate compound $Fp(THF)^{+}PF_6^{-}$[14] with the ($\eta^1$-O) formates **5** and **6**, respectively (eq 5). These mixed tungsten-iron (**9**) and rhenium-iron (**10**) bridging formate salts are isolated in 70-80% yields after precipitating from dichloromethane-diethyl ether. They reprecipitate intact from dichloromethane or nitromethane solutions even after sitting for six hours. We did not detect **9** and **10** disproportionating to mixtures of their homobimetallic bridging carboxylates **4/7** and **4/8**.

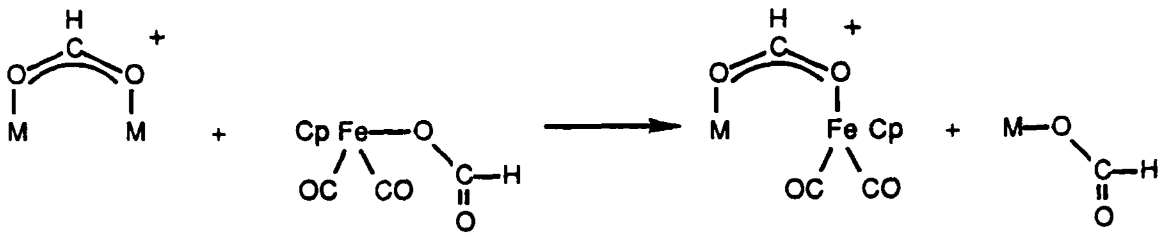


(5)

| | | |
|---|---|---|
| **5** | M = $W(CO)_3Cp$ | **9** |
| **6** | M = Re(NO)(CO)Cp | **10** |

Diagnostic formate absorptions in the $^1H$ NMR and IR spectra of the iron-tungsten and iron-rhenium bridging formate complexes **9** and **10** clearly differentiate them from their homobimetallic counterparts **4**, **7**, and **8**. The formate absorption in the NMR spectrum of **9** ($CD_3NO_2$) at δ 7.15, for example; differs from those for **4** (δ 7.03) and **7** (δ 7.21). Although separate Cp singlets occur for **9** at δ 6.05 (W center) and at 5.33 (Fp center), these are within 0.04ppm of the corresponding absorptions for **4** and for **7**. IR spectral $\nu_{sym}(CO_2)$ absorptions for the rhenium-containg μ-formates **8** and **10** and for $Fp_2(O_2CH)^{+}$ (**4**) vary over a 40 $cm^{-1}$ range even though their higher energy $\nu_{asym}$ ($CO_2$) absorptions appear within 15$cm^{-1}$ of one another. Corresponding Δν valves for **4** (212 $cm^{-1}$), **8** (245 $cm^{-1}$), and **10** (227 $cm^{-1}$) therefore distinguish **10**.

Differances in the $^1H$ NMR spectra of **9** and **10** vs their homobimetallic analogs facilitated direct monitoring of the reactions between FpOC(O)H (**3**) and the bis-tungsten (**7**) and bis-rhenium (**8**) μ-formates (eq.6). The objective of studying these reactions was to determine the lability of bimetallic formates **7** and **8** and to incorporate FpOC(O)H (**3**) into a bimetallic formate structure, thereby converting homobimetallic μ-formates **7** and **8** into their heterobimetallic counterparts **9** and **10**, respectively. No reaction between **3** and **7** is evident by $^1H$ NMR spectral monitoring after 10 hours in $CD_3NO_2$ solution (22°C): the Fp formate (**3**) does not exchange into the μ-formate **7** to release $Cp(CO)_3W\text{-}OC(O)H$ (**5**).



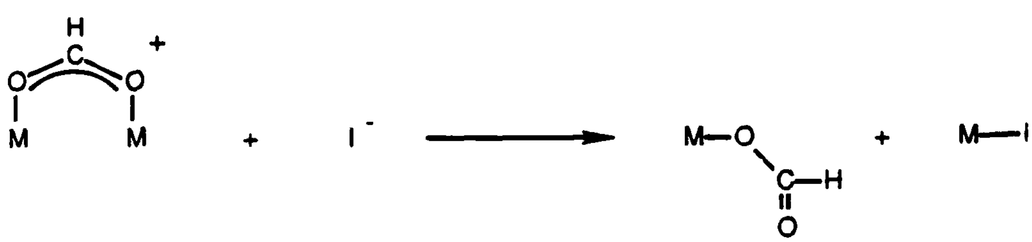

(6)

**7** M = $W(CO)_3Cp$ **9**

**8** M = Re(NO)(CO)Cp **10**

The bis-rhenium μ-formate **8**, however, proved to be more labile under these conditions. Within ten hours, 86% of the iron formate **3** incorporates into **7** concomitant with release of Cp(NO)(CO)ReOC(O)H (**5**) and the mixed iron-rhenium μ-formate **10**.

