electrophiles in their addition reactions with alkenes. A sharp decrease in k_i/k_t was observed when R in **1** was changed from Me to H. Similar trends are also observed when aryl substituents (X) in **1** (R = H) are successively changes from electron-withdrawing (Cl) to electron-donating (MeO) groups (see Table II). This supports the idea[2e,3,4] that there is substantial hydride character associated with the migrating hydrogen and concomitant positive charge development at the origin of the migration.[5]

(5) The substitutent effects on the intercepts k_i/k_2 are rather unexpected. Assuming that k_2 is not affected by substituents on the α-phenyl ring, one would expect that the values of k_i/k_2 should be decreased as the ring substituents are changed from electron-donating to -withdrawing groups. Observed parabolic deviations from linearity may imply that intermolecular process is not unaffected by the ring substituent. Presumably, orientation of the phenyl group may affect the electronic as well as steric nature of the chlorocarbene.

## Chemistry of New Heteronuclear Bridging Hydrides: (μ-H)[Fe(CO)₄M(CO)₅]⁻ (M = Cr, Mo, W)

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The prevalence of hydride ligands at centers of metal aggregation is a well-known feature of transition-metal hydride chemistry.[1] In fact the chemistry of the VIB carbonyl hydrides is dominated by bridging hydrides, $(\mu\text{-H})M_2(CO)_{10}^-$ (M = Cr, Mo, W), in which the hydride bridge is supported neither by a M–M bond nor by bridging carbonyls.[2] In contrast, the structure of $(\mu\text{-H})Fe_2(CO)_8^-$ contains two bridging CO groups as well as an Fe–Fe bond.[3] Although the chemistry of heteronuclear bridging hydrides should prove important to the establishment of relative M–H bond stabilities and metal-to-metal hydride-transfer capabilities, only a few have been well characterized.[4,5] Our studies of the highly reactive monomeric VIB carbonyl hydrides, $HM(CO)_5^-$,[6] indicate that they are good sources of H⁻ with the ability to transfer H⁻ to both carbon and metal centers. Pursuant of such chemical characterizations we detected in the reaction of $HW(CO)_5^-$ with $Fe(CO)_5$ the iron formyl, $HC(O)Fe(CO)_4^-$, the iron hydride, $HFe(CO)_4^-$, $(\mu\text{-H})W_2(CO)_{10}^-$, and, as well, a new species believed to be the heteronuclear bimetallic $(\mu\text{-H})FeW(CO)_9^-$, **1c⁻**. In subsequent work a clean synthesis of the title anions was developed, a preliminary X-ray structural analysis of PPN⁺**1c⁻** has been done,[7] and some interesting and unanticipated chemical reactivity patterns have been observed.

An efficient synthesis (80–90% yield) of PPN⁺(μ-H)FeM-(CO)₉⁻ (M = Cr, Mo, W) is based on the aggregation of HFe-(CO)₄⁻ with photochemically generated THF·M(CO)₅ (eq 1).

$$THF\cdot M(CO)_5 + PPN^+HFe(CO)_4^- \xrightarrow[\text{room temperature}]{THF}$$
$$PPN^+(\mu\text{-H})FeM(CO)_9^- \quad (1)$$
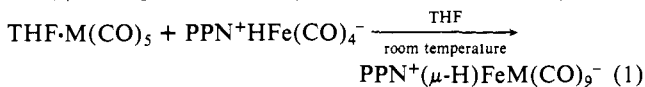
1a⁻, M = Cr; **1b⁻**, M = Mo; **1c⁻**, M = W

