Contribution from the Department of Chemistry,
Rensselaer Polytechnic Institute, Troy, New York 12180-3590

Homo- and Heterobimetallic $\mu(\eta^1\text{-O}:\eta^1\text{-O}')$ Formate Complexes $(\text{M–OCHO–M}')^+\text{PF}_6^-$ [M, M′ = $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})(\text{NO})\text{Re}$, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{W}$, and $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}$]: Their Synthesis, Solution Lability, and Reactivity toward Hydride Donors

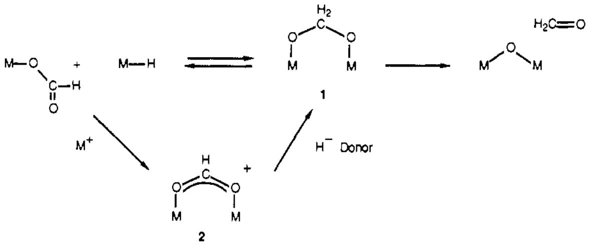
Chung C. Tso and Alan R. Cutler*

Received October 17, 1988

The rhenium and tungsten η^1-O formates Cp(NO)(CO)Re–OC(O)H and $\text{Cp(CO)}_3\text{W–OC(O)H}$ are available through protonolysis ($\text{HBF}_4\text{–HCO}_2\text{H}$) of their methyl complexes. These formates, in turn, afford homobimetallic ReRe and WW $\mu(\eta^1\text{-O,O}')$ formates M–OCHO–M$^+$ upon reacting with the requisite organometallic Lewis acid [M–H/Ph_3C^+]. Analogous heterobimetallic μ-formates FpRe and FpW [Fp = $\text{Cp(CO)}_2\text{Fe}$] also are prepared by 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 $\text{Cp(CO)}_3\text{W–OCHO–W(CO)}_3\text{Cp}^+$ give only the W formate and $\text{Cp(CO)}_3\text{W–H(D)}$; no evidence was found for hydride (deuteride) adding to the carboxylate carbon of the formate bridge.

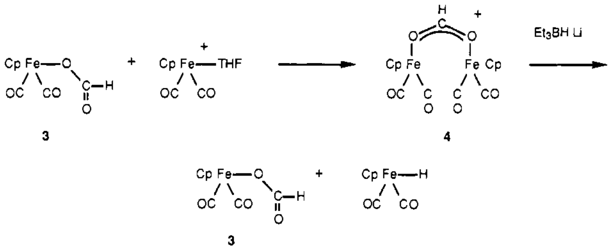
Introduction

Many examples of organometallic hydrido compounds that incorporate CO_2 to give η^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 and the *gem*-diolate intermediate $\text{M–OCH}_2\text{O–M}$ (**1**) subsequently extruding formaldehyde (eq 1).[2] Reduction of bimetallic $\mu(\eta^1\text{-O}:\eta^1\text{-O}')$ formates M–OCHO–M$^+$ (**2**) also potentially provides another synthetic route to examples of **1** (eq 1). Our goal is to examine this latter route by synthesizing examples of 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) $\mu(\eta^1\text{-O}:\eta^1\text{-O}')$ formate complex **4** by coordinating FpOC(O)H (**3**) with the Lewis acid Fp$^+$ (eq 2).[4] A noteworthy observation concerning this bimetallic formate **4** is that nucleophilic hydride donors react with it by an apparent dissociatve 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 acetonitrile do not give the substitution-inert $\text{Fp(CH}_3\text{CN)}^+$. Intermediacy of **1** is inconsistent with the results of a labeling 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 Fp–OCHDO–Fp.[4]



(2)

We now report syntheses of the formate complexes $\text{Cp(CO)}_3\text{W–OC(O)H}$ (**5**) and Cp(NO)(CO)Re–OC(O)H (**6**), the homobimetallic $\mu(\eta^1\text{-O}:\eta^1\text{-O}')$ formate compounds **7** [**2**: M = $\text{W(CO)}_3\text{Cp}$] and **8** [**2**: M = Re(CO)(NO)Cp], and the heterobimetallic analogs **9** [**2**: M_2 = $\text{W(CO)}_3\text{Cp}$ and $\text{Fe(CO)}_2\text{Cp}$] and **10** [**2**: M_2 = Re(NO)(CO)Cp and $\text{Fe(CO)}_2\text{Cp}$]. The reactions of nucleophiles, including hydride donors, with the bimetallic formates **7**–**10** received considerable emphasis.

The third-row tungsten and rhenium centers in **7**–**10** potentially impart higher stability–lower reactivity to their complexes; we therefore 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]

---

(1) (a) Behr, A. *Ang. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (d) Darensbourg, D. J.; Bauch, C. G.; Ovalles, C. *Rev. Inorg. Chem.* **1985**, *7*, 315. (e) Inoue, S.; Koinuma, H. *Rev. Inorg. Chem.* **1984**, *6*, 291. (f) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (g) Behr, A. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel Publishers: Boston, MA, 1983; p 169. (h) Ito, T.; Yamamoto, A. In *Organic and Bio-Organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982; Chapter 3. (i) Sneedon, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, F. W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 50.4.

