Notes

Equilibrium Constants for Homolysis of Metal–Metal-Bonded Organometallic Dimers in Cyclohexane Solution. Reaction of the (MeCp)Mo(CO)$_3$ Radical with the Nitroxide Radical Trap TMIO

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Summary: Equilibrium constants for the homolyses of the (MeCp)$_2$Mo$_2$(CO)$_6$, Cp$_2$Fe$_2$(CO)$_4$, and Mn$_2$(CO)$_{10}$ dimers at 23 (±1) °C in cyclohexane solution are reported ($K_{eq,Mo}$ = [1.1 (±0.1)] × 10^{-17}; $K_{eq,Fe}$ = [2.0 (±0.1)] × 10^{-17}; $K_{eq,Mn} < 2.4 \times 10^{-19}$). The crystal structure of the (MeCp)Mo(CO)$_2$(TMIO) adduct, formed by reaction of TMIO with (MeCp)Mo(CO)$_3$ radicals, is also reported. (TMIO is the nitroxide radical trap 1,1,3,3-tetramethylisoindoline-2-oxyl). TMIO is a superior trap for (MeCp)Mo(CO)$_3$ radicals, reacting 77 times faster than CCl$_4$ in benzene at 23 °C.

Equilibrium constants for the homolysis of several Cr–Cr-bonded organometallic dimers[1] and for the bulky (η^5-C$_5$Ph$_5$)$_2$Mo$_2$(CO)$_6$ dimer[2] have been reported (Table I):[3,4]

$$M_2L_{2n} \overset{K_{eq}}{\rightleftharpoons} 2ML_n \tag{1}$$

M_2L_{2n} = metal carbonyl dimer; ML_n = *free* radical[5]

For these dimers, substantial concentrations of the free radicals exist in room-temperature solution because of the weak metal–metal bonds. It is important to recognize that dimers with stronger metal–metal bonds also exist in equilibrium with their free-radical monomers. In this note, we report the equilibrium constants for the (MeCp)$_2$Mo$_2$(CO)$_6$, Cp$_2$Fe$_2$(CO)$_4$, and Mn$_2$(CO)$_{10}$ dimers in cyclohexane solution. (Equilibrium constants in CH$_3$CN, measured by electrochemical methods, were recently reported.[7] Cyclohexane was used in this study because of the possibiity that 19-electron adducts may form in acetonitrile.[8]) Although the equilibrium constants are relatively small, the concentrations of the radicals at equilibrium are significantly greater than the steady-state concentrations of the radicals in typical chain reactions. The homolyses and subsequent equilibria can therefore have important consequences in the quantitative interpretation of metal radical reactions, particularly in those chain reactions in which metal radicals can act as initiators.[9] Also reported herein are results pertaining to the use of TMIO (1,1,3,3-tetramethylisoindoline-2-oxyl) as a trapping agent for organometallic radicals.

Results and Discussion

Strategy for Obtaining K_{eq}. The equilibrium constants for eq 1 were obtained by using the expression $K_{eq} = k_f/k_r$, where k_f is the rate constant for the formation of free radicals from the dimers and k_r is the rate constant for combination of two metal radicals. Values for k_f were obtained by quantitatively trapping the free radicals produced by homolysis of the metal–metal bond, and values for k_r were taken from flash photolysis studies reported in the literature.[10–12] For reasons discussed below,

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[1] (a) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643. (b) Goh, L. Y.; Khoo, S. K.; Lim, Y. Y. *J. Organomet. Chem.* **1990**, *399*, 115.

[2] Mao, F.; Sur, S. K.; Tyler, D. R. *Organometallics* **1991**, *10*, 419.

[3] For nonquantitative examples of other dimers in equilibrium with radicals, see: (a) Tyler, D. R.; Goldman, A. S. *J. Organomet. Chem.* **1986**, *311*, 349. (b) Herrick, R. S.; Herrington, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42. (c) Kidd, D. R.; Cheng, C. P.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4103. (d) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496. (e) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, *2*, 775.

[4] Note that eq 1 is for the equilibrium of a dimer with two *free* radicals. The reaction proceeds through a caged radical pair as shown:

$$M_2L_{2n} \underset{k_c}{\overset{k_1}{\rightleftharpoons}} \underset{\text{caged radical pair}}{[L_nM^\bullet\,{}^\bullet ML_n]} \underset{k_{-1}}{\overset{k_d}{\rightleftharpoons}} \underset{\text{free radicals}}{2\,{}^\bullet ML_n}$$

The rate constant k_f (for the formation of free radicals from the dimers) in eq 2 is given by $k_f = [1 - F_c]k_1$, where F_c is the cage efficiency factor, defined as $F_c = k_c/(k_c + k_d)$. Likewise, k_r is a composite rate constant given by F_ck_{-1}. See ref 5 and 6 for further details. The equilibrium constants we report in this paper are for the dimers in equilibrium with the *free* radicals.

