Design, Stabilization, and Efficiency of Organometallic "Electron Reservoirs". 19-Electron Sandwiches η^5-$C_5R_5Fe^I$-η^6-$C_6R'_6$, a Key Class Active in Redox Catalysis

Sir:

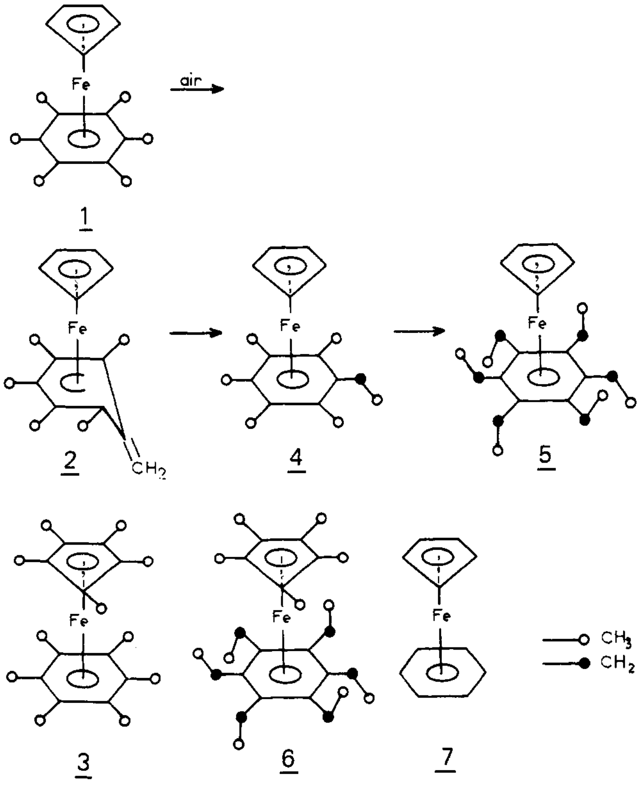
As a remarkable example of the use of transition metals in activation of arenes,[1] we showed in a recent communication[2] that dioxygen can take up one H atom from η-C_5H_5Fe-η^6-$C_6(CH_3)_6$ (**1**) under mild conditions, giving **2** (Scheme I). It was proposed that this reaction proceeds by electron transfer to form $O_2^{-}\cdot$, an intermediate now recognized[3] as responsible for the destruction of living cells by O_2.

Viewing the energetic and bioenergetic importance of such redox systems, we report now the design, characterization, and redox efficiency of the 19-electron complexes CpFe-arene to serve as electron reservoirs[4] with high redox potentials (up to −1.9 V vs. SCE). In addition we suggest a relationship between their electronic structure and stabilization and present the first crystal structure of a mixed 19-electron complex.[5,6] Whereas the parent $C_5H_5FeC_6H_6$ is unstable,[7] we find that analogues with six alkyl groups on the benzene ligand are stable in many solvents and catalytically active and, depending on the substituents (CH_3 or C_2H_5), show unusual solid-state and solution properties.

1 is best synthesized by stirring a DME solution of $\mathbf{1}^+BF_4^-$ with Na/Hg (1%) amalgam (15 min, 25 °C). After removal of DME in vacuo, the residue is extracted with pentane which, upon standing at −40 °C overnight, affords green black crystals of **1** (90% yield): mass spectrum M^+ calcd 283.115, found 283.115; sublimation at 70 °C (0.2 μHg); $\mu_{\text{eff}} = 1.84 \pm 0.1\ \mu_B$ by the Gouy method from 69 to 293 K; ^{1}H NMR (δ, ppm, $C_6D_5CD_3$) 35.01 (C_5H_5), −2.15 ($C_6(CH_3)_6$), 22 °C; ^{13}C NMR (δ, ppm, $C_6D_5CD_3$) 449 and 584 (ring carbons), −35.9 (CH_3). Anal. Calcd: C, 72.09; H, 8.22; Fe, 20.37. Found: C, 71.81; H, 8.23; Fe, 20.55.