(2) (a) Etievant, P.; Tainturier, G.; Gautheron, B. *C. R. Seances Acad. Sci., Ser. C* **1976**, *283*, 233. Etievant, P.; Gautheron, B.; Tainturier, G. *Bull. Soc. Chim. Fr.* **1978**, 292. (b) Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269. Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1985**, *107*, 6278. (c) Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877.

(3) Transition organometallic η^1-O alkoxide compounds commonly undergo β-deinsertion of a metal hydride complex to give organic aldehydes. (a) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805 and references cited. (b) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546. (c) Wilczewski, T.; Boche'nska, M.; Biernat, J. F. *J. Organomet. Chem.* **1981**, *215*, 87.

(4) Tso, C. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1242.

(5) (a) Treichel, P. M.; Vincenti, P. J. *Inorg. Chem.* **1985**, *24*, 228. (b) Cesarotti, E.; Anyoletta, M.; Walker, N. P. C.; Hursthouse, M. B.; Vefghi, R.; Schofield, P. A.; White, C. *J. Organomet. Chem.* **1985**, *286*, 343. Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761. (c) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151. (d) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251. (e) Tobe, M. L. *Inorganic Reaction Mechanisms*; Thomas Nelson and Sons: London, 1972. Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders Co.: Philadelphia, PA, 1977; Chapter 7.

(6) (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *23*, 1. (b) Stewart, R. P.; Okamoto, N.; Graham, W. A. G. *J. Organomet. Chem.* **1972**, *42*, C32. Sweet, J. R.; Graham, W. A. G. *Ibid.* **1979**, *173*, C9. (c) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811. (d) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982. (e) Casey, C. P.; Andrews, M. A.; Rinz, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 741. (f) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *Ibid.* **1980**, *102*, 1927. Tam, W.; Wong, W.; Gladysz, J. A. *Ibid.* **1979**, *101*, 1589.

0020-1669/90/1329-0471$02.50/0

the phosphine-substituted analogue 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 co-workers recently reported a stable tungsten-containing bimetallic alkoxide $Cp(CO)_3W–CH_2CH_2O–Zr(Cl)Cp_2$, which upon heating or photolyzing 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 by 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} absorptión; 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 microanalyses were done by MicAnal, Tucson, 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 for 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 (η^5-C_5H_5)$(CO)_3W$–OC(O)H (5). To a yellow dichloromethane solution (40 mL) of $Cp(CO)_3W–CH_3$ (2.06 g, 5.77 mmol) was added first 88% formic acid (0.45 mL, 8.6 mmol) and then with efficient stirring $HBF_4·OEt_2$ (1.1 mL, 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 (6.00 g, 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 being concentrated under reduced pressure. Recrystallization from dichloromethane–heptane offered a red crystalline solid (1.351 g) 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); $^{13}C\{^1H\}$ 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. Calcd for $C_9H_6O_5W$: C, 28.58; H, 1.59. Found: C, 28.11; H, 1.60.

Preparation of (η^5-C_5H_5)$(CO)_3W$–OCHO–$W(CO)_3$(η^5-C_5H_5)$^+PF_6^-$ (7). A bright yellow dichloromethane solution (20 mL) containing $Ph_3C^+PF_6^-$ (0.412 g, 1.06 mmol) was cooled (−78 °C) and was treated with $Cp(CO)_3WH$ (0.355 g, 1.06 mmol) in dichloromethane solution (10 mL). 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 (1.5 h). 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, and the filtrate was concentrated under reduced pressure (20 mL) and added dropwise to 100 mL of diethyl ether. This precipitated $[Cp(CO)_3W]_2(OCHO)^+PF_6^-$ (**7**) as a reddish brown microcrystalline solid that was filtered out, washed with ether, and vacuum dried: 0.537 g (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); $^{13}C\{^1H\}$ NMR (CH_2Cl_2) δ 240.4 (trans-CO), 234.6 (cis-CO), 195.6 (OCHO; $^1J_{CH}$ = 219.3 Hz, 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 (5.0 mL) of $[Cp(CO)_3W]_2(OCHO)^+PF_6^-$ (**7**) (81 mg, 0.10 mmol) was added $(n\text{-}Bu)_4N^+I^-$ (37 mg, 0.10 mmol). IR spectral monitoring of the red solution (0.5 h) established quantitative conversion to $Cp(CO)_3W$–I (2039, 1960 (br) cm^{-1}) and $Cp(CO)_3W$–OC(O)H (**5**).

Preparation of (η^5-C_5H_5)$(CO)_3W$–OCHO–$Fe(CO)_2$(η^5-C_5H_5)$^+PF_6^-$ (9). $Cp(CO)_3WOC(O)H$ (**5**) (0.421 g, 1.11 mmol) and $Cp(CO)_2Fe(THF)^+PF_6^-$ (0.438 g, 1.11 mmol) were dissolved in 25 mL of dichloromethane. After 5 h, IR spectral monitoring of the red solution indicated complete conversion of $Cp(CO)_3W–OCHO–Fe(CO)_2Cp^+PF_6^-$ (**9**): 2068, 2025 [ν(CO)] [$Cp(CO)_2Fe$], 2063, 1958 (br) [ν(CO)] [$Cp(CO)_3W$], 1577 cm^{-1} [$\nu(CO_2)$]. This solution was filtered through Celite, and the combined filtrates were concentrated to 10 mL before being added dropwise to excess ether (50 mL). The resulting red-orange precipitate was filtered out and was reprecipitated from dichloromethane–ether (15–60 mL): yield 0.561 g (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.