Following methanol precipitation of excess PPN⁺HFe(CO)₄⁻, filtration, and partial solvent removal, addition of hexane precipitated the product as a yellow or yellow-orange powder. Recrystallization from concentrated methanol/hexane solutions
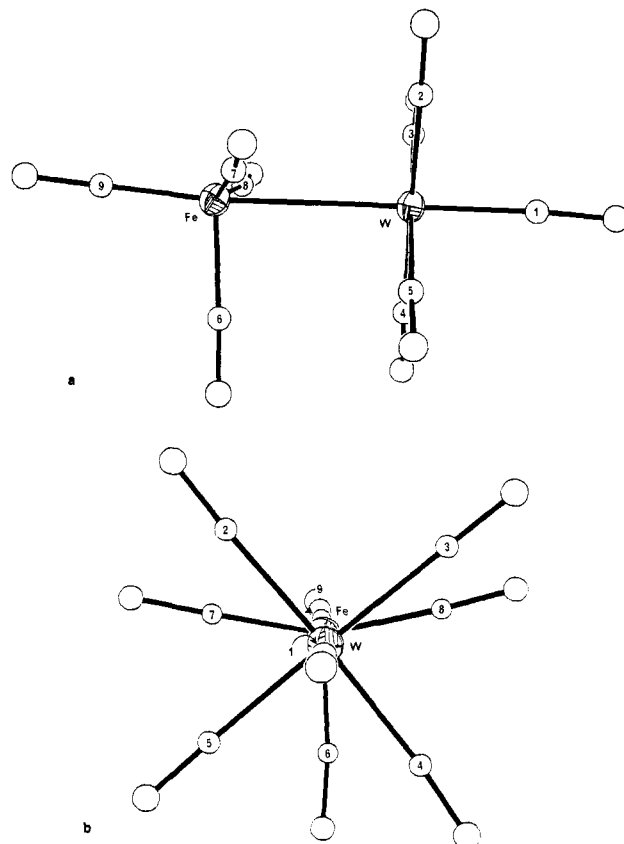
Figure 1. (a) ORTEP drawing of $(\mu\text{-H})FeW(CO)_9^-$ showing 50% probability ellipsoids of the W and Fe atoms. Carbons and oxygens are drawn as spheres. The W is in an octahedral setting with all C–W–C bond angles in the range 87.8–91.4°. Pertinent bond lengths and bond angles: Fe–W, 2.989 (2); W–Cl, 1.92 (2); W–C2, 2.05 (2); W–C3, 2.01 (2); W–C4, 2.03 (2); W–C5, 2.05 (2); Fe–C6, 1.81 (2); Fe–C7, 1.81 (2); Fe–C8, 1.74 (2); Fe–C9, 1.75 (2) Å; C7–Fe–C6, 99.2 (7)°; C8–Fe–C6, 101.6 (7)°; C8–Fe–C7, 147.6 (8)°; C9–Fe–C6, 99.5 (7)°; C9–Fe–C7, 100.2 (8)°; C9–Fe–C8, 100.4 (7)°. (b) An end-on view of $(\mu\text{-H})FeW(CO)_9^-$ showing the linear, staggered nature of the heterobimetallic.

yielded analytically pure samples.[8] As solids these salts may be handled in air for short periods; solutions are air sensitive.

The complex ν(CO) IR spectra of all **1⁻** show no bands in the bridging CO region.[8] The ¹³C NMR spectrum of PPN⁺**1c⁻** in THF at −80 through +50 °C showed three resonances which at 23 °C are positioned at 218.1, 203.9, and 203.0 ppm, of approximate intensities 4:1:4. These are assigned to $Fe(CO)_4$, $W(CO)_{trans}$, and $W(CO)_{cis}$, respectively.[9] The hydride chemical shifts for **1a⁻**, **1b⁻**, and **1c⁻** are (at −14.6, −11.5, and −11.8 ppm, respectively) upfield of both $HM(CO)_5^-$ and $HFe(CO)_4^-$. The observed J_{WH} of 15.0 Hz is much smaller than that for $HW(CO)_5^-$ (52.5 Hz),[6] $(\mu\text{-H})W_2(CO)_{10}^-$ (42.0 Hz), $(\mu\text{-H})WCr(CO)_5^-$ (38.4 Hz),[10] $Ph_3PAuHW(CO)_5$ (37 Hz),[5] or $(\mu\text{-H})_2W_2(CO)_8^{2-}$ (30 Hz).[11]

The X-ray crystal structure[12] of PPN⁺**1c⁻** showed no bridging CO's, a structural feature similar to the parent $(\mu\text{-H})W_2(CO)_{10}^-$.

