means of bonding electrons is expected to be proportional to the densities of the bonding electrons at the respective nuclei; thus, the coupling of the nuclei will be greater the larger the s character of the overlapping hybrid atomic orbitals that form the bond between them. Similar principles apply to tin–proton coupling in methyltin compounds in which the interaction takes place across two bonds. Assuming that the hybridization of carbon remains constant,[41] changes in $J$ can be attributed to variation in the amount of s character in the s–p hybrid orbitals of tin directed to the methyl group.

Taking tetramethyltin (with $J(^{119}\text{Sn–CH}_3) = 54$ cps) as the basis for comparison, the decreasing coupling constants observed in $(CH_3)_3SnCo(CO)_4$, $(CH_3)_2Sn[Co(CO)_4]_2$, and $CH_3Sn[Co(CO)_4]_3$ suggest that the tin orbitals bonding to carbon in these compounds possess *less* than the 25% s character expected in the four equivalent orbitals of tetramethyltin. This implies that the tin orbitals bonding to cobalt are enriched in s character, in accordance with Bent's rule.[36] While undoubtedly oversimplified, this appears to provide a useful interim viewpoint from which metal–metal bonds of this type may be regarded.

**Acknowledgment.**—We thank the National Research Council of Canada for support of this work.

[41] An assumption supported by the small variation of $J(^{13}CH_3)$ in related compounds. In $(CH_3)_3SnMn(CO)_5$, $J(^{13}CH_3) = 129.2$ cps,[13] differing only slightly from the value of 128 cps reported for tetramethyltin.[40]

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# Kinetic Studies of Group VI Metal Carbonyl Complexes. IV. Substitution Reactions of *o*-Phenanthroline Complexes of Chromium Hexacarbonyl[1]

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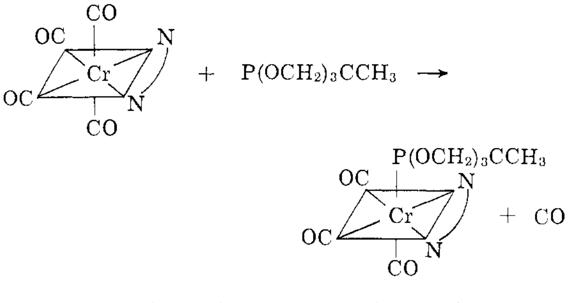
$Cr(CO)_4$(X-*o*-phen) reacts with $P(OCH_2)_3CCH_3$, L, at a rate which is independent of the concentration of L to form *cis*-$Cr(CO)_3$(L)(X-*o*-phen) as the only reaction product. The rate of reaction of $Cr(CO)_4$(X-*o*-phen) is however dependent on the basicity of the X-*o*-phen chelate in a manner which is predictable from a linear free energy expression. The reaction rate dependence on the p$K_a$ of X-*o*-phen is contrary to what would be predicted from current $\pi$-bonding theories since the reaction rate was found to increase with increasing p$K_a$ of the chelate. The C–O stretching frequencies of the $Cr(CO)_4$(X-*o*-phen) complexes decrease with increasing basicity of X-*o*-phen. This would be predicted from $\pi$-bonding theory but does not explain the observed rate trend. The increases in reaction rates with increasing chelate p$K_a$ are discussed in terms of a stabilized transition state and in terms of labilizing and nonlabilizing ligands.

## Introduction

The complexes, $M(CO)_4$(dipy), where M = Cr, Mo, or W, have been found to undergo substitution reactions with phosphites, L, to form $M(CO)_3$(L)(dipy).[2,3] These reactions were observed to proceed under unusually mild conditions and occurred even faster for the analogous 4,4′-dimethyl-2,2′-dipyridyl complexes. This result indicated that the more basic dipyridyl ligand significantly labilized the CO groups. Since a number of substituted *o*-phenanthrolines, X-*o*-phen, were available to us, the present study was undertaken in an attempt to examine the relationship between the rate of CO replacement in $M(CO)_4$(X-*o*-phen) and the basicity of the *o*-phenanthroline.