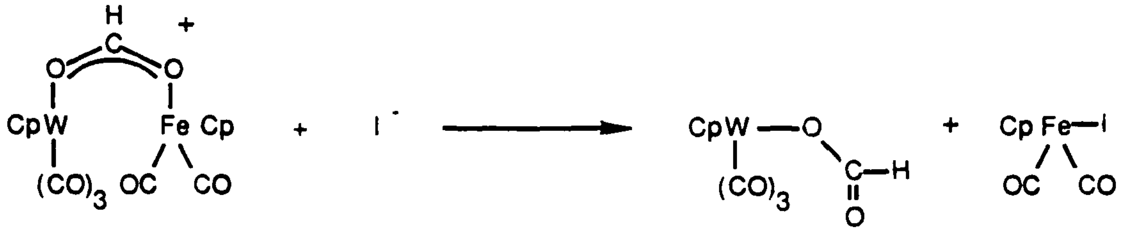
Iodide cleavage of the bimetallic formates **7** and **8** is a characteristic reaction (eq 7) that is particularly amenable to monitoring by IR spectroscopy. These reactions go to completion within 0.5 hour and release the starting formate complex plus a known metal iodide compound (eq 7). The intense IR spectral formate absorption $\nu_{asym}(CO_2)$ thus shifts to higher energy. One equivalent of iodide also leaves the heterobimetallic formates; these reactions are regioselective. The tungsten-iron μ-formate **9** produces exclusively $Cp(CO)_3W\text{-}OC(O)H$ (**5**) (eq 8), whereas the rhenium-iron μ-formate **10** delivers FpOC(O)H (**3**) (eq 9).



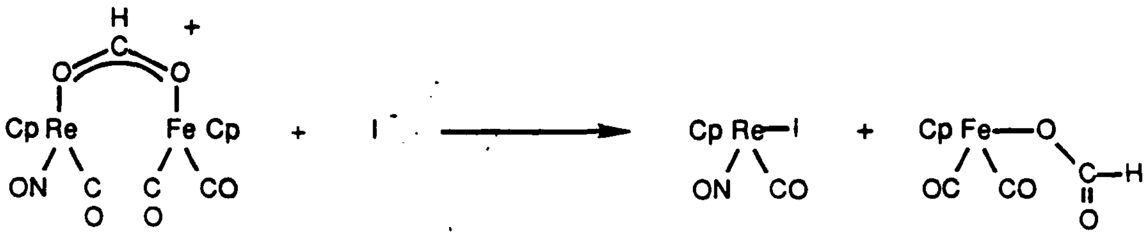

(7)

**7** M = $W(CO)_3Cp$ **5**

**8** M = Re(NO)(CO)Cp **6**



9 5 (8)

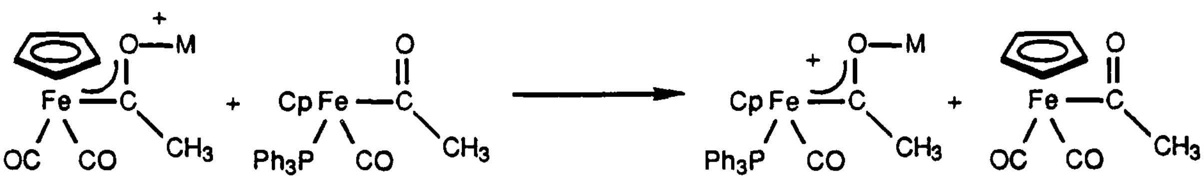


10 3 (9)

A pattern thus emerges in which the rhenium center on the bimetallic μ-formates **8** and **10** is considerably more labile than the corresponding tungsten centers on **7** and **9**. FpOC(O)H (**3**) displaces Cp(NO)(CO)ReOC(O)H (**6**) from the bis-rhenium formate **8**, but is unreactive towards the bis-tungsten congener **7** (eq 6). Iodide preferentially displaces on the rhenium center of the rhenium-iron μ-formate **9** (eq 8), but attacks at the Fp center on the tungsten-iron μ-formate **10** (eq 9).

This pattern is consistent with our earlier observations on the solution lability of bimetallic-μ($\eta^1$-C: $\eta^1$-O) acetyl compounds $[Cp(CO)_2Fe\text{-}C(CH_3)O\text{-}M]^+$, which exchange their $FpCOCH_3$ fragment for $Cp(PPh_3)(CO)FeCOCH_3$ in dichloromethane (eq 10).[34] The facility of these reactions depends on the choice of ($\eta^1$-O)-bound metal; after 18h (20°C), the extent of exchange varies: M=Re(NO)(CO)Cp (100%) > $Fe(CO)_2Cp$ (80%) > $W(CO)_3Cp$ (30%). These exchange reactions do not involve dissociation of the bimetallic acetyl (to $FpCOCH_3$ plus $M^+$) as determined by independent studies, but entail nucleophilic displacement of the acetyl complex $Cp(PPh_3)(CO)FeCOCH_3$ at the ($\eta^1$-O) bound metal M.