[5] Koenig, T.; Finke, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 2657.

[6] Koenig, T.; Hay, B. P.; Finke, R. G. *Polyhedron* **1988**, *7*, 1499.

[7] (a) Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 8245. (b) Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 3784.

[8] For recent reviews, see: (a) Tyler, D. R.; Mao, F. *Coord. Chem. Rev.* **1990**, *97*, 119. (b) Tyler, D. R. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; p 338. Also see ref 34.

[9] Castellani, M. P.; Tyler, D. R. *Organometallics* **1989**, *8*, 2113.

[10] Different flash photolysis studies have determined slightly different k_r values for the same dimer even when the reaction conditions are essentially identical. For consistency, we decided to use the back-reaction rate constants tabulated in ref 11 on p 209. If subsequent work finds better k_r values, the K_{eq} values reported herein are easily corrected. See the table in ref 11, p 209, for specific details and references regarding the flash photolysis studies.

[11] Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

[12] Different solvents have different values for F_c[4] and therefore the rate constants for the back-reactions should be measured in the same solvent as the rate constants for the forward reactions. F_c depends on several factors, most notably the viscosity of the solvent.[5,6,13,14]

[13] Koenig, T.; Fischer, H. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, p 157.

[14] Koenig, T. In *Organic Free Radicals*; Pryor, W. A.; Ed.; ACS Symposium Series 69; American Chemical Society: Washington, DC, 1978; Chapter 3.

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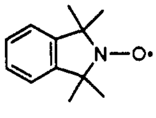
Table I. k_f, k_r, K_{eq}, **and Metal–Metal Bond Dissociation Energies for Selected Metal–Metal-Bonded Carbonyl Dimers at 23 °C in Cyclohexane**

dimer	k_f (s^{-1})	k_r (M^{-1} s^{-1})	K_{eq} (M)	solvent	M–M BDE (ΔH^*) (kcal/mol)
$Cp_2Cr_2(CO)_6$			4.5×10^{-4} [a]	toluene, THF	13[a]
$(\eta^5\text{-}C_5Me_5)_2Cr_2(CO)_6$			3.6×10^{-2} [b]	toluene	18.3 ± 0.6[b]
$(\eta^5\text{-}C_5Ph_5)_2Mo_2(CO)_6$			$[8.7 (\pm 5.1)] \times 10^{-5}$ [c]	toluene	
$(MeCp)_2Mo_2(CO)_6$	$[3.3 (\pm 0.3)] \times 10^{-8}$ [d]	3.1×10^9	$[1.1 (\pm 0.1)] \times 10^{-17}$ [e]	cyclohexane	33[f]
$(MeCp)_2Mo_2(CO)_6$	$[2.8 (\pm 0.3)] \times 10^{-8}$ [g]	3.1×10^9	$[9.0 (\pm 1)] \times 10^{-18}$ [e]	cyclohexane	
$Cp_2Mo_2(CO)_6$			7.1×10^{-17} [h]	0.1 M TBAH/CH_3CN	
$Cp_2Fe_2(CO)_4$	$[6.5 (\pm 0.3)] \times 10^{-8}$ [d]	3.2×10^9	$[2.0 (\pm 0.1)] \times 10^{-17}$ [e]	cyclohexane	27[i]
$Cp_2Fe_2(CO)_4$			1.7×10^{-17} [j]	0.5 M TBAH/CH_3CN	
$Cp_2Fe_2(CO)_4$			4.0×10^{-19} [j]	0.1 M TBAH/CH_3CN	
$Mn_2(CO)_{10}$	$<4.6 \times 10^{-10}$ [k]	1.9×10^9	$<2.4 \times 10^{-19}$ [e]	cyclohexane	38[l]
$Mn_2(CO)_{10}$			5.2×10^{-19} [j]	0.5 M TBAH/CH_3CN	
$Mn_2(CO)_{10}$			2.4×10^{-21} [h]	0.1 M TBAH/CH_3CN	

[a] Reference 1a. [b] Reference 1b. [c] Reference 2. [d] From reaction with CCl_4. [e] This work. [f] References 47 and 30. [g] From reaction with TMIO. [h] Reference 7b. [i] Reference 27. [j] Reference 7a. [k] Measured in neat CCl_4. [l] References 7b, 11, and 48.

two traps were used, CCl_4 and the nitroxide TMIO.[15] The reactions with CCl_4 will be discussed first.



