76SF00034, for support of this research. We wish to thank Matthey Bishop, Inc., Malvern, Pa., for the loan of the iridium used in this study. We thank Wayne Tikkanen for assistance and advice in use of the Varian CFT-20.

Registry No. [Ir(bpy)$_2$H$_2$O(bpy)]Cl$_3$, 62793-15-1.

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Site of M–CO Bond Breaking and Fluxionality in (*o*-Phenanthroline)tetracarbonylmetal Systems[1,2]

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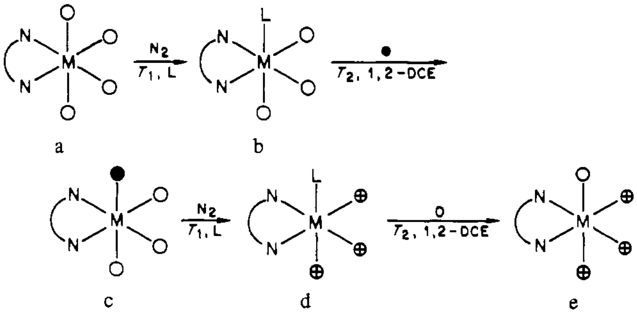
Since the controversy as to the site of Mn–C bond breaking in ligand-dissociation reactions of Mn(CO)$_5$Br (whether axial or equatorial[3])[4–9] and the discovery that five-coordinate intermediates derived through such a process may be fluxional on the time scale of the ligand-substitution process,[10] there has been a great interest in the elucidation of that site in substituted octahedral metal carbonyl systems and the determination of the extent of that fluxionality, if any. The systems Mn(CO)$_5$Br,[11,12] *cis*-Mn(CO)$_4$(PPh$_3$)(Br),[13] Re(CO)$_5$Br,[13] *cis*-Re(CO)$_4$(PPh$_3$)(Br),[13] (bpy)Cr(CO)$_4$,[14,15] (phen)Cr(CO)$_4$ (phen = *o*-phenanthroline),[14–16] and (diphos)Cr(CO)$_4$[17] [diphos = 1,2-bis(diphenylphosphino)ethane] have all been investigated in this context. Recently, also, it has been proposed that under kinetic control, product stereochemistry must reflect the site of initial M–CO bond breaking, regardless of possible fluxionality of the intermediate thus produced, in systems in which the incoming nucleophile creates little steric congestion during the substitution process.[18]

To ascertain whether the observed patterns of reactivity—stereospecific or highly stereoselective *axial* loss of CO and fluxional intermediates—hold for M = Mo and W as well as for Cr in the group 6B systems, the site of bond breaking and the extent of intermediate fluxionality have been determined for (phen)M(CO)$_4$ (M = Mo, W). Those results are the subject of this report.

Experimental Section

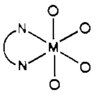
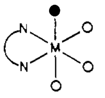
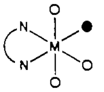
The method chosen for determination of the site of bond breaking—stereospecific introduction of a ^{13}CO label (90 mol %) and determination of its fate during the ligand-substitution process—is similar to that previously employed in the (phen)Cr(CO)$_4$ and (bpy)Cr(CO)$_4$ studies.[15] The substrates (phen)Mo(CO)$_4$ and (phen)W(CO)$_4$ and the *fac*-(CH$_3$CN)(phen)M(CO)$_3$ complexes which are employed in the sterospecific enrichment were prepared through standard procedures.[19,20] Scheme I sets forth the experimental conditions and the transformations employed in these studies.

Scheme I



M = Mo, T_1 = 50 °C, T_2 = 0 °C
M = W, T_1 = 82 °C, T_2 = 22 °C
N N = phen, ○ = ^{12}CO, ● = ^{13}CO, ⊕ = "scrambled" sites, L = CH$_3$CN

Table I. Site of Bond Breaking and Degree of Scrambling in (phen)M(CO)$_4$ Complexes (M = Mo, W)

isotopic species	fraction present		
		exptl	
	theory[a]	(phen)Mo(CO)$_4$ T_2 = 0 °C	(phen)W(CO)$_4$ T_2 = 22 °C
	0.5266	0.554	0.533
	0.1568	0.150	0.155
	0.3017	0.281	0.297

[a] For 100% scrambling and exclusive axial loss of CO. See ref 16.