Similarly, η^5-$C_5(CH_3)_5Fe$-η^6-$C_6(CH_3)_6$ (**3**)[8] and η^5-$C_5(CH_3)_5Fe$-η^6-$C_6(C_2H_5)_6$ (**6**)[8] are obtained as ivory green crystals (60–80% yields after recrystallization from pentane at −40 °C) by Na/Hg reduction of the cationic precursors.[9]

Scheme I



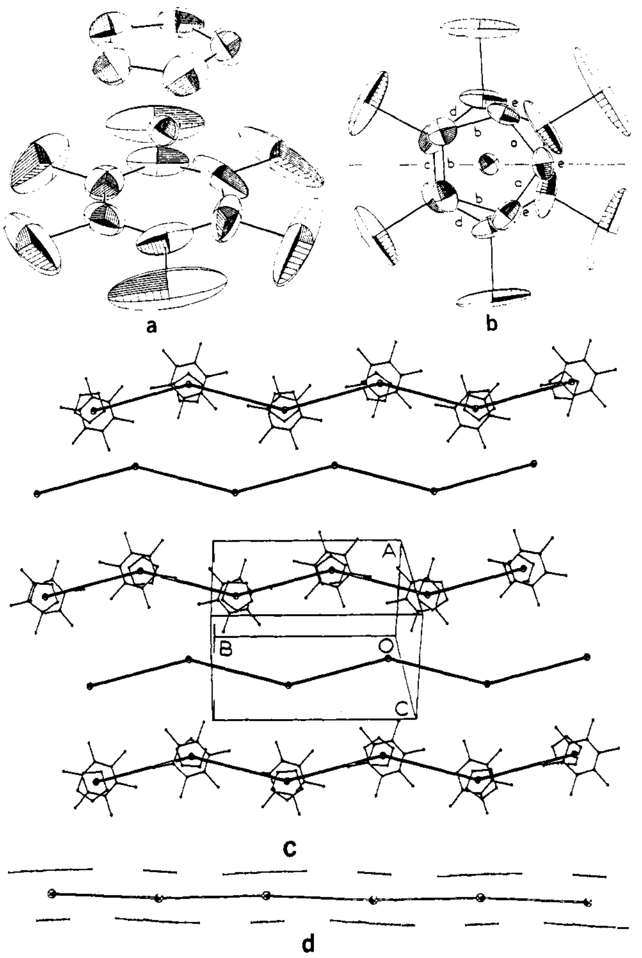


Figure 1. (a) Perspective view of η^5-C_5H_5Fe-η^6-$C_6(CH_3)_6$ (**1**). The vibrational ellipsoids are drawn at the 50% probability level. (b) Projection on the cyclopentadienyl ring. The vibrational ellipsoids are drawn at the 30% probability level. The dihedral angle between the two rings is 0.82°. Bond distances: $\bar{a}$ = 1.371 (6); $\bar{b}$ = 1.403 (6); c = 1.293 (8); $\bar{d}$ = 1.366 (9); $\bar{e}$ = 1.428 (9) Å. Average internal angles: $\hat{c}(C_5H_5)$, 108.00 (25); $\hat{c}(C_6Me_6)$, 119.99 (56)°. Fe-C_5H_5, 1.79 (1); Fe-C_6Me_6, 1.58 (1) Å; the methyl groups are slightly bent toward the metal according to the steric demand of the metal-carbon orbital interaction ($\bar{\alpha}$ = 1.32°). Note the overall C_s symmetry of the molecule. (c) Perspective view of the structure along the normal to the layers. For sake of clarity, only the iron atom chains of the upper layer are depicted. (d) Projection of a chain onto a plane perpendicular to layers of mixed Cp and arene rings.

Reaction of the THF solution of **1** with dry air, followed by addition of 1 mol of CH_3I at 25 °C and metathesis with aqueous HPF_6, affords $\mathbf{4}^+PF_6^-$ [9] which, upon Na/Hg reduction, gives **4**.[11] The reaction mixture $\mathbf{1}^+PF_6^-$ + excess *t*-BuOK + excess CH_3I in THF (1 h, 25 °C) gives $\mathbf{5}^+PF_6^-$, the reduction of which affords **5**.[8] Alternatively $\mathbf{5}^+$ is synthesized by successive contacts of **1**, **2**, or **4** with Na/Hg/O_2 + CH_3I (THF, 25 °C, 4 h) (Scheme I).