TMIO

Method for Determining the Homolytic Rate Constants. Considerable prior work has shown that organometallic radicals can be trapped with halogen atom donors; in particular, CCl_4 is an excellent trap (eq 2).[11,16–20]

$$L_nM^{\bullet} + CCl_4 \rightarrow L_nM\text{–}Cl + ({}^{\bullet}CCl_3) \qquad (2)$$

$$L_nM^{\bullet} = CpMo(CO)_3,\ CpFe(CO)_2,\ Mn(CO)_5$$

Over a period of several weeks to months, degassed solution of the dimers in cyclohexane containing 2 M CCl_4 reacted in the dark (23 °C):[21]

$$L_nM\text{–}ML_n + 2CCl_4 \rightarrow 2ML_nCl + (2CCl_3) \qquad (3)$$

The rates of reaction 3 were monitored by following the disappearance of the dimers using electronic absorption spectroscopy. The rate constants thus obtained for the disappearance of the dimers will be those for free-radical formation if *all* of the free radicals are trapped by 2 M CCl_4 *and* if homolysis is the only process contributing to the disappearance of $L_nM\text{–}ML_n$. The first requirement was established in a straightforward fashion by showing that the quantum yields for the photochemical analogs of reaction 3 are saturated at 2 M CCl_4.[16,20,22] (It is well-established that irradiation ($\lambda > 540$ nm) of metal–metal-bonded dimers leads to homolysis of the metal–metal bonds.[11,19]) No increase was observed in the photolytic quantum yield for concentrations greater than 0.4 M CCl_4.[20,23] Thus, every free radical generated photochemically is trapped with 2 M CCl_4. By implication, every free radical generated thermally in eq 3 will also be trapped by 2 M CCl_4 because the steady-state concentration of free radicals is certainly lower in the slower thermal reactions.

The second requirement (that homolysis should be the only pathway contributing to the disappearance of the dimers) is a concern because Poë showed that $Cp_2Mo_2(CO)_6$ reacted with $CHBr_3$ or $C_2H_2Cl_4$ to form $CpMo(CO)_3X$ (X = Br, Cl) in decalin solution at 72 °C by two pathways: one pathway was the homolytic pathway and the other was a pathway that was second-order in halocarbon (and thus third-order overall).[24] However, the halocarbon-dependent pathway can be discounted in this study because we found no dependence of the rate on [CCl_4].

Several other mechanisms may also contribute to the disappearance of the dimers in reaction 3. However, various mechanistic arguments also rule out these pathways. These arguments rely on the fact that the rates of disappearance determined by using CCl_4 and TMIO as traps are identical. The discussion of the additional possible mechanisms is necessarily presented in the final section of this note, after a discussion of the TMIO results.

Homoytic Rate Constants and K_{eq} Values from the Reactions with CCl_4. In a typical experiment, a 2.00×10^{-3} M solution of $Cp_2Fe_2(CO)_4$ in 2 M CCl_4 was prepared in the dark and the disappearance of $Cp_2Fe_2(CO)_4$ periodically monitored by electronic absorption spectroscopy at 524 nm.[25] The disappearance of the dimer followed first-order kinetics; the average of three trials yielded a rate constant of $[6.5 (\pm 0.3)] \times 10^{-8}$ s^{-1}.[26] Meyer and Huheey[28] reported $k_r = 3.2 \times 10^9$ M^{-1} s^{-1} in cyclohexane (23 °C), and thus K_{eq} is $[2.0 (\pm 0.1)] \times 10^{-17}$ M (23 °C). Infrared spectroscopy of the reaction solution showed the

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(15) Beckwith, A. L. J.; Bowry, V. W.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632.

(16) The rate constant for Cl atom abstraction from CCl_4 by $CpMo(CO)_3$ radicals is 2×10^4 M^{-1} s^{-1}.[11] Recombination of two free $CpMo(CO)_3$ radicals cannot compete with this abstraction reaction.

(17) (a) Gasanov, R. G.; Sadykhov, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 993. (b) Song, J.-S.; Bullock, R. M.; Creutz, C. *J. Am. Chem. Soc.* **1991**, *113*, 9862.

(18) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388.

(19) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(20) Covert, K. C.; Askew, E.; Grunkemeier, J.; Koenig, T.; Tyler, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 10 446.

(21) Control experiments showed that no disappearance of the dimers occurred in the absence of CCl_4.

(22) In a recent paper[20] we showed that no trapping of caged-pair radicals will occur in 2 M CCl_4/cyclohexane solution. See ref 4 for a more complete mechanistic description of reaction 2.

(23) Saturation probably occurs at much lower concentrations; 0.4 M CCl_4 just happened to be the lowest concentration we tried.

(24) Amer, S.; Kramer, G.; Poë, A. *J. Organomet. Chem.* **1981**, *220*, 75.

(25) Tyler, D. R.; Schmidt, M. A.; Gray, H. B. *J. Am. Chem. Soc.* **1979**, *101*, 2753.