$(n\text{-}Bu)_4N^+I^-$ (37 mg, 0.10 mmol) was added to a dichloromethane solution (2.5 mL) containing $Cp(CO)_3W–OCHO–Fe(CO)_2Cp^+PF_6^-$ (**9**) (70 mg, 0.10 mmol). Results of IR spectral monitoring (0.5 h) were consistent with quantitative cleavage of **9** to $Cp(CO)_3WOC(O)H$ (**5**) and $Cp(CO)_2Fe$–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 (η^5-C_5H_5)$(CO)_3W$–OCHO–$Fe(CO)_2$(η^5-C_5H_5)$^+PF_6^-$ (9). A solution of $[Cp(CO)_3W]_2(OCHO)^+PF_6^-$ (**7**) (32 mg, 0.037 mmol) and $Cp(CO)_2FeOC(O)H$ (**3**) (8.3 mg, 0.037 mmol) in CD_3NO_2 (0.4 mL) was prepared in a NMR tube. ^1H NMR spectral monitoring of the red solution over 24 h 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 (0.4 mL) of $[Cp(CO)_2Fe]_2(OCHO)^+PF_6^-$ (**4**) (24 mg, 0.044 mmol) and $Cp(CO)_3WOC(O)H$ (**5**) (17 mg, 0.044 mmol) afforded similar results (10 h). 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**) (76 mg, 0.089 mmol) was dissolved in 6.0 mL of dichloromethane and was cooled to −78 °C. A tetrahydrofuran solution of $LiDBEt_3$ (0.09 mL, 0.09 mmol) was added dropwise, and the unchanged red solution was maintained at −78 °C (0.5 h). After warming to room temperature (over 1.0 h), solvent was removed under reduced pressure (30 mmHg, 1 h), 0.8 mL of $CDCl_3$ (purified by passing through activity 1 alumina) was added to the solid, and the solution was filtered through a bed of alumina (4 × 4 mm diameter) in order to remove a trace of suspended material. ^1H NMR spectral measurements were recorded. Absorptions for $Cp(CO)_3WOC(O)H$ (**5**), $Cp(CO)_3WH/Cp(CO)_3WD$ [δ 5.50 (Cp), −7.30 (W–H)], and $[Cp(CO)_3W]_2$ (δ 5.39), in addition to those of residual THF and CH_2Cl_2, 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-

---

(7) Buhro, W. E.; Georgiou, S.; Fernandez, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. Fernandez, J. M.; Emerson, K.; Larsen, R. H.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8268.

(8) (a) Beck, W.; Olgemöller, B. J. *Organomet. Chem.* **1977**, *127*, C45. Olgemöller, B.; Beck, W. *Chem. Ber.* **1981**, *114*, 867. (b) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339.

(9) Jacobsen, E. N.; Trost, M. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 8092.

(10) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

(11) Dauben, H. J.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem,* **1960**, *25*, 1442.

(12) King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, 156.

(13) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

(14) (a) Reger, D. L.; Coleman, C. *J. Organomet. Chem.* **1977**, *131*, 153. (b) Schmidt, E. K. G.; Thiel, C. H. *J. Organomet. Chem.* **1981**, *220*, 87. (c) Rosenblum, M.; Scheck, D. *Organometallics* **1982**, *1*, 397. (d) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1984**, *276*, 55; **1986**, *304*, 181. Schumann, H. *Ibid.* **1986**, *299*, 169. (e) Schumann, H. *J. Organomet. Chem.* **1985**, *293*, 75.

(15) Fergusson, S. B.; Sanderson, L. J.; Shackleton, T. A.; Baird, M. C. *Inorg. Chim. Acta* **1984**, *83*, L45. Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, *21*, 1275.