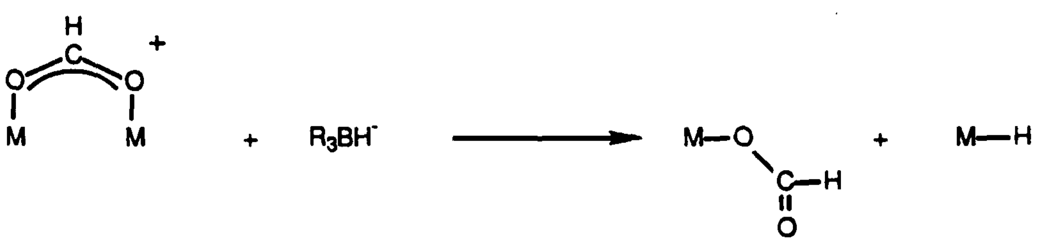
Of the three bimetallic formate complexes $M\text{-}OCHO\text{-}M^+$ [**4**, M=Fp; **7**, M=$W(CO)_3Cp$; **8**, M=Re(NO)(CO)Cp], the bis-tungsten **7** -- containing the least labile center M -- should be the most likely to undergo nucleophilic hydride addition at the bridging formate-carbon (eq 1).



(10)

M = $Fe(CO)_2Cp$, $Re(NO)(CO)Cp$, $W(CO)_3Cp$

Both μ-formates **7** and **8**, however, react with one equivalent of the monohydride donors $LiHBEt_3$ or $KHB(O\textit{i}\text{-}Pr)_3$ and immediately give a formate complex (**5** or **6**, respectively) and metal hydride (eq 11). These reactions occur quantitatively as ascertained by IR spectral monitoring; subsequent addition of $CCl_4$ transforms $Cp(CO)_3WH$ (i.e., the reduction product of **7**) into $Cp(CO)_3WCl$.[35] Upon removal of solvent and workup, the reaction mixture changes as dimeric $[Cp(CO)_3W]_2$ forms at the expenses of the tungsten hydride. Overall, reduction of **7** and **8** offers results analogous to those observed for their iodide cleavage and for hydride transfer to $FpOCHOFp^+$ (**4**).



(11)

**7** M = $W(CO)_3Cp$ **5**

**8** M = $Re(NO)(CO)Cp$ **6**

We used the reaction between **7** and $LiDBEt_3$ as a probe into the intermediacy of a gem-diolate complex **1** (M=$W(CO)_3Cp$). If deuteride addition to **7** occurs at the formate carbon then the resulting $Cp(CO)_3W\text{-}OCHDO\text{-}W(CO)_3Cp$ would fragment into approximately equal concentrations of labeled **5**, $Cp(CO)_3WOC(O)D$, and unlabeled **5**. Since $^1H$ NMR spectral monitoring of this reaction established that at least 90% unlabeled tungsten formate **5** forms, transience of $Cp(CO)_3W\text{-}OCHDO\text{-}W(CO)_3Cp$ contributes only a very minor pathway at best Inference of a 48:52 mixture of $Cp(CO)_3WH$ / $Cp(CO)_3WD$ by relative integration intensities of the Cp and tungsten hydride signals is consistent with established free-radical reactivity for this tungsten hydride complex.[35] We conclude that hydride-deuteride transfer to **7** occurs by nucleophilic attack at a tungsten center with displacement of $Cp(CO)_3WOC(O)H$ (**5**), a result analogous to that observed in reducing $FpOCHOFp^+$ (**4**).

We cannot vigorously exclude reduction of **7** by single-electron-transfer from the borohydride reogent,[36] the resulting neutral $Cp(CO)_3WOCHOW(CO)_3Cp$ then fragmenting into **5** and the seventeen-electron $Cp(CO)_3W$. The absence of dimeric $[Cp(CO)_3W]_2$ (and of $Fp_2$ in the reduction of **4**) as a kinetic product is inconsistent with intermediacy of a high-energy organometallic "radical",[35] however.

## Conclusions

The homobimetallic bridging-formate compounds $Cp(CO)_3W\text{-}OCHO\text{-}W(CO)_3Cp^+PF_6^-$ (**7**) and $Cp(NO)(CO)Re\text{-}OCHO\text{-}Re(NO)(CO)Cp^+PF_6^-$ (**8**) were prepared because of the potential of their tungsten and rhenium centers for stabilizing a variety of $C_1$ ligands. A surprising observation is the substantially higher lability of the rhenium center on **8** vs the tungsten center on **7**. Both **7** and **8**, however, rapidly intercept one equivalent of iodide or of a nucleophilic hydride donor to release the neutral ($\eta^1$-O) formate **5** and **6**, respectively. This hydride delivery does not give a gem-diolate intermediate **1**, as ascertained by the results of a labeling study involving **7** and $LiDBEt_3$. We favor a dissociative interchange ($I_D$) pathway[5] for these displacement reactions; involvement of a pure dissociative mechanism is inconsistent with the solution stability of the heterobimetallic μ-formates $FpOCHOM^+$ [**9**, M=$W(CO)_3Cp$ and **10**, M=$Re(NO)(CO)Cp$] and of $FpOCHOFp^+$ (**4**).

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