5 (or **6**) reacts further with 1 mol of O_2 (end point by color change from deep green to pale yellow) to give the salt $\mathbf{5}^+O_2^-\cdot$ (or $\mathbf{6}^+O_2^-\cdot$) (the temperature-dependent ESR spectra characterize $O_2^-\cdot$[3]) providing further evidence for $O_2^-\cdot$ as an intermediate in the loss of one H atom: $\mathbf{1} + O_2 \rightarrow \mathbf{2}$.

The ESR spectra[10] of **1**, **3**, **4**, and **5** (observed in frozen DME solutions only below 180 K) show 3 g values (rhombic Jahn-Teller distortion[10]) close to **2**, consistent with d^7 complexes with significant metal character for the singly occupied e^*_{1g}.[10]

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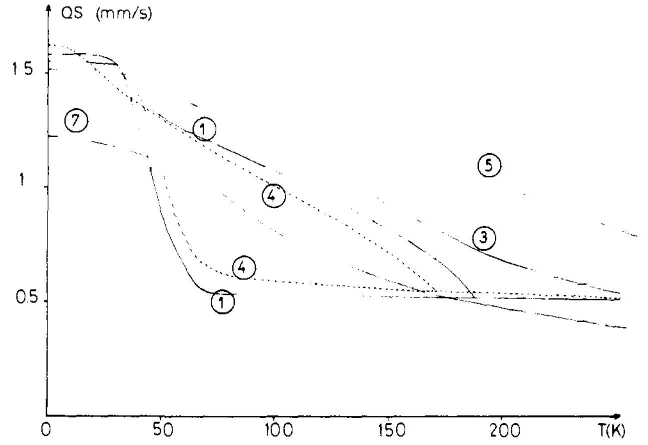

Figure 2. ^{57}Fe Mössbauer spectroscopy at zero field: temperature dependence of the quadrupole splitting (QS). Isomer shifts are constant (0.73-0.75 mm s^{-1}). Numbering corresponds to that in Scheme I.

The crystal structure of **1**[11] (Figure 1) shows that it is a true 19-electron complex. Both rings are planar and parallel. The Fe-C_5H_5 (ring centroid) distance of 1.79 (1) Å is significantly longer than that in 18-electron complexes of Fe[9] and is the longest Fe-Cp bond ever measured by X-ray. This suggests that the antibonding e^*_{1g} orbital involves the e_1 level of C_5H_5 at least as much as that of the arene ligand (Fe-$C_{C_5H_5}$ = 2.144 (4), Fe-$C_{C_6(CH_3)_6}$ = 2.100 (7) Å). The shape of the CH_3 ellipsoids arises from a libration and/or rotation of the benzene ligand rather than from a disorder since the X-ray powder pattern becomes more accurate on cooling to 180 K.[14c] The remarkable packing (Figure 1c,d) consists of alternating layers of coplanar Cp and arene rings parallel to the quasi-linear chains of iron atoms (angle 150°, Fe-Fe distance 7.61 Å) running along the the *b* axis, a situation not otherwise encountered in metallocene packings.

The Mössbauer spectra of $C_5H_5FeC_6H_6$, **7** (263 K) and of **1**, **3**, **4**, **5**, and **6** (293 K) show a quadruple doublet with QS values (IS = 0.73-0.75 mm s^{-1}; QS = 0.4-0.6 mm s^{-1}) $\simeq$ 1.5 mm s^{-1} smaller than those for the related cations (IS = 0.41-0.45 mm s^{-1}; QS = 1.8-2 mm s^{-1}) corresponding to 65-75% metal character[13] for the e^*_{1g} singly occupied by the 19th electron.[13] An intriguing feature is the splitting below 170 K into two doublets for **1.** This is correlated with the alternating layers resulting from the difference of ring sizes (Figure 1d); the doublets of **3** and **7,** in which the ligands have nearly the same size, do not split, but the QS values show a large temperature dependence (Figure 2) due to a nonaxial potential consistent with a Jahn-Teller effect (thermal population of the upper Kramers doublet; see Figure 2; e^*_{1g} splitting = 120-140 cm^{-1}) characteristic of this d^7 Fe(I) series.[14]