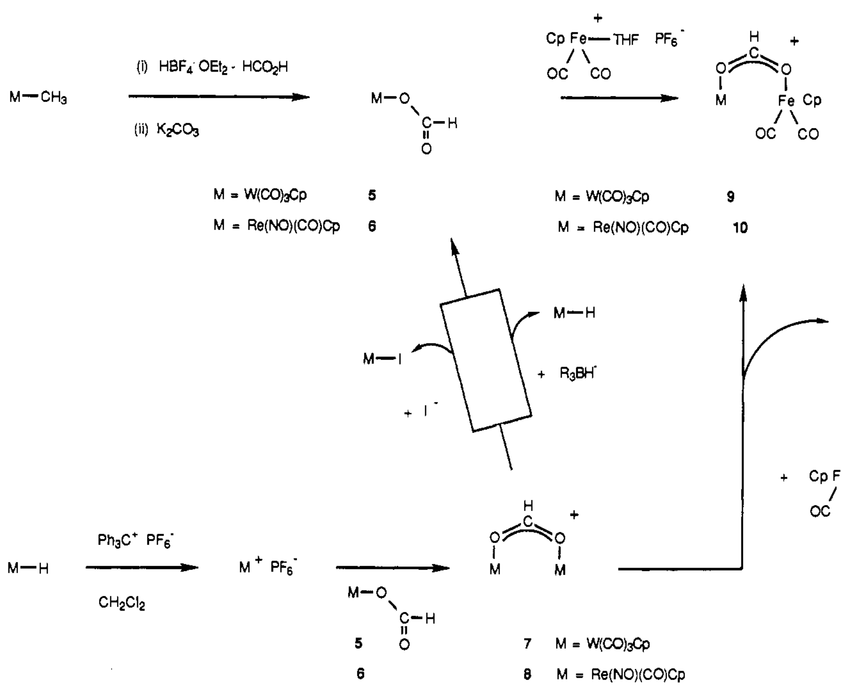
(16) Reference 12, pp 114, 175.

(17) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85.

(18) Burckett-St. Laurent, J. C. T. R.; Field, J. S.; Haines, R. J.; McMahon, M. *J. Organomet. Chem.* **1979**, *181*, 117.

(19) Hames, B. W.; Kolthammer, B. W. S.; Legzdins, P. *Inorg. Chem.* **1981**, *20*, 650. Graham, W. A. G.; Sweet, J. R. *J. Organomet. Chem.* **1983**, *241*, 45.

Scheme I



$(CO)_3WH$ (5.0:0.48) were calculated.

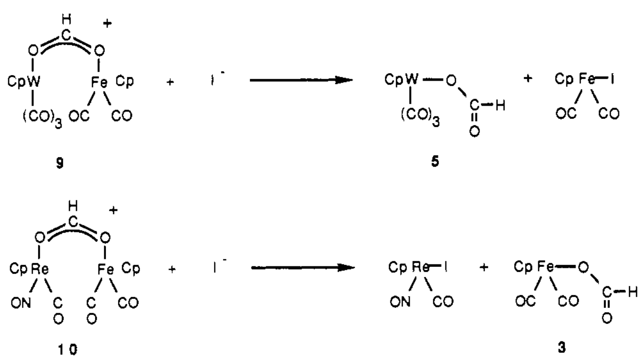
Preparation of (η^5-C_5H_5)(NO)(CO)Re–OC(O)H (6). A dichloromethane solution (25 mL) of Cp(NO)(CO)ReCH$_3$ (0.200 g, 0.617 mmol) was treated with 88% formic acid (0.04 mL, 0.93 mmol) and then $HBF_4·OEt_2$ (0.12 mL, 0.87 mmol) with vigorous stirring. Immediate gas evolution (presumably methane) concurrent 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 [ν(CO)], 1725 (br) [ν(NO)] cm^{-1}. Anhydrous potassium carbonate (0.5 g, 3.3 mmol) 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 (0.158 g, 73% yield) after crystallization from dichloromethane–heptane: IR (CH_2Cl_2) 1992 [ν(CO)], 1727 [ν(NO)], 1641 cm^{-1} [$\nu(CO_2)$]; IR (KBr) 1987, 1961 (sh) [ν(CO)], 1732 (sh), 1700 [ν(NO)], 1638 [$\nu_{asym}(CO_2)$], 1255 [$\nu_{sym}(CO_2)$] cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.46 (s, OCHO), 5.86 (s, Cp); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 199.6 (CO), 170.1 (OCHO; $^1J_{C-H}$ = 208.2 Hz, gated decoupling), 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 (η^5-C_5H_5)(NO)(CO)Re–OCHO–Re(CO)(NO)(η^5-C_5H_5)$^+PF_6^-$ (8). To a dichloromethane solution (20 mL) of $Ph_3C^+PF_6^-$ (0.168 g, 0.433 mmol), which was kept at −78 °C, was added dropwise a dichloromethane solution (6 mL) of Cp(NO)(CO)ReH (0.134 g, 0.432 mmol). The initially red-orange solution formed a yellow-orange suspension (0.75 h) to which Cp(NO)(CO)ReOC(O)H (**6**) (0.153 g, 0.432 mmol) was added with vigorous stirring. The suspension was warmed to room temperature (1 h); by then a yellow-orange solution was evident. This was filtered throught Celite, and the filtrate was concentrated to 10 mL and added slowly to 60 mL of diethyl ether to give a yellow-brown precipitate. Reprecipitation afforded [Cp(NO)(CO)Re]$_2$(OCHO)$^+PF_6^-$ (**8**) (0.276 g, 79% yield): IR (CH_2Cl_2) 2012 [ν(CO)], 1749 [ν(NO)], 1561 cm^{-1} [$\nu(CO_2)$]; IR (KBr) 1982 [ν(CO)], 1720 (br) [ν(NO)], 1560 [$\nu_{asym}(CO_2)$], 1315 cm^{-1} [$\nu_{sym}(CO_2)$]; ^{1}H NMR (CD_3NO_2) δ 7.72 (s, OCHO), 6.13 (s, Cp); $^{13}C\{^1H\}$ NMR (CH_2Cl_2) δ 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; H, 1.36. Found: C, 19.59; H, 1.45.