(26) Cutler and Rosenblum[27] measured the following activation parameters for homolysis of the metal–metal bond over the temperature range 60–100 °C in *benzene* solution: $\Delta H^{\ddagger} = 26.9 \pm 2.7$ kcal/mol, $\Delta S^{\ddagger} = 2.0 \pm 3.2$ cal mol^{-1} K^{-1}. Extrapolation to 23 °C yields $k_f = 2.42 \times 10^{-7}$ s^{-1}, a value in reasonable agreement with our value of $[6.5 (\pm 0.3)] \times 10^{-8}$ s^{-1} in hexane/2 M CCl_4.

(27) Cutler, A. R.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *120*, 87.

(28) Hughey, J. L.; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440.

formation of $CpFe(CO)_2Cl$ ($\nu(C{\equiv}O)$ = 2055, 2011 cm^{-1}) but no other products.

The value of k_f for $(MeCp)_2Mo_2(CO)_6$, obtained by the same method, is $k_f = [3.3\ (\pm0.3)] \times 10^{-8}\ s^{-1}$ (23 °C), and the calculated equilibrium constant is $K_{eq} = [1.1\ (\pm0.1)] \times 10^{-17}$ M.[29,32]

In the case of $Mn_2(CO)_{10}$, neat CCl_4 was used as the solvent. No disappearance of the dimer had occurred after 75 days, leading to $K_{eq} < 2.4 \times 10^{-19}$ M. (This value represents the uncertainty of 0.003 in the absorbance readings of our Beckman DU spectrophotometer.[33])

The equilibrium constants for the dimers are summarized in Table I. As expected, the K_{eq} values correlate with the metal–metal bond dissociation energies of the dimers.[7] The equilibrium constants in cyclohexane are close in value to those measured by Pugh and Meyer in CH_3CN (also reported in Table I).[7] The differences in the two sets of data are likely attributed to differences in solvation of the radicals. For example, the slightly larger value for K_{eq} of $Cp_2Mo_2(CO)_6$ in CH_3CN compared to that in cyclohexane probably reflects the tendency of $CpMo(CO)_3$ radicals to form 19-electron species in the coordinating CH_3CN solvent.[36]

Reactions with TMIO. As briefly discussed above, the reactions of metal carbonyl dimers with halocarbons can be mechanistically complex.[24,27] It seemed prudent therefore to obtain an independent measurement of k_f by using a non-halocarbon trap. For that reason, experiments to measure the k_f values for the homolysis reactions were repeated using 80 mM TMIO, a nitroxide radical trap, in place of the CCl_4.[15]

The dark reaction of $(MeCp)_2Mo_2(CO)_6$ with TMIO (eq 4) has the same rate constant within experimental error ($k_f = [2.8\ (\pm0.3)] \times 10^{-8}\ s^{-1}$ (23 °C)) as the reaction with CCl_4. The structure of the $(MeCp)Mo(CO)_2(TMIO)$ product in reaction 4 was determined by X-ray crystallography (Figure 1, Tables II–IV).[38]

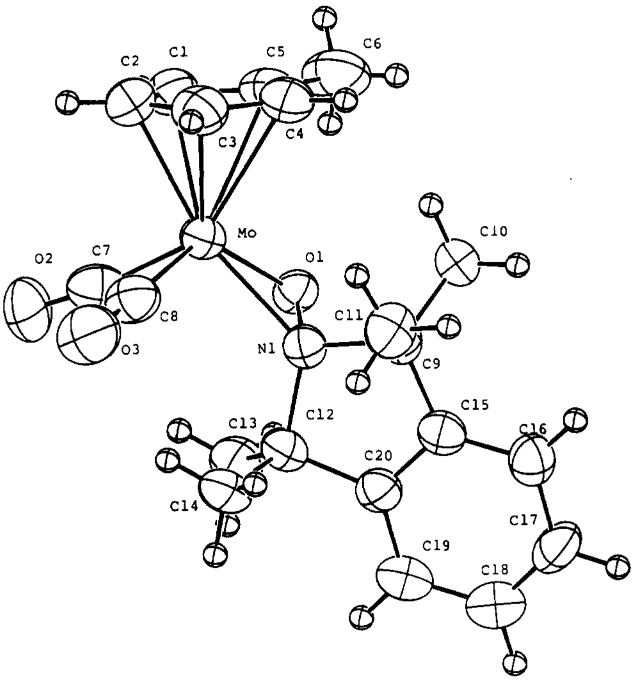
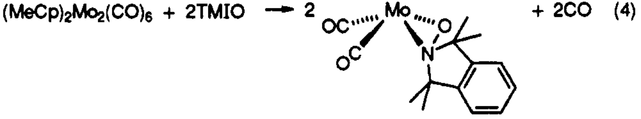


Figure 1. Molecular structure of the $(MeCp)Mo(CO)_2(TMIO)$ complex.