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(2) Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176.

(3) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

(4) (a) Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Inorg. Chem.* **1979**, *18*, 136. (b) Leblanc, J. C.; Reynoud, J. F.; Moise, C. *J. Organomet. Chem.* **1983**, *244*, C24.
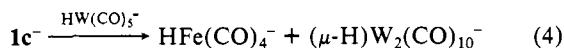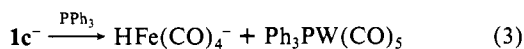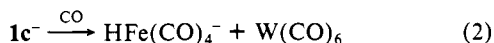
(5) Green, M.; Orpen, A. G.; Salter, I. D.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 813.

(6) Darensbourg, M. Y.; Slater, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 5914.

(7) PPN⁺ = bis(triphenylphosphine)iminium, Ph₃P–N–PPh₃⁺.

(8) Elemental anal. (Mic Anal Organic Microanalysis, Tucson, AZ). Calcd for Ph₃PNPPh₃⁺HFeW(CO)₉⁻ (Found): C, 52.40 (52.26); H, 3.03 (3.06); N, 1.36 (1.44). ν(CO) IR (THF solution) (PPN⁺**1a⁻**) 2057 vw, 2012 w, 2000 m, sh, 1942 s, 1911 m, sh, 1880 m, br cm⁻¹, (PPN⁺**1b⁻**) 2062 vw, 2005 m, sh, 1950 s, 1922, m, 1885 m, br cm⁻¹, (PPN⁺**1c⁻**) 2063 vw, 2009 m, sh, 1940 s, 1911 m, sh, 1870 m, br cm⁻¹.

(9) The CO sites on Fe are presumed to be rapidly interconverting.

(10) Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

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(12) Data were collected on an Enraf-Nonius CAD-4 computer automated diffractometer at −103 °C using Mo Kα radiation. Space group is P1̄ (Z = 2) with a = 14.099 (5) Å, b = 11.601 (5) Å, c = 14.148 (5) Å, α = 95.53 (3)° β = 118.23 (3)°, γ = 92.39 (3)°. Intensity data were collected for 5671 reflections, of which 3635 were unique and measured >3σ(I) and were used for structure refinement. With a unit weighting scheme, R = 0.059.

However, the metal–metal distance of 2.989 (2)Å is well within bonding range, unlike the tungsten parent but like $(\mu\text{-H})Fe_2(CO)_8^-$. The *ORTEP* plots of Figure 1a,b indicate strict octahedral coordination geometry about tungsten and a distorted trigonal-bipyramidal geometry about iron. The M–M bond and (presumed) bridging hydride serves to complete the coordination spheres of each metal. In contrast to the TBP geometry of $HFe(CO)_4^-$ in which all equatorial C–Fe–C angles are near 120°,[13] the C7–Fe–C8 angle of **1c⁻** has opened to 147.6(8)° and is staggered with respect to the same position as is C2 and C3 on the W centers. The position about which this stagger occurs is the most probable location for the H⁻ ion. Preliminary results indicate that the location of the H⁻ ion will prove successful; however, what presently appears as a slight disordering of the carbonyls on the W prevents its positive identification at the current level of refinement ($R = 0.059$). Its projected position is just off the Fe–W bond axis. In view of the similarity of the $(OC)_{ax}$–Fe–$(CO)_{eq}$ bond angles in **1c⁻** to those of $HFe(CO)_4^-$ (ca. 100° in both) it is tempting to assume that the hydride is more closely associated with the Fe than the W and that $HFe(CO)_4^-$ is serving as a unit ligand to $W(CO)_5^0$. Indeed *most* of the chemical reactions presented below are supportive of this notion. However, we have also noted one major difference in the reactivity of $HFe(CO)_4^-$ as derived from **1c⁻** vs. that of pure $HFe(CO)_4^-$ (vide infra). Hence further speculation on this structure is declined at this time.[14]
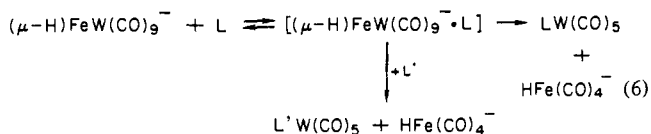
The dimer disrupts in the presence of added ligands, eq 2–4