Treating a dichloromethane solution of **8** (3.0 mL, 0.10 mmol) with excess n-$Bu_4N^+I^-$ immediately afforded a red-brown solution: IR 2000 (br) [ν(CO)], 1730 (br) [ν(NO)], 1641 cm^{-1} [$\nu(CO_2)$].

Preparation of (η^5-C_5H_5)(NO)(CO)Re–OCHO–Fe(CO)$_2$(η^5-C_5H_5)$^+$-PF_6^- (10). A mixture of Cp(NO)(CO)ReOC(O)H (**6**) (0.112 g, 0.316 mmol) and Cp(CO)$_2$Fe(THF)$^+PF_6^-$ (0.125 g, 0.316 mmol) was prepared as a dark red dichloromethane solution (6.0 mL). After 4 h, IR spectral monitoring confirmed quantitative conversion to Cp(NO)(CO)Re–OCHO–Fe(CO)$_2$Cp$^+PF_6^-$ (**10**): 2070, 2020 [ν(CO)], 1751 [ν(NO)], 1572 cm^{-1} [$\nu(CO_2)$]. The solution was filtered through Celite, and the red product (**10**) was isolated by precipitating in excess ether (50 mL) and reprecipitating from dichloromethane–ether: yield 0.168 g (78%); IR (KBr) 2070, 2015 (br) [ν(CO)], 1748 (br) [ν(NO)], 1575 [ν_{asym}-(CO_2)], 1348 cm^{-1} [$\nu_{sym}(CO_2)$]; ^{1}H NMR (CD_3NO_2) δ 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.

Scheme II



A dichloromethane solution (3.0 mL) containing Cp(NO)(CO)ReOCHOFe(CO)$_2$Cp$^+PF_6^-$ (**10**) (67 mg, 0.10 mmol) was treated with n-$Bu_4N^+I^-$ (37 mg, 0.10 mmol). IR spectral analysis of the red solution (0.5 h) established quantitative cleavage of **10** to Cp(NO)(CO)ReI and Cp(CO)$_2$FeOC(O)H (**3**): 2058, 2000 (br) [ν(CO)], 1735 [ν(NO)], 1617 cm^{-1} [$\nu(CO_2)$]. 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 [(η^5-C_5H_5)(NO)(CO)Re]$_2$(OCHO)$^+PF_6^-$ (8) and (η^5-C_5H_5)(CO)$_2$FeOC(O)H (3). A CD_3NO_2 solution (0.4 mL, predried by passage through alumina) of [Cp(NO)(CO)Re]$_2$(OCHO)$^+PF_6^-$ (**8**) (28 mg, 0.035 mmol) and Cp(CO)$_2$FeOC(O)H (**3**) (8 mg, 0.035 mmol) was examined by ^{1}H NMR spectroscopy. After 1 h, a 1.0:1.0:1.76:1.76 ratio of Cp(NO)(CO)ReOC(O)H (**6**)–Cp(NO)(CO)ReOCHOFe(CO)$_2$Cp$^+$ (**10**)–Cp(CO)$_2$FeOC(O)H (**3**)–[Cp(NO)(CO)Re]$_2$(OCHO)$^+$ (**8**) was quantified by integration of Cp and of formate absorptions. No other organometallic species were detected. After 10 h, 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

The transformations observed in this work are summarized in Schemes I and II. We synthesized 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)$_3$WCH$_3$[13] and Cp(NO)(CO)ReCH$_3$[6b,c] first with tetrafluoroboric acid etherate–formic acid and then with potassium carbonate afforded **5** and **6** as air-stable red crystalline solids in 60–75% yields (Scheme I). Characterization of these formate species as detailed in the experimental section is straightforward.

Homobimetallic tungsten (**7**) and rhenium (**8**) bridging formate compounds are readily available by treating the Lewis acids Cp(CO)$_3$W$^+$PF$_6^-$[20] and Cp(NO)(CO)Re$^+$PF$_6^-$[21] with the requisite η^1-O formate complex. These Lewis acids reagents M$^+$PF$_6^-$, in turn, were generated by the standard procedure[22] of abstracting hydride from metal hydrido complexes with Ph$_3$C$^+$PF$_6^-$. We isolated both $\mu(\eta^1$-O:η^1-O$')$ formates **7** and **8** in moderate yields (60–80%) as air-stable brownish hexafluorophosphate salts.

Heterobimetallic formate complexes **9** and **10** are the products of reacting the labile tetrahydrofuranate compound Fp(THF)$^+$PF$_6^-$[14] with the η^1-O formates **5** and **6**, respectively. 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 6 h. We did not detect **9** and **10** disproportionating to mixtures of their homobimetallic bridging carboxylates **4**/**7** and **4**/**8**.