Table II. Crystallographic Information for $C_{20}H_{23}MoNO_3{\cdot}0.5C_6H_6$

composition	$C_{20}H_{23}MoNO_3{\cdot}0.5C_6H_6$
fw	460.4
space group	$P\bar{1}$
a	9.117(3) Å
b	9.767(6) Å
c	12.543(3) Å
α	85.37(3)°
β	87.29(2)°
γ	72.51(3)°
V	1062(2) Å^3
Z	2
d_{calc}	1.440 g cm^{-3}
T	20 °C
λ	0.710 69 Å
μ	6.23 cm^{-1}
no. of obs rflns	2355 ($I \geq 3\sigma(I)$)
$R(F_o)^a$	0.057
$R_w(F_o)^b$	0.070

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.



The use of TMIO as a trap for metal radicals has not previously been reported. It was of interest therefore to compare quantitatively its trapping ability to that of CCl_4. Competitition experiments using photogenerated metal radicals gave the relative rates of $(MeCp)Mo(CO)_3$ radical trapping by CCl_4 compared to TMIO. Thus, irradiation (λ < 520 nm) of benzene solutions containing both CCl_4 and TMIO gave $(MeCp)Mo(CO)_3Cl$, CCl_3–TMIO, and $(MeCp)Mo(CO)_2(TMIO)$ in yields that depended on the relative concentrations of CCl_4 and TMIO (eq 5). Quantitative analysis of the results of this competitition indicated that the rate constant for the decarbonylative trapping of the metal free radical by TMIO is 77 times faster than Cl atom abstraction from CCl_4; thus, $k_{TMIO} \simeq 1.5 \times 10^6\ M^{-1}\ s^{-1}$ (23 °C).[16]

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(29) Poë et al.[30] measured activation parameters for homolysis of the Mo–Mo bond in the $Cp_2Mo_2(CO)_6$ complex in *decalin* over the temperature range 70–135 °C ($\Delta H^\ddagger$ = 32.5 ± 0.5 kcal/mol, $\Delta S^\ddagger$ = 13.4 ± 1.3 cal mol^{-1} K^{-1}). These values lead to $k_f = 5.2 \times 10^{-9}\ (\pm1.2 \times 10^{-9})\ s^{-1}$ at 23 °C, a value considerably smaller than our measured value. Decalin is more viscous than cyclohexane or CCl_4 (0.92 cP for CCl_4 at 23 °C[31] vs ~2.5 cP for decalin at 70 °C[29]), and to a certain extent the slower rate for net homolysis in decalin probably reflects a larger F_c value in this solvent.

(30) Amer, S.; Kramer, G.; Poë, A. J. *J. Organomet. Chem.* **1981**, *209*, C28.

(31) Barrer, R. M. *Trans. Faraday Soc.* **1943**, *39*, 48.

(32) The rate constant k_r for $Cp_2Mo_2(CO)_6$ was used in the calculation because the value for $(MeCp)_2Mo_2(CO)_6$ is unavailable from the flash photolysis studies.[11] The MeCp complex was employed in our experiments because the Cp complex was too insoluble in the cyclohexane/CCl_4 solvent to allow accurate absorbance measurements.

(33) Mn–Mn bond homolysis was shown to be negligible compared to Mn–CO bond dissociation in the substitution reactions of $Mn_2(CO)_{10}$,[34,35] as determined by mass spectroscopic and infrared spectroscopic techniques. However, the detection limits for these techniques are such that the existence of a small homolysis equilibrium for $Mn_2(CO)_{10}$ cannot be excluded. For example, Coville, Stolzenberg, and Muetterties[34] report a detection limit for homolysis products of ~3%.

(34) Coville, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2499.

(35) (a) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Chem.* **1982**, *21*, 1699 and references therein. (b) Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 4031 and references therein.

(36) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325.

(37) See Schemes VI and VIII in ref 11, for examples. Also see: Biddulph, M. A.; Davis, R.; Wilson, F. I. C. *J. Organomet. Chem.* **1990**, *387*, 277 for proposed examples in the $Mn_2(CO)_{10}$ system.

(38) For synthetic purposes, the $(MeCp)Mo(CO)_2(TMIO)$ product ($\nu(C{\equiv}O)$ = 1944, 1834 cm^{-1} in toluene) is formed in essentially quantiative yield by irradiation (λ > 520 nm) of the $(MeCp)_2Mo_2(CO)_6$ dimer in benzene solution in the presence of 2 equiv of TMIO.