The qualitative determination of the amount and position of the label in structures c and e (Scheme I) was made through use of a Perkin-Elmer Model 621 grating spectrophotometer and a JEOL FT-100 Fourier transform NMR spectrometer as described previously.[16] Results (experimentally determined percentages in the three predominant reaction products, nonlabled, and singly labeled either axial or equatorial), together with calculated results based on exclusive axial loss and subsequent statistically random label distribution, are presented in Table I.

Results and Discussion

In contrast to (phen)Cr(CO)$_4$,[21] which undergoes ligand exchange exclusively via a unimolecular, ligand-dissociation path, both (phen)Mo(CO)$_4$ and (phen)W(CO)$_4$ react by way of a two-term rate law (eq 1) indicative of two competitive

$$-d[(\text{phen})M(CO)_4]/dt = k_1[(\text{phen})M(CO)_4] + k_2[(\text{phen})M(CO)_4][L] \quad (1)$$

reaction paths.[22] There is very strong evidence that these two paths, dissociation (D) and a dissociative interchange (I$_d$), are very closely related;[23,24] that both reaction paths afford the

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(1) Octahedral Metal Carbonyls. 51.
(2) Taken from: Asali, K. J. Ph.D. Dissertation, North Texas State University, Denton, TX, 1979.
(3) Axial refers to an arrangment in which the carbonyl in question is trans to another carbonyl.
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axially substituted substitution product for a wide variety of L (eq 2) is consistent with this conclusion.

$$(phen)M(CO)_4 + L \rightarrow fac\text{-}(L)(phen)M(CO)_3 + CO \qquad (2)$$

Displacement of acetonitrile from *fac*-$(CH_3CN)(phen)M(CO)_3$ (M = Mo, 0°C; M = W, 22 °C) by ^{13}CO affords stereospecifically labeled *fac*-$(^{13}CO)(phen)M(CO)_3$ products. Reaction of these species with acetonitrile and then with ^{12}CO (Scheme I) affords mixtures of products (Table I) which, when assayed for ^{13}CO, demonstrate that reaction of $(phen)M(CO)_4$ with acetonitrile to afford *fac*-$(CH_3CN)(phen)M(CO)_3$ occurs exclusively via dissociation of an axial CO and that the carbonyls "scramble" statistically during the conversion. There is every reason to ascribe the scrambling process to the five-coordinate species produced via the D path, consistent with obervation for other systems, for which theoretical interpretations have been discussed in detail.[11-17]

The observation that only the *fac*-$(L)(phen)M(CO)_3$ products are obtained and that these products mirror the site of M–CO bond fission is consistent with the "quasi microscopic reversibility" argument (vide supra),[18] which is predicated on the nondiscriminating nature of the $[(phen)Mo(CO)_3]$ intermediates formed via M–CO bond fission.

The results for $(phen)M(CO)_4$ (M = Mo, W) are thus analogous to those for $(phen)Cr(CO)_4$, for which exclusive *axial* loss of CO and statistical scrambling of carbonyls in the resulting five-coordinate intermediate was also observed.[15,16] Thus the identity of the metal atom appears to exert little influence on these features of the ligand-exchange process in such group 6B metal carbonyl complexes.

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Registry No. $(phen)Mo(CO)_4$, 15740-78-0; $(phen)W(CO)_4$, 14729-20-5.