The unsubstituted *o*-phenanthroline complexes, $M(CO)_4$(*o*-phen),[4] and their products of reaction with phosphines, L, and phosphites, $M(CO)_3$(L)(*o*-phen),[4,5] have already been prepared. Analogous complexes of the substituted *o*-phenanthrolines have been prepared and their reaction products with phosphines and phosphites identified. For comparison, the $M(CO)_4$(1,2-diamino-2-methylpropane) complexes were synthesized and their reactions with phosphites examined.

All of the $M(CO)_4$(N–N) complexes, where N–N is an *o*-phenanthroline or 1,2-diamino-2-methylpropane, have been found to react with phosphines and phosphites according to eq 1. The kinetics of these reactions



(1)

have been investigated for the molybdenum and tungsten as well as the chromium complexes. The current paper reports the kinetic results for the $Cr(CO)_4$(X-*o*-phen) reaction. A subsequent paper will

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[1] Presented at the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30, 1965.

[2] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965).

[3] J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965).

[4] G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

[5] L. W. Houk and G. R. Dobson, *J. Chem. Soc., Sect. A*, 317 (1966).

treat the analogous molybdenum and tungsten reactions.

## Experimental Section

**Preparation and Purification of Materials.**—The substituted *o*-phenanthroline complexes, $M(CO)_4$(X-*o*-phen), were prepared by refluxing 1:1 molar ratios of the metal hexacarbonyl and X-*o*-phen in toluene (when M was Cr or Mo) or xylene (when M was W). These preparations, which are analogous to those reported for some dipyridyl complexes,[6] were found to be satisfactory only when electron-withdrawing groups (5-nitro, 5,6-dichloro, and 4,7-diphenyl) were not present in the *o*-phenanthroline.

*Anal.* Calcd for $Mo(CO)_4$(3-$CH_3$-*o*-phen): C, 50.7; H, 2.49. Found: C, 50.5; H, 2.30.

*Anal.* Calcd for $Mo(CO)_4$(3,4,7,8-tetramethyl-*o*-phen): C, 54.1; H, 3.60. Found: C, 54.1; H, 4.09.

The other $M(CO)_4$(X-*o*-phen) complexes were identified from their infrared spectra in the C–O stretching region (Table II).

Complexes of the *o*-phenanthrolines substituted by 5-nitro, 5,6-dichloro, and 4,7-diphenyl were prepared by the ultraviolet irradiation of an acetone solution containing a 1:1 molar ratio of the appropriate metal hexacarbonyl and substituted *o*-phenanthroline. The irradiations were carried out under a nitrogen atmosphere for a period of between 4 and 6 hr. The complexes were isolated from the acetone solutions by evaporating the solvent at reduced pressure and purified by recrystallizing the crude product from dichloromethane at −80°.

$Mo(CO)_4$(1,2-diamino-2-methylpropane) was prepared by refluxing 0.65 g of $Mo(CO)_6$ and 1 ml of 1,2-diamino-2-methylpropane in 10 ml of toluene for 30 min. The reaction solution was allowed to cool to room temperature and pentane was added. Upon cooling in an ice–water bath, a good yield of the desired light yellow compound was obtained. The complex was purified by recrystallizing three times from dichloromethane at −80°.

*Anal.* Calcd for $Mo(CO)_4$(1,2-diamino-2-methylpropane): C, 32.5; H, 4.06. Found: C, 32.7; H, 3.93.

The analogous 1,2-diamino-2-methylpropane complex of Cr was prepared in about 20% yield by ultraviolet irradiation for 8 hr of a solution composed of 20 ml of dry tetrahydrofuran, 0.60 g of $Cr(CO)_6$, and 1 ml of freshly distilled 1,2-diamino-2-methylpropane. The product precipitated upon treatment of the solution with water. The yield was found to be very sensitive to traces of impurities in the reagents and to traces of air. The complex was purified by recrystallization from toluene and identified by comparing its C–O stretching spectrum with that of the analogous Mo complex.