Table III. Atomic Coordinates ($\times 10^4$; Mo, $\times 10^5$) and Equivalent Isotropic Thermal Parameters ($Å^2$)[a]

atom	x	y	z	B_{eq}
Mo	20063(7)	56945(7)	28339(5)	3.46(4)
O(1)	–102(5)	7025(5)	3341(3)	3.4(3)
O(2)	955(8)	3069(7)	2435(5)	6.4(5)
O(3)	3215(7)	4801(8)	534(5)	6.7(5)
N(1)	152(6)	7598(6)	2314(4)	3.2(4)
C(1)	3157(10)	4508(9)	4392(7)	4.9(6)
C(2)	4231(10)	4181(10)	3536(7)	4.8(6)
C(3)	4554(9)	5443(11)	3168(7)	5.1(6)
C(4)	3748(10)	6566(10)	3844(7)	5.1(6)
C(5)	2882(10)	5975(10)	4591(6)	4.9(6)
C(6)	1845(12)	6718(13)	5477(7)	7.0(8)
C(7)	1228(10)	4138(11)	2576(6)	5.0(6)
C(8)	2767(10)	5172(10)	1381(7)	4.8(6)
C(9)	270(8)	9149(8)	2292(6)	3.5(5)
C(10)	430(9)	9581(9)	3409(6)	4.4(5)
C(11)	1642(9)	9250(9)	1557(6)	4.6(6)
C(12)	–1173(8)	7629(8)	1554(5)	3.6(5)
C(13)	–2130(9)	6689(10)	2022(7)	4.9(6)
C(14)	–496(10)	7116(10)	472(6)	4.8(6)
C(15)	–1237(9)	10048(9)	1820(5)	3.7(5)
C(16)	–1832(10)	11540(9)	1758(6)	4.3(5)
C(17)	–3289(10)	12158(9)	1332(6)	4.8(6)
C(18)	–4136(10)	11332(11)	1000(7)	5.5(7)
C(19)	–3530(10)	9829(10)	1051(6)	4.9(6)
C(20)	–2046(8)	9202(8)	1464(5)	3.6(5)
C(21)[b]	3417(16)	671(15)	4862(20)	5.2(3)
C(22)[b]	4401(35)	373(28)	3934(16)	7.3(5)
C(23)[b]	5981(28)	–267(24)	4101(17)	6.0(4)
C(24)[c]	3593(34)	716(31)	5436(36)	3.4(5)
C(25)[c]	3872(45)	726(36)	4244(36)	4.1(7)
C(26)[c]	5219(59)	39(38)	3943(25)	4.2(6)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j]$. [b] Refined isotropically; site occupancy factor 0.70. [c] Refined isotropically; site occupancy factor 0.30.

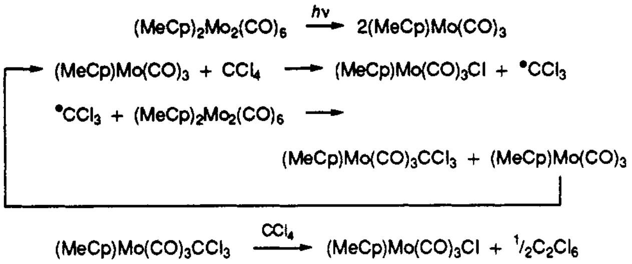
Table IV. Selected Bond Lengths (Å) and Angles (deg)

Mo–O(1)	2.075(5)	Mo–C(7)	1.917(10)
Mo–N(1)	2.182(6)	Mo–C(8)	1.970(9)
Mo–C(1)	2.315(8)	O(1)–N(1)	1.399(7)
Mo–C(2)	2.288(8)	O(2)–C(7)	1.171(10)
Mo–C(3)	2.316(8)	O(3)–C(8)	1.165(9)
Mo–C(4)	2.455(8)	N(1)–C(9)	1.548(9)
Mo–C(5)	2.442(7)	N(1)–C(12)	1.567(9)
Mo–Cp[a]	2.037(6)		

Cp–Mo–O(1)	114.3(3)	Mo–O(1)–N(1)	75.0(3)
Cp–Mo–N(1)	133.3(3)	Mo–N(1)–O(1)	66.7(3)
Cp–Mo–C(7)	118.6(3)	Mo–N(1)–C(9)	123.4(4)
Cp–Mo–C(8)	113.5(3)	Mo–N(1)–C(12)	125.8(4)
O(1)–Mo–N(1)	38.3(2)	O(1)–N(1)–C(9)	113.6(5)
O(1)–Mo–C(7)	94.6(3)	O(1)–N(1)–C(12)	110.9(5)
O(1)–Mo–C(8)	129.9(3)	C(9)–N(1)–C(12)	107.4(5)
N(1)–Mo–C(7)	103.3(3)	Mo–C(7)–O(2)	170.8(8)
N(1)–Mo–C(8)	95.5(3)	Mo–C(8)–O(3)	177.0(8)
C(7)–Mo–C(8)	75.3(4)		

[a] Cp = cyclopentadienyl ring centroid.