Iodide cleavage of the bimetallic formates **7** and **8** is a characteristic reaction (Scheme II) that is particularly amenable to monitoring by IR spectroscopy. These reactions are complete within 0.5 h and release the starting formate complex plus a known metal iodide compound. The intense IR spectral formate absorption $\nu_{\text{asym}}(\text{CO}_2)$ thus shifts to higher energy. One equivalent of iodide also cleaves the heterobimetallic formates; these reactions are regioselective. The tungsten-iron μ-formate **9** produces exclusively Cp(CO)$_3$W-OC(O)H (**5**), whereas the rhenium–iron μ-formate **10** delivers FpOC(O)H (**3**).

Both μ-formates **7** and **8** react with 1 equiv of the monohydride donors LiHBEt$_3$ or KHB(O-*i*-Pr)$_3$ and immediately give a formate complex (**5** or **6**, respectively) and metal hydride (Scheme I). These reactions occur quantitatively as ascertained by IR spectral monitoring; subsequent addition of CCl$_4$ transforms Cp(CO)$_3$WH (i.e., the reduction product of **7**) into Cp(CO)$_3$WCl.[23] Upon removal of solvent and workup, the reaction mixture changes as dimeric [Cp(CO)$_3$W]$_2$ forms at the expenses of the tungsten hydride. Overall, reduction **7** and **8** offers results analogous to those observed for their iodide cleavage and for hydride transfer to FpOCHOFp$^+$ (**4**).

Discussion

Preparation of Formate Complexes. The presence of unidentate η^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)$_3$WX and Cp(NO)(CO)ReX. The intense carboxylate stretching frequencies are particularly diagnostic for covalent η^1-O formate species as opposed to η^2-O,O$'$ chelating formate structures. Higher energy $\nu_{\text{asym}}(\text{CO}_2)$ absorptions, for example, appear above 1600 cm^{-1}. A more conclusive observation is that differences in the carboxylate stretching frequencies, $\Delta\nu = \nu_{\text{asym}}(\text{CO}_2) - \nu_{\text{sym}}(\text{CO}_2)$, for **5** (343 cm^{-1}) and for **6** (383 cm^{-1}) are in the expected range for η^1-O formate ligands.[24]

The corresponding tungsten acetate Cp(CO)$_3$W-OC(O)CH$_3$ has been reported by two research groups.[9,25] Werner and coworkers[25] recently prepared it by protonating Cp(CO)$_3$WCH$_3$ with HBF$_4$–CH$_3$CO$_2$H; they also confirmed the η^1-O acetate bonding by means of its X-ray structure determination. Warming this η^1-O acetate drives it over to the η^2-O,O$'$ chelating structure Cp(CO)$_2\overline{\text{W–OC(O)}}CH_3$.[25] Reversible interconversion of η^1-O and η^2-O,O$'$ carboxylate ligands (including both formate and acetate) recently has been reported for *trans*-(PPh$_3$)$_2$(CO)$_2$(NO)W–OC(O)R/(PPh$_3$)$_2$(CO)(NO)$\overline{\text{W–OC(O)}}$R[26] and for the Mo(II) systems (PR$'_3$)$_2$(CO)$_2$[RC(O)O]$\overline{\text{Mo–OC(O)}}$R (R$'$ = Et, Ph).[27] Under the conditions of our experiments, we did not observe any transformation of the η^1-O formate complexes **5** and **6** (and **3**) to analogous chelating η^2-O,O$'$ formate structures.

Two observations on the preparative route used in obtaining formate complexes **5** and **6** are worth noting. First, protolytic cleavage of transition-metal methyl compounds with strong acid (e.g., HBF$_4$) generally affords labile organometallic Lewis Acids.[22] We previously reported that treating FpCH$_3$ with HBF$_4$·OR$_2$ gives first the covalent fluoroborate complex FpFBF$_3$ and then the labile etherates (Fp·OR$_2$)$^+$BF$_4^-$ (R = Me, Et).[28] Similar intermediates presumably transpire during protonation of starting tungsten and rhenium methyl compounds. Indeed, both the tungsten Lewis acid Cp(CO)$_3$WFBF$_3$ and its etherate Cp(CO)$_3$W·OEt$_2^+$ are known, although Beck prepared them after abstracting hydride from Cp(CO)$_3$WH.[20]

Analogous rhenium Lewis acids and their formate derivatives also are available. Sweet and Graham[21] obtained the rhenium Lewis acid Cp(NO)(CO)Re$^+$ as its labile 3,4-η^2-C$_6$H$_5$CHPh$_2$ adduct by abstracting hydride with Ph$_3$C$^+$ from Cp(NO)(CO)ReH. Gladysz and co-workers[29] generated Cp(NO)(PPh$_3$)Re$^+$ by protonating the methyl compound Cp(NO)(PPh$_3$)ReCH$_3$; the η^1-O formate derivative Cp(NO)(PPh$_3$)ReOC(O)H is available by this route. Beck's group[30] characterized the rhenium Lewis acid (CO)$_5$ReFBF$_3$, which results from the reaction of (CO)$_5$ReCH$_3$ and Ph$_3$C$^+$BF$_4^-$, and prepared the analogous formate (CO)$_5$ReOC(O)H. The η^1-O formate complex (α,α'-bipyridine)(CO)$_3$ReOC(O)H forms as the product of CO$_2$ "insertion" into the corresponding rhenium hydride.[31]