The solvent, 1,2-dichloroethane, used in the kinetic studies was purified by fractional distillation. The bicyclic phosphite ligand, $P(OCH_2)_3CCH_3$, was prepared as described in the literature.[7]

**Determination of Reaction Rates.**—The infrared spectra of the $Cr(CO)_4$(X-*o*-phen) complexes exhibit four C–O stretching absorptions. During the course of reaction with $P(OCH_2)_3CCH_3$ according to eq 1, these four absorptions disappear, and the three absorptions of the product, $Cr(CO)_3[P(OCH_2)_3CCH_3]$(X-*o*-phen), increase in intensity. Because there is no overlap with product bands, the highest frequency C–O stretching band at about 2010 $cm^{-1}$ was followed as it disappeared with time. Linear plots of $\ln (A - A_\infty)$, where $A$ is the absorbance at any time and $A_\infty$ is the absorbance at infinite time, *vs.* $t$ had slopes which were the pseudo-first-order rate constants, $k_{obsd}$, for the reaction. The rate constants are presented in Table I.

The kinetic studies were carried out in a two-compartment reaction vessel which was also fitted with a side-arm stopcock to allow the reaction mixture to be maintained under a nitrogen atmosphere. The top of the vessel was sealed with a serum cap. At the beginning of a run a solution of the complex was pipetted into one compartment of the vessel and the ligand solution was pipetted into the other. These solutions were allowed to equilibrate thermally in a constant-temperature bath for about 30 min before the reactant solutions were thoroughly mixed by tilting the vessel. Concentrations of the $Cr(CO)_4$(X-*o*-phen) complexes were approximately $5 \times 10^{-3}$ *M*. Absorbance readings at about 2010 $cm^{-1}$ were made on the solution by withdrawing samples with a syringe at appropriate time intervals.

Average deviations for the rate constants, $k_{obsd}$, were less than 3%. A general nonlinear least-squares computer program[8] was used to calculate values of the activation parameters and their standard deviations.

**Product Identification.**—The metal carbonyl product of reaction 1 exhibits three strong absorptions characteristic of the $M(CO)_3$(L)(X-*o*-phen) complexes.[5] The reaction proceeds quantitatively according to eq 1 with no side products. The reaction products usually were identified by their infrared spectra. Since the reaction solutions were so dilute, it would not have been possible to isolate the product but in one case it was isolated on a preparative scale. A 1,2-dichloroethane solution of 0.80 g of $Mo(CO)_4$(3,4,7,8-tetramethyl-*o*-phen) and 0.70 g of $P(OCH_2)_3CCH_3$ was refluxed for 1 hr under nitrogen. After cooling to room temperature and filtering, the product was precipitated with hexane. It was washed several times with hexane and dried under vacuum.

*Anal.* Calcd for $Mo(CO)_3[P(OCH_2)_3CCH_3]$[3,4,7,8-tetramethyl-*o*-phen]: C, 51.1; H, 4.43. Found: C, 51.0; H, 4.54.

The infrared spectrum (Table II) of this compound was identical with that observed at infinite time for the reaction between $Mo(CO)_4$(3,4,7,8-tetramethyl-*o*-phen) and $P(OCH_2)_3CCH_3$. All of the $M(CO)_4$(X-*o*-phen) complexes reacted with L to form products, $M(CO)_3$(L)(X-*o*-phen), having very similar spectra.

During the reaction of $Mo(CO)_4$(1,2-diamino-2-methylpropane) with $P(OCH_2)_3CCH_3$ three products are formed. Two of the products, *cis*-$Mo(CO)_4[P(OCH_2)_3CCH_3]_2$[9] and *cis*-$Mo(CO)_3[P(OCH_2)_3CCH_3]_3$, were observed and identified in the reaction of $Mo(CO)_4$(dipy) with $P(OCH_2)_3CCH_3$.[3] Their identity here was established on the basis of their C–O stretching spectra. The third product, *cis*-$Mo(CO)_3[P(OCH_2)_3CCH_3]$[1,2-diamino-2-methylpropane], was identified from a comparison of the reaction product spectrum with the spectrum of the compound prepared in the following manner: 0.63 g of $Mo(CO)_4$(1,2-diamino-2-methylpropane) and 0.35 g of $P(OCH_2)_3CCH_3$ were refluxed in 1,2-dichloroethane for 1.5 hr. Upon slowly cooling to room temperature, light brown crystals separated. After filtering, the crystals were washed with pentane and dried, then washed with water, 6 *N* HCl, water, and 20 ml of acetone. It was finally dried under vacuum.