$$\textbf{1c}^- \xrightarrow{\text{CO}} HFe(CO)_4^- + W(CO)_6 \qquad (2)$$

$$\textbf{1c}^- \xrightarrow{\text{PPh}_3} HFe(CO)_4^- + Ph_3PW(CO)_5 \qquad (3)$$

$$\textbf{1c}^- \xrightarrow{\text{HW(CO)}_5^-} HFe(CO)_4^- + (\mu\text{-H})W_2(CO)_{10}^- \qquad (4)$$

(THF solvent). When the anion is allowed to stand in THF solution at room temperature, eq 5, the same products as in eq

$$\textbf{1c}^- \xrightarrow[\text{dec}]{\Delta} HFe(CO)_4^- + W(CO)_6 \qquad (5)$$
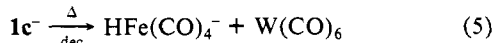
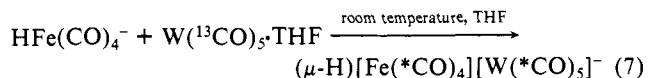2 are obtained, presumably by the standard decomposition pathway as a variety of labile $LW(CO)_5$ species.[15] In all cases of dimer disruption the H⁻ ligand consistently remained with $HFe(CO)_4^-$. Attempts were made to force the opposite heterolytic cleavage yielding $HW(CO)_5^-$ and $[Fe(CO)_4^0]$. For example, it is known that CO_2 inserts into W–H bonds of $HW(CO)_5^-$ (but not easily into $HFe(CO)_4^-$)[16] to yield $(OC)_5WOC(O)H^-$.[17] Also $W(CO)_5\cdot THF$ is trapped by $HW(CO)_5^-$ at time of mixing to yield the very stable $(\mu\text{-H})W_2(CO)_{10}^-$. Nevertheless neither CO_2 nor $W(CO)_5\cdot THF$ reacted with **1c⁻**.

The dimer cleavage reactions (3) and (4) proceeded at the same rate with half-lives of ca. 5–6 h, measured at $[\textbf{1c}^-] = 0.0048$ M, $[PPh_3] = 0.10$ M, and $[HW(CO)_5^-] = 0.0048$ M. The decomposition reaction (5) was slower ($t_{1/2} \sim$ days), because the initial products of cleavage, $HFe(CO)_4^-$ and $W(CO)_5^0$, recombine (eq 1). Unexpectedly, in the presence of CO-saturated THF, [CO] estimated at 0.01 to 0.02 M,[18] **1c⁻** had a half-life of ca. 10 min (eq 2). Furthermore in the presence of both CO (~ 0.02 M) and PPh_3 (0.01 M) a reaction equally rapid as (2) occurs; however, the product distribution (85% $W(CO)_5PPh_3$ and 15% $W(CO)_6$) is the same as a similar mixture of CO, PPh_3, and photochemically generated $THF\cdot W(CO)_5$. This suggests that the CO that promotes

the dimer cleavage does not necessarily trap the coordinatively unsaturated species produced! A reaction pathway consistent with this result is shown in eq 6.

$$(\mu\text{-H})FeW(CO)_9^- + L \rightleftharpoons [(\mu\text{-H})FeW(CO)_9^- \cdot L] \longrightarrow LW(CO)_5$$
$$\downarrow {\scriptstyle +L'} \qquad\qquad +$$
$$L'W(CO)_5 + HFe(CO)_4^- \qquad HFe(CO)_4^- \quad (6)$$