We note that the metallocarboxylic acid Cp(NO)(CO)ReC(O)OH, a tautomer of the rhenium η^1-O formate **6**, has been characterized. The Casey[6e] and Graham[6d] research groups obtained this stable metallocarboxylic acid by adding hydroxide to the carbonyl salt Cp(NO)(CO)$_2$Re$^+$. We recently reported using this metallocarboxylic acid in the synthesis of the heterobimetallic $\mu(\eta^1$-C:η^2-O,O$')$ carbon dioxide complex Cp(NO)(CO)ReCO$_2$Zr(Cl)Cp$_2$.[32] Distinguishing between **6** and its tautomer is straightforward by IR and ^{1}H 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 η^1-O formic acid derivatives. Their deprotonation (K$_2$CO$_3$) affords the isolated η^1-O formates, which in turn react with HBF$_4$ to regenerate these labile formic acid complexes.

---

(20) (a) Beck, W.; Schloter, K. *Z. Naturforsch., B* **1978**, *33B*, 1214. (b) Sunkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 231. Appel, M.; Sacher, W.; Beck, W. *J. Organomet. Chem.* **1987**, *322*, 351.

(21) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135.

(22) Beck, W.; Sunkel, K. *Chem. Rev.* **1988**, *88*, 1405.

(23) Turaki, N. N.; Huggins, J. M. *Organometallics* **1986**, *5*, 1703 and references cited.

(24) (a) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed; Wiley: New York, 1986; p 231.

(25) Werner, H.; Roll, J.; Zolk, R.; Thometzek, P.; Linse, K.; Ziegler, M. *Chem. Ber.* **1987**, *120*, 1553.

(26) Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876. Holl, M. M.; Hillhouse, G. L.; Folting, K.; Huffman, J. C. *Organometallics* **1987**, *6*, 1522.

(27) Brower, D. C.; Winston, P. B.; Tonker, T. L.; Templeton, J. L. *Inorg. Chem.* **1986**, *25*, 2883. Riera, V.; Arnaiz, F. J.; Herbosa, G. G. *J. Organomet. Chem.* **1986**, *315*, 51.

(28) Cutler, A. R.; Todaro, A. B. *Organometallics* **1988**, *7*, 1782.

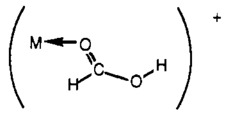
(29) (a) Fernandez, J. M.; Gladysz, J. A. *Inorg. Chem.* **1986**, *25*, 2672. (b) Merrifield, J. H.; Gladysz, J. A. *Organometallics* **1983**, *2*, 782. Merrifield, J. H.; Fernandez, J. M.; Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 4022.

(30) (a) Beck, W.; Raab, K.; Nagel, U.; Steimann, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 526. Raab, K.; Beck, W. *Chem. Ber.* **1985**, *118*, 3830. (b) Raab, K.; Olgemöller, B.; Schloter, K.; Beck, W. *J. Organomet. Chem.* **1981**, *214*, 81. Raab, K.; Nagel, U.; Beck, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 1466.

(31) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500.

(32) Tso, C. C.; Cutler, A. R. *J. Am. Chem. Soc.* **1986**, *108*, 6069.

(33) (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosenblum, M. *J. Organomet. Chem.* **1980**, *187*, 253. (b) Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298.



M = W(CO)$_3$Cp

M = Re(NO)(CO)Cp

Analogous structures having the organic carbonyl functional group coordinated through the organometallic electrophile are well-known.[22,23] Examples of η^1-O aldehyde and ketone complexes bearing Cp(CO)$_3$W$^+$,[20] Cp(NO)(CO)Re$^+$,[6d] Cp(NO)(PPh$_3$)Re$^+$,[7] and (CO)$_5$Re$^+$[30b] organometallic moieties have been characterized.

Bridging Formate Complexes. A combination of IR and ^{1}H and ^{13}C NMR spectral data and combustion microanalytical data suffice to unambiguously characterize the homobimetallic 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-C(O)OCH$_2$-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)$_3$WOC(O)H (**5**) also have two carbonyl absorptions (with a 2:1 intensity ratio), but these correspond to magnetically nonequivalent cis and trans carbonyls.[34]

Diagnostic formate absorptions in the ^{1}H 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$_3$NO$_2$) 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 0.04 ppm of the corresponding absorptions for **4** and for **7**. IR spectral ν_{syn}(CO$_2$) absorptions for the rhenium-containing μ-formates **8** and **10** and for Fp$_2$(O$_2$CH)$^+$ (**4**) vary over a 40-cm^{-1} range even though their higher energy ν_{asym}(CO$_2$) absorptions appear within 15 cm^{-1} of one another. Corresponding $\Delta\nu$ values for **4** (212 cm^{-1}), **8** (245 cm^{-1}) and **10** (227 cm^{-1}) therefore distinguish **10**.