Contribution from the CNEN-CSN-Casaccia, Laboratorio
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Observations on the Structural Characterization of the Di-μ-hydroxo-octaaquodiiron(III) Dimer

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Morrison et al.[1] concluded from EXAFS (extended X-ray absorption fine structure) work on $Fe(ClO_4)_3$ in 0.023 M $HClO_4$ aqueous solution that the dominant species present is di-μ-hydroxo-octaaquodiiron(III)$[(H_2O)_4Fe(OH)_2Fe(H_2O)_4{}^{4+}]$; this conclusion is in disagreement both with the results of our X-ray work on solutions of similar composition[2] and with our general knowledge of such solutions.

The hydrolysis of iron(III) has been extensively studied. Different authors reached the conclusion that no appreciable amounts of soluble hydrolysis products are present when real equilibrium is established.[3-5] However, attainment of the final equilibrium is very slow in these solutions, requiring several years at 25 °C.[6] Consequently, many of the studies on iron(III) hydrolysis have been performed with supersaturated solutions, i.e., solutions unstable with respect to the precipitation of Fe^{3+} hydroxides. Nevertheless, this fact does not affect the conclusions drawn regarding the equilibria in solutions since the rate of precipitation is negligible as compared to that of complexation. This point has been well outlined by Ciavatta and Grimaldi,[5] who purposely investigated supersaturated solutions of Fe^{3+} in 3 M $NaClO_4$. It is then possible to demonstrate the presence of hydrolysis complexes in supersaturated solutions. Among the various hydrolysis complexes, the above described dimer can be dominant in suitable chemical conditions. Figure 1 shows the distribution of complexes calculated from the equilibrium constants potentiometrically determined by Hedstrom[7] (quoted by Morrison[1]) in 3 M $NaClO_4$ (the use of other reliable constants from Biedermann[8] or Ciavatta,[5] also obtained in 3 M $NaClO_4$, substantially gives the same results). Assuming now that the equilibrium constants are approximately valid for concentrated solutions, an hypothesis that has been proved to hold in many cases,[9] we can see from Figure 1 that neither Morrison's so-

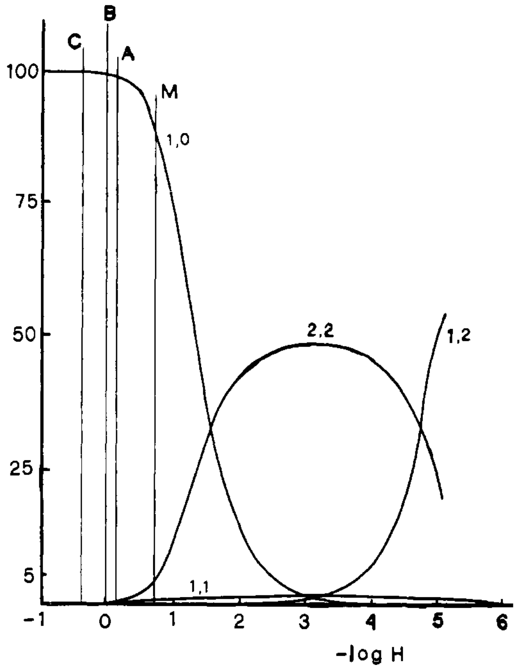

Figure 1. Distribution of Fe^{3+} hydrolysis complexes as a function of the free H^+ concentration with use of the equilibrium constants of ref 7. The various *p,q* index on the distribution lines refer to the different $Fe_p(OH)_q{}^{3p-q}$ complexes. Vertical lines show the expected complex distributions for the following solutions: M (by Morrison et al.[1]) = 1.819 M $Fe(ClO_4)_3$ –0.023 M $HClO_4$; A = 1.50 M $Fe(ClO_4)_3$ –0.72 M $HClO_4$; B = 2.24 M $Fe(ClO_4)_3$ –1.08 M $HClO_4$; C = 1.825 M $Fe(ClO_4)_3$ –2.56 M $HClO_4$. Since polynuclear complexes are formed, the complex distribution is iron concentration dependent, and the one reported has been evaluated for the chemical conditions of Morrison's solution. The distribution, however, is substantially the same for the other solutions which have been thus indicated by vertical lines on the same figure.

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