Attempts to isolate $C_5(CH_3)_5FeC_6H_6$ as a solid from its DME solution lead to dimerization through the benzene ring during evaporation of the solvent even at −50 °C.[15] This shows that hypermethylation of a ring pushes the spin density onto the other ligand, an observation consistent with the long Cp-Fe distance found for **1** (vide supra).

Since hypermethylation raises the e_{1g} ring level involved in the e^*_{1g} HOMO, it decreases the eigenvector of this ligand in e^*_{1g}. Thus hyperalkylation of the benzene ring, not that of Cp, stabilizes the d^7 sandwich (as e_{1g} Cp > e_{1g} C_6H_6).[16] Since e^*_{1g} has ~70% metal character, a slight increase of the benzene eigenvector in e^*_{1g} probably increases drastically the tendency to dimerization (sandwiches of the second and third row transition metals with more than 18 electrons have not been isolated).[17]

Therefore, the sandwiches designed here are ideal "electron reservoirs". A dramatic example is the efficiency of **1** as a stable redox catalyst for the electroreduction of NO_3^- to NH_3 in aqueous 0.1 N LiOH, a reaction otherwise not feasible in water, which now proceeds with infinite turnovers at the potential (−1.8 V vs. SCE) at which $\mathbf{1}^+$ is reversibly reduced to **1.**[18] Since alkylation of the sandwich rings displaces the redox potential toward more negative values ($\simeq$0.02 V vs. CH_3), the more energetic electron reservoirs are the fully alkylated sandwiches **3** and **6** ($E_{1/2}$ = −1.9 V vs. SCE, aqueous LiOH).

Acknowledgments. We are grateful to Professors M. Caïs (Haifa, Israel) and M. McGlinchey (McMaster University, Canada) for stimulating discussions during their sabbatical leave in Rennes[19a] and to Professor A. Rassat (CENG, Grenoble), for ESR facilities. CNRS is acknowledged for financial support (ATP No. 3801).

References and Notes

(1) For a recent and comprehensive review, see G. W. Parshall, *J. Mol. Catal.*, **4**, 263 (1978).

(2) D. Astruc, E. Roman, J. R. Hamon, and P. Batail, *J. Am. Chem. Soc.*, **101**, 2240 (1979).

(3) A. M. Michelson, J. M. McCord, and I. Fridovitch, "Superoxide and Superoxide Dismutase", Academic Press, New York, 1977.

(4) By the term "electron reservoir" we mean a highly reduced species which is one half of a totally reversible redox catalytic system in which both the oxidized and reduced forms are stable and isolable. Although a plethora of organometallic redox systems exist, they suffer from either the instability of one of the forms or a low redox potential such as the other d^7 19-electron sandwiches known[5,6] (see, for example, U. Koele, *J. Organomet. Chem.*, **152**, 225 (1978), **157**, 327 (1978)). Note that cobaltocene reacts with O_2 to give a peroxide (H. Kojima, S. Takahashi, and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 230 (1973)).

(5) The crystal structures of cobaltocene[5a] and (bisborabenzene)cobalt[5b] (d^7) are known: (a) W. Bunder and E. Weiss, *J. Organomet. Chem.*, **92**, 65 (1976); (b) G. Huttner, B. Krieg, and W. Gartzke, *Chem. Ber.*, **105**, 3424 (1972).

(6) For a comprehensive discussion of the electronic structure of cobaltocene and other d^7 sandwiches, see J. H. Ammeter, *J. Magn. Reson.*, **30**, 299 (1978).