Scheme I. Hypothetical Chain Mechanism for the Reaction of $(\mathrm{MeCp})_2\mathrm{Mo}_2(\mathrm{CO})_6$ with CCl_4



$$(\mathrm{MeCp})_2\mathrm{Mo}_2(\mathrm{CO})_6 \xrightarrow{h\nu} \underset{\text{free radicals}}{2(\mathrm{MeCp})\dot{\mathrm{M}}\mathrm{o}(\mathrm{CO})_3} \xrightarrow{\mathrm{TMIO} + \mathrm{CCl}_4} (\mathrm{MeCp})\mathrm{Mo}(\mathrm{CO})_2(\mathrm{TMIO}) + (\mathrm{MeCp})\mathrm{Mo}(\mathrm{CO})_3\mathrm{Cl} + \mathrm{Cl}_3\mathrm{C{-}TMIO} + \mathrm{CO} \quad (5)$$

No *net* dark reaction occurred between $\mathrm{Cp_2Fe_2(CO)_4}$ and TMIO in cyclohexane. However, photochemical experiments monitored by infrared spectroscopy showed that TMIO does react with photogenerated $\mathrm{CpFe(CO)_2}$ radicals, but the reaction is reversible. Thus, irradiation ($\lambda > 520$ nm) of a THF solution of $\mathrm{Cp_2Fe_2(CO)_4}$ in the presence of TMIO in an infrared cell gave a product tentatively identified as $\mathrm{CpFe(CO)_2(TMIO)}$ by comparison to other $\mathrm{CpFe(CO)_2X}$ species.[39] The product back-reacted over several hours in the dark to re-form the starting materials. Because the product back-reacted to re-form the starting materials (and was thus unacceptable for the long-term trapping reactions), its definitive identification was not pursued. Note that because the k_f value for $\mathrm{Cp_2Fe_2(CO)_4}$ measured with $\mathrm{CCl_4}$ cannot be independently duplicated with TMIO, it is probably best to consider the k_f value obtained in the $\mathrm{CCl_4}$ experiment an upper limit for the homolysis rate constant.

Alternative Pathways. It has been frequently suggested to the authors that the $\mathrm{CCl_3}$ radicals produced in reaction 3 might react with a dimer and lead to a chain mechanism as shown in Scheme I.[40] Because TMIO cannot participate in chain mechanisms of this type, the identical rate constants for metal-radical trapping by $\mathrm{CCl_4}$ and TMIO strongly suggest there is no chain component in the reaction of $(\mathrm{MeCp})_2\mathrm{Mo}_2(\mathrm{CO})_6$ with $\mathrm{CCl_4}$.

It might also be argued that reaction 3 follows an electron-transfer pathway, involving either the rate-determining oxidation or reduction of the metal dimer. This mechanism is also unlikely, because of the large mismatch in redox potentials between the dimers and $\mathrm{CCl_4}$ or TMIO. For example, the $\mathrm{Cp_2Mo_2(CO)_6}^{+/0}$ couple is 0.9 V vs SCE in $\mathrm{CH_3CN}$[7] and the $\mathrm{CCl_4/CCl_3 + Cl^-}$ couple varies between –0.45 and –1.25 V vs NHE in various organic solvents.[41] Thus, $\mathrm{CCl_4}$ will not spontaneously oxidize $\mathrm{Cp_2Mo_2(CO)_6}$. Likewise, the fact that the reactions of $\mathrm{Cp_2Mo_2(CO)_6}$ with TMIO and $\mathrm{CCl_4}$ occur at the same rate eliminates from consideration any mechanism involving bimolecular reaction of the trap with the $\mathrm{Cp_2Mo_2(CO)_6}$ in a rate-determining step.

One final alternative mechanistic possibility is the rate-determining dissociation of an M–CO bond in an initial step. In fact, several papers describe the reactions of *photochemically* generated coordinatively unsaturated metal carbonyl dimers with halocarbons.[37] The products of such reactions may be the same as those formed by reaction of the metal radicals with the halocarbons, but

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(39) The product tentatively identified as $\mathrm{CpFe(CO)_2(TMIO)}$ has bands at 2012 and 1960 $\mathrm{cm^{-1}}$ (THF). For comparison, the $\mathrm{CpFe(CO)_2CH_3}$ complex has bands at 2010 and 1965 $\mathrm{cm^{-1}}$ in $\mathrm{CCl_4}$ (Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 113). The suggested pathway for formation of this product is

$$\mathrm{Cp_2Fe_2(CO)_4} \overset{h\nu}{\rightleftharpoons} 2\mathrm{CpFe(CO)_2} \overset{\mathrm{TMIO}}{\rightleftharpoons} 2\mathrm{CpFe(CO)_2(TMIO)}$$

No net reaction occurs, we suggest, because CO loss from the $\mathrm{CpFe(CO)_2(TMIO)}$ adduct to form a stable, chelated TMIO product is slow. CO loss from the sterically bulkier $\mathrm{CpMo(CO)_3(TMIO)}$ is apparently rapid, which leads to the net reaction shown in eq 4.