Differences in the ^{1}H NMR spectra of **9** and **10** vs their homobimetallic analogues facilitated direct monitoring of the reactions between FpOC(O)H (**3**) and the bis(tungsten) (**7**) and bis(rhenium) (**8**) μ-formates (Scheme I). 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 ^{1}H NMR spectral monitoring after 10 h in CD$_3$NO$_2$ solution (22 °C): the Fp formate (**3**) does not exchange into the μ-formate **7** to release Cp(CO)$_3$W–OC(O)H (**5**). The bis(rhenium) μ-formate **8**, however, proved to be more labile under these conditions. Within 10 h, 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**.

A pattern thus emerges in which the rhenium centers on the bimetallic μ-formates **8** and **10** are 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 toward the bis(tungsten) congener **7**. Iodide preferentially displaces on the rhenium center of the rhenium–iron μ-formate **9** but attacks at the Fp center on the tungsten–iron μ-formate **10** (Scheme II).

This pattern is consistent with our earlier observations on the solution lability of bimetallic μ(η^1-C:η^1-O) acetyl compounds [Cp(CO)$_2$Fe–C(CH$_3$)O–M]$^+$, which exchange their FpCOCH$_3$ fragments for Cp(PPh$_3$)(CO)FeCOCH$_3$ in dichloromethane (eq 3).[35] The facility of these reactions depends on the choice of η^1-O-bound metal; after 18 h (20 °C), the extent of exchange varies: M = Re(NO)(CO)Cp (100%) > Fe(CO)$_2$Cp (80%) > W(CO)$_3$Cp (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 η^1-O-bound metal M.

(3)

M = Fe(CO)$_2$Cp, Re(NO)(CO)Cp, W(CO)$_3$Cp

Of the three bimetallic formate complexes M–OCHO–M$^+$ (**2**) [i.e., M = Fp (**4**), M = W(CO)$_3$Cp (**7**), M = Re(NO)(CO)Cp **8**)], 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).

We used the reaction between **7** and LiDBEt$_3$ as a probe into the intermediacy of a *gem*-diolate complex **1** (M = W(CO)$_3$Cp). If deuteride addition to **7** occurs at the formate carbon, then the resulting Cp(CO)$_3$W–OCHDO–W(CO)$_3$Cp would fragment into approximately equal concentrations of labeled **5**, Cp(CO)$_3$WOC(O)D, and unlabeled **5**. Since ^{1}H NMR spectral monitoring of this reaction established that at least 90% unlabeled tungsten formate **5** forms, transience of Cp(CO)$_3$W–OCHDO–W(CO)$_3$Cp contributes only a very minor pathway at best. Inference of a 48:52 mixture of Cp(CO)$_3$WH/Cp(CO)$_3$WD by relative integration intensities of the Cp and tungsten hydride signals is consistent with established free-radical reactivity for this tungsten hydride complex.[23] We conclude that hydride–deuteride transfer to **7** occurs by nucleophilic attack at a tungsten center with displacement of Cp(CO)$_3$WOC(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 reagent,[36] the resulting neutral Cp(CO)$_3$WOCHOW(CO)$_3$Cp then fragmenting into **5** and the 17-electron Cp(CO)$_3$W. The absence of dimeric [Cp(CO)$_3$W]$_2$ (and of Fp$_2$ in the reduction of **4**) as a kinetic product is inconsistent with intermediacy of a high-energy organometallic "radical",[23] however.

Conclusions

The homobimetallic bridging formate compounds Cp(CO)$_3$W–OCHO–W(CO)$_3$Cp$^+$PF$_6^-$ (**7**) and Cp(NO)(CO)Re–OCHO–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 1 equiv of iodide or of a nucleophilic hydride donor to release the neutral η^1-O formates **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$^+$ [M = W(CO)$_3$Cp (**9**) and M = Re(NO)(CO)Cp (**10**)] and of FpOCHOFp$^+$ (**4**).

Acknowledgment. Support from the Office of Naval Research and from the National Science Foundation, Grant CHE-8305484, is gratefully acknowledged.

---

(34) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852. Barnett, K. W.; Slocum D. W. *J. Organomet. Chem.* **1972**, *44*, 1.

(35) Cutler, A. R.; Todaro, A. B.; Forschner, T. C.; Chung, C. C.; LaCroce, S. J. Manuscript in preparation.

(36) (a) Touchard, D.; Fillaut, J.-L.; Khasnis, D. V.; Dixneuf, P. H.; Mealli, C.; Masi, D.; Toupet, L. *Organometallics* **1988**, *7*, 67. (b) Chanon, M. *Acc. Chem. Res.* **1987**, *20*, 214. (c) Astruc, D. *Acc. Chem. Res.* **1986**, *19*, 377. Michaud, P.; Lapinte, C.; Astruc, D. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 97. Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755. (d) Wagner, W. R.; Rastetter, W. H. *J. Org. Chem.* **1983**, *48*, 294. (e) Ashby, E. C.; Goel, A. B.; DePriest, R. N.; Prasad, H. S. *J. Am. Chem. Soc.* **1981**, *103*, 973. Ashby, E. C.; Goel, A. B.; DePriest, R. N. *Ibid.* **1980**, *102*, 7779.