(7) Both decomplexation and dimerization of $C_5H_5FeC_6H_6$ (**7**) occur at 20 °C in the solid state or in pentane. Fast decomplexation was observed in coordinating solvents: (a) D. Astruc and R. Dabard, *C. R. Acad. Sci. Paris, Ser. C*, **269**, 689 (1969); (b) C. Moinet, E. Roman, and D. Astruc, *J. Organomet. Chem.*, **128**, C45 (1977); (c) A. N. Nesmeyanov, N. A. Vol'kenau, L. S. Shilovtseva, and V. A. Petrakova, *ibid.*, **61**, 329 (1973).

(8) Mass spectra (molecular peaks): **3,** calcd 353.193, found 353.193; **4,** calcd 297.130, found 297.130; **5,** calcd 367.209, found 367.209; **6,** calcd 437.287, found 437.287. **3:** ^{1}H NMR (δ, ppm, Me_4Si, C_6D_6, 28 °C), CH_3 of the C_6 (or C_5) rings at −21.73 (or 30.85); ^{13}C NMR (δ, ppm, C_6D_6), CH_3 of Cp at −136.7. Additional resonances at 7.71, −0.20, and −1.66 ppm (^{1}H) and 54.6, 19.6, and 16.7 (^{13}C) may be due to partial reversible decoordination (the benzene solution is brown at 28 °C; pentane and THF solution are green). **5:** ^{1}H NMR (δ, ppm, $C_6D_5CD_3$, 28 °C), C_5H_5 at −39.80 and −42.10, CH_2 at −7.02, CH_3 at 4.80; ^{13}C NMR −37.7 and −2.7; additional ^{1}H signals at 3.80, 2.23, and 1.91; additional ^{13}C signals at 77.6, 22.0, and 16.9 (CH_2); also signals at 1.42 (^{1}H) and 0.8 (^{13}C) for CH_3, $\mu_{eff} = 1.85 \pm 0.1\ \mu_B$. Sublimation at 5 mmHg: **3,** 105 °C; **5,** 40 °C.

(9) $\mathbf{3}^+PF_6^-$ (or $\mathbf{6}^+PF_6^-$) is obtained in 40% (or 25%) yield by reacting $C_5(CH_3)_5Fe(CO)_2Br$–$C_6(CH_3)_6$– (or $C_6(C_2H_5)_6$–) $AlCl_3$ (1:3:2) for 12 h at 180 °C, followed by metathesis with aqueous HPF_6. Consistent data for the cations $\mathbf{3}^+$, $\mathbf{4}^+$, $\mathbf{5}^+$, and $\mathbf{6}^+$ (PF_6^-) will be published later.

(10) *g* values: **1,** 1.864, 2.000, 2.063; **3,** 1.912, 2.002, 2.062; **4,** 1.850, 2.006, 2.053; **5,** 1.896, 2.003, 2.059. For a detailed analysis of the Jahn–Teller effect in metallocenes, see ref 5, 13, and J. H. Ammeter, *J. Chem. Phys.*, **57**, 678 (1972).

(11) Crystal data and refinement results: $C_{17}H_{23}Fe$, monoclinic; a = 8.363 (6), b = 14.710 (8), c = 11.845 (5) Å; β = 93.98 (6)°; space group $P_{2_{1/n}}$; Z = 4. A suitable crystal mounted under inert atmosphere in a glass capillary was used to collect X-ray diffraction data on a Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation and ω–2θ scans; 2657 unique data with $2\theta < 60°$ were used in subsequent refinement. Atoms were located through direct method (MULTAN) and difference Fourier syntheses. Structure was refined to a current residual R index on F_o of 0.070 ($R\omega$ = 0.063), with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms of the Cp ring were located.

(12) For a recent discussion of Fe–Cp distances, see G. M. Reiner, I. Bernal, H. Brunner, and M. Mushiol, *Inorg. Chem.*, **17**, 783 (1978).

(13) The monoelectronic 3d function being $\simeq$2 mm s^{-1} for a degenerate e^*_{1g} MO (F. Varret, *J. Phys. C*, **37**, 437 (1976)), one can calculate 1.3–1.5/2 = 65–75% metal character for e^*_{1g} for the d^7 Fe(I) series. However this neglects the relaxation of the other d orbitals; 67% was found by ESR in cobaltocene (J. H. Ammeter, N. Ostwald, and R. Bucher, *Helv. Chim. Acta*, **58**, 671 (1975)).