In contrast to both parent dimers, $(\mu\text{-H})W_2(CO)_{10}^-$ and $(\mu\text{-H})Fe_2(CO)_8^-$, **1c⁻** is highly CO labile. When ^{13}CO is used in reaction 2 *both* products are found to be highly enriched. Extensive ligand exchange has thus occurred on the intact dimer prior to disruption. The reaction described by eq 7 was run in an

$$HFe(CO)_4^- + W(^{13}CO)_5\cdot THF \xrightarrow{\text{room temperature, THF}} $$
$$(\mu\text{-H})[Fe(*CO)_4][W(*CO)_5]^- \quad (7)$$

$$* = \text{mixture of } {}^{13}CO \text{ and } {}^{12}CO$$

attempt to generate $(\mu\text{-H})[Fe(^{12}CO)_4][W^{13}CO)_5]^-$. However, both the $\nu(CO)$ IR spectrum, taken within 5 min of mixing, and the 23 °C ^{13}C NMR spectrum, recorded within a few hours of synthesis, indicated that the label was equally distributed over the Fe and W centers. Hence it is impossible to tell whether the CO exchange is specific for one metal center.

In conclusion, the structure of a newly synthesized heterobimetallic, $(\mu\text{-H})FeW(CO)_9^-$, has been determined and found to be intermediate between that of its homobimetallic parents. The dimer heterolytically disrupts with the hydride ligand remaining on the iron center. The new anion shows reactivity with CO remarkably different from both parent molecules. The reason for this reactivity difference is currently under investigation.

(13) Smith, M. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95*, 2388.

(14) The X-ray crystal structures of PPh₄⁺$(\mu\text{-H})FeW(CO)_9^-$ and of PPh₄⁺$(\mu\text{-H})FeCr(CO)_9^-$ are under investigation. Large crystals of the latter, hopefully suitable for neutron diffraction analysis, have been obtained.

(15) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* **1973**, *12*, 1286.

(16) Evans, G. O.; Newell, C. J. *Inorg. Chim. Acta* **1978**, *31*, L387.

(17) Darenbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223.

(18) We have estimated the concentration of CO in a CO-saturated THF solution at 22 °C to be similar to that of acetone (8.8×10^{-3} M at 20 °C) or diethyl ether (1.6×10^{-2} M at 0 °C) whose values were taken from: "International Critical Tables"; 1933: Vol. III, p 265.

Heterocycles in Synthesis: Chiral Amino Acids/Dipeptides via a Novel Photooxidative Cleavage of Trisubstituted Imidazoles

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Although heteroaromatic nuclei have demonstrated potential to serve as latent functional group equivalents,[1] use of the imidazole ring in this capacity, to our knowledge, is without precedent.[2] We envisioned a general, asymmetric synthesis of N-protected amino

(1) Some recent examples: (a) Furans: Van Royen, L. A.; Mijngheer, R.; De Clerq, P. J. *Tetrahedron Lett.* **1983**, *24*, 3145. (b) Isoxazoles: L'abbe, G.; Godts, F.; Toppet, S. *Ibid.* **1983**, *24*, 3149. (c) Oxazoles: Wasserman, H. H.; Lu, T.-J. *Ibid.* **1982**, *23*, 3831 and references therein. Jacobi, P. A.; Walker, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4611. Levin, J. I.; Weinreb, S. M. *Ibid.* **1983**, *105*, 1397. (d) Thiazoles: Biskupiak, J. E.; Ireland, C. M. *J. Org. Chem.* **1983**, *48*, 2302. (e) Groth, U., Schollkopf, U. *Synthesis* **1983**, 37.

(2) Grimmett, M. R. *Adv. Heterocycl. Chem.* **1980**, *27*, 241. Grimmett, M. R. *Ibid.* **1970**, *12*, 103.