(40) Analogous chain mechanisms have been reported for the reaction of halogens with metal carbonyl dimers (see: Brodie, N. M. J.; Poë, A. J. *NATO ASI Ser., Ser. C* **1989**, *257*, 345. Poë, A. *Chem. Br.* **1983**, *19*, 997) and for the reactions of dithiols with metal carbonyl dimers (see: Abrahamson, H. B.; Freeman, M. L. *Organometallics* **1983**, *2*, 679).

(41) Eberson, L. *Acta Chem. Scand.* **1982**, *36B*, 533.

the metal halide products are not formed quantitatively because of the initial loss of CO. Although M–CO dissociation may be occurring to some extent, it is absolutely certain that M–M bond homolysis is also occurring. Numerous experiments establish this fact. For example, Cp/MeCp exchange experiments with $Cp_2Fe_2(CO)_4$ and $(MeCp)_2Fe_2(CO)_4$ in the dark established that Fe–Fe homolysis occurs with these dimers.[42] Also consistent with Fe–Fe homolysis is the observation that addition of dppe to a solution of $Cp_2Fe_2(CO)_4$ in the dark led to the formation of radical-derived disproportionation products.[42] Likewise, the slow disproportionation reactions of $Cp_2Mo_2(CO)_6$ with added ligands (in the dark) is taken as evidence for slow thermolysis of the Mo–Mo bond at room temperature.[43] Finally, the close agreement of the $K_{\mathrm{eq,cyclohexane}}$ values measured herein with the values reported in CH_3CN (obtained by an altogether different procedure[7]) is another indication that the major reaction involved in eq 3 is M–M homolysis.

Experimental Section

Materials and Supplies. $(MeCp)_2Mo_2(CO)_6$[44] and $Cp_2Fe_2(CO)_4$[45] were synthesized as previously described. $(MeCp)_2Mo_2(CO)_6$ was recrystallized three times from THF/hexane and dried in vacuo prior to use. $Cp_2Fe_2(CO)_4$ was recrystallized once from THF/hexane and dried in vacuo. No THF was detected (<5 mol %) in ^{1}H NMR spectra of the dried samples in $CDCl_3$ solution. $Mn_2(CO)_{10}$ was obtained from Strem Chemical Co. and purified by three recrystallizations from hexane. Cyclohexane was distilled twice from sodium and freeze–pump–thaw degassed prior to use. CCl_4 was freshly distilled from P_2O_5 and freeze–pump–thaw degassed prior to use. TMIO was synthesized as previously supported[15] and purified by sublimation (35 °C; 10^{-4} Torr). Unless stated otherwise, all reaction solutions were scrupulously protected from light.

Reactions and Instrumentation. The dark reactions were carried out in cuvettes equipped with vacuumtight stopcocks and a bulb sidearm for freeze–pump–thaw degassing the solutions. Solutions (5 mL) of $(MeCp)_2Mo_2(CO)_6$ (8×10^{-4} M), $Cp_2Fe_2(CO)_4$ (2×10^{-3} M), or $Mn_2(CO)_{10}$ (1×10^{-3} M) in cyclohexane containing either CCl_4 (2 M) or TMIO (8×10^{-2} M) were prepared in a darkened glovebox (Vacuum Atmospheres Co.). The samples were removed from the glovebox, frozen, transferred to a darkroom, and then degassed by four freeze–jump–thaw cycles. A Beckman DU or a Perkin-Elmer Lambda 6 spectrophotometer was used to measure the absorbances of the solutions every 3–7 days (at 510 nm ($\epsilon = 1860\ M^{-1}\ cm^{-1}$) for $Cp_2Mo_2(CO)_6$, at 524 nm ($\epsilon = 770\ M^{-1}\ cm^{-1}$) for $Cp_2Fe_2(CO)_4$, or at 342 nm ($\epsilon = 21\,000\ M^{-1}\ cm^{-1}$) for $Mn_2(CO)_{10}$[46]). The reactions were allowed to proceed until a precipitate of the metal chloride product appeared (generally about 10% conversion). The cuvettes were kept at 23 (±1) °C.

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Supplementary Material Available: Text giving a description and tables giving the details of crystallographic collection, bond distances and angles, anisotropic thermal parameters, calculated parameters for hydrogen atoms, torsion angles, and least-squares planes (16 pages). Ordering information is given on any current masthead page.

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