(14) (a) That one doublet of **1** does not depend on temperature in the range of 60–295 K indicates a site in a dynamic JT situation due to minimum asymmetry of the external potential. Spectra of **4** (bulky ethyl substituents) and of **1** in frozen decalin or in **2** as host lattice (10% of **1,** cosublimation) show no splitting (like pure **3** and **8**) consistent with largely asymmetric potential. See J. H. Ammeter and J. M. Brom, Jr., *Chem. Phys. Lett.*, **27**, 380 (1974). (b) For a rare example of Jahn–Teller effect observed by

Mössbauer spectroscopy, see G. Garcin, P. Imbert, and G. Jehanno, *Solid State Commun.*, **21**, 545 (1977). (c) The X-ray powder pattern recorded at 80 K is different from that recorded at 293 K, but no thermal event is observed by low temperature DTA in agreement with a second-order phase transition around 170 K (Dr. J. Pannetier, private communication).

(15) (a) We could characterize η^5-$C_5(CH_3)_5Fe$–η^6-C_6H_6 as an Fe(I) monomeric green species by the Mössbauer spectrum of a frozen DME solution at 77 K: IS = 0.73 mm s^{-1}; QS = 0.82 mm s^{-1}. Dimer (η^5-$C_5(CH_3)_5Fe$–η^5-C_6H_6–$)_2$: ^{1}H NMR (δ, C_6D_6), CH_3 at 1.60 (s, 15), cyclohexadienyl at 1.60–1.80 (m, 3), 3.60 (m, 2), and 5.12 (m, 1). (b) d^7 $CpFePh(CH_3)_n$ can be isolated as solids at −20 °C and characterized by Mössbauer spectroscopy (n = 1, 5; parameters are in the same range as for d^7 Fe(I) sandwiches noted in text). Dimerization (in the solid state, not in solution) is slow (~10 min) for n = 1, 5 at −10 °C and for n = 2, 3, 4 at −20 °C.

(16) K. D. Warren, *Struct. Bonding (Berlin)*, **27**, 45 (1976).

(17) For instance, $[\eta^6$-$C_6(CH_3)_6]_2M$ (Re, Te) dimerize spontaneously at low temperature in spite of the hypermethylation (E. O. Fischer and M. F. Schmidt, *Chem. Ber.*, **99**, 2206 (1966)) as Cp_2M (Ir, Rh) (E. O. Fischer and H. Waversick, *J. Organomet. Chem.*, **5**, C59 (1966)).

(18) The efficiency of this redox catalysis is still enhanced on solubilization of both **1** and **1**$^+$ by means of introducing a carboxylate group on the Cp ring; then $k(NO_3^- \rightarrow NH_3) = 10^2$ mol^{-1} L s^{-1}. (a) D. Astruc, A. Darchen, and C. Moinet, Colloque D.G.R.S.T., Paris, Dec 15th, 1978; (b) A. Buhet, A. Darchen, and C. Moinet, *J. Chem. Soc., Chem. Commun.*, 447 (1979).

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Mechanism of the Reaction between Organo Transition Metal Alkyls and Hydrides. A Model for the Aldehyde-Forming Step in the Oxo Process

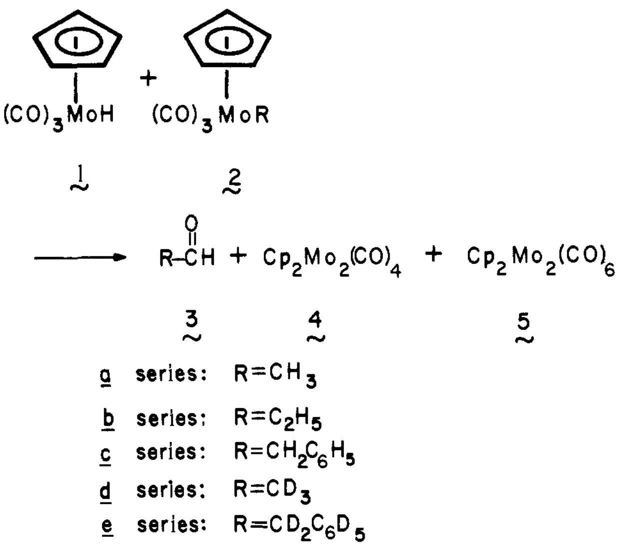
Sir:

The identification of primary reaction steps in organo transition metal chemistry (e.g., oxidative addition, reductive elimination, β-elimination, etc.) was an important advance in understanding organometallic reaction mechanisms.[1] These steps, characteristic of processes which occur at a single metal center, are now being augmented by the identification of steps which involve more than one metal.[2] One such process which has appeared repeatedly recently is the reaction of a metal hydride and a metal alkyl (or acyl) to give a product containing a new C–H bond:

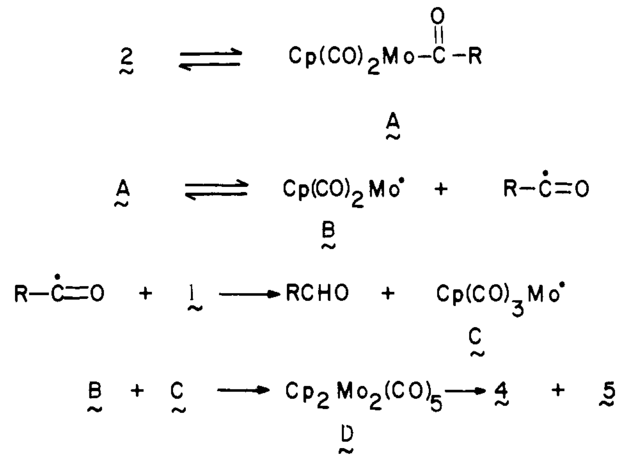
$$M\text{-}H + M'\text{-}R \rightarrow R\text{-}H + M\text{-}M' \qquad (1)$$

An early example was the observation made by Breslow and Heck[3] that $HCo(CO)_4$ and $CH_3COCo(CO)_4$ led rapidly to acetaldehyde, a process which was, however, discounted (perhaps prematurely[4]) as the source of aldehyde in the hydroformylation reaction. Later Schwartz uncovered another example in an iridium system.[5] Norton and his co-workers have investigated such a process in an osmium alkyl hydride, a study which led to the unusual postulate of reductive elimination of *alkane* from an acyl hydride intermediate.[6] More recently still, Halpern and co-workers have shown that benzylpentacarbonylmanganese and hydridopentacarbonylmanganese react to give toluene in a process for which they have proposed a mechanism involving initial homolysis of the benzylmanganese bond, followed by rapid hydrogen transfer from $HMn(CO)_5$ to the benzyl radical intermediates so formed.[7]

Scheme I



Scheme II



The growing ubiquity and apparent facility of metal hydride–metal alkyl reactions makes it important to have good mechanistic information available on these processes. After briefly surveying the reactions of several well-characterized hydrides and alkyls, we discovered that molybdenum hydride **1** and corresponding alkyls **2** undergo an especially clean and quantitative reaction which leads to aldehyde **3** and dimers **4** and **5** (Scheme I). The methyl and ethyl complex **2a** and **2b** are converted into aldehydes **3a** and **3b** at temperatures between 25 and 50 °C, **2b** reacting substantially more rapidly. Yields are quantitative and no trace of alkanes are observed. These reactions give clean second-order kinetics; rate constants are listed in Table I.

Table I. Rate Constants for Reaction between $CpMo(CO)_3H$ and $CpMo(CO)_3R$ in THF-d_8[a]

alkyl	T, °C	k, M^{-1} s^{-1}
2a	50	2.5×10^{-4}
2b	50	4.0×10^{-3}
2b	25	8.5×10^{-4}
2c	50	2.5×10^{-5}
6a	50	2.3×10^{-4}

[a] Rates measured by monitoring disappearance of starting material resonances in the 180-MHz NMR spectrum.