*Anal.* Calcd for $Mo(CO)_3[P(OCH_2)_3CCH_3]$[1,2-diamino-2-methylpropane]: C, 34.6; H, 5.06. Found: C, 34.8; H, 5.44.

The analogous reaction of $Cr(CO)_4$(1,2-diamino-2-methylpropane) with $P(OCH_2)_3CCH_3$ yielded only $Cr(CO)_3[P(OCH_2)_3CCH_3]$[1,2-diamino-2-methylpropane] as identified from its infrared spectrum which was essentially identical with that of the previously characterized $Mo(CO)_3[P(OCH_2)_3CCH_3]$[1,2-diamino-2-methylpropane]. If $Cr(CO)_3[P(OCH_2)_3CCH_3]$[1,2-diamino-2-methylpropane] is allowed to remain in the presence of excess $P(OCH_2)_3CCH_3$, the chelate ligand is slowly displaced to give *cis*-$Cr(CO)_3[P(OCH_2)_3CCH_3]_3$.

**Infrared Spectra.**—All the kinetic measurements were made on a Beckman IR-8 infrared spectrophotometer. Infrared frequency measurements as in Table II were made on a Beckman

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(6) M. H. B. Stiddard, *J. Chem. Soc.*, 4712 (1962).

(7) J. G. Verkade, T. J. Hutteman, M. K. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).

(8) R. H. Moore, based on a report from Los Alamos Scientific Laboratory, LA2367, plus addenda. We thank Mr. J. P. Birk for modification of this program for use on the present computer facilities.

(9) In the earlier work on the $Mo(CO)_4$(dipy) system the geometry of $Mo(CO)_4[P(OCH_2)_3CCH_3]_2$ was incorrectly reported as having the *trans* configuration. A reevaluation of the infrared and nmr spectra of this complex indicates that the configuration is more probably *cis:* J. G. Verkade, R. E. McCarley, D. G. Hendricker, and A. Vandenbroucke, unpublished results.

IR-9 and are estimated to be accurate to ±1 $cm^{-1}$ but reproducible to ±0.5 $cm^{-1}$.

## Results

The C–O stretching frequencies of the $M(CO)_4$-(X-*o*-phen) complexes are very similar to those of the long-known $Mo(CO)_4$(*o*-phen) but shift to lower wavenumber as the $pK_a$[10] of the X-*o*-phen increases (Table II). Also given in Table II are the C–O stretching frequencies of two of the products of reaction, $Cr(CO)_3[P(OCH_2)_3CCH_3]$[X-*o*-phen]. The results of the kinetic studies of reaction 1 are presented in Table I and indicate that the rate of CO replacement is independent of the concentration of $P(OCH_2)_3CCH_3$. Thus for all of the $Cr(CO)_4$(X-*o*-phen) complexes and for $Cr(CO)_4$(1,2-diamino-2-methylpropane) their rates of reaction obey the following rate law

$$\text{rate} = k_1[Cr(CO)_4(X\text{-}o\text{-phen})] \qquad (2)$$

Since the reactions proceed according to a first-order rate law, the pseudo-first-order rate constant, $k_{obsd}$, and $k_1$ are the same.

## Discussion

A variety of $Cr(CO)_4$(X-*o*-phen) complexes and $Cr(CO)_4$(1,2-diamino-2-methylpropane) react with $P(OCH_2)_3CCH_3$ to form the CO-substituted product of the geometry represented in eq 1. This geometrical assignment has been made by others[4,15] on the basis of the number and intensity of the C–O stretching absorptions. That all of these reactions gave products with three strong C–O stretching absorptions is strong evidence that the designated isomer is the only one formed in any of these reactions.

Since all of these complexes react at rates which are independent of the $P(OCH_2)_3CCH_3$ concentration, the rate-determining step presumably involves the dissociation of a CO group from the reactant complex

$$Cr(CO)_4(\text{chelate}) \xrightarrow[\text{slow}]{-CO} Cr(CO)_3(\text{chelate}) \xrightarrow[\text{fast}]{+P(OCH_2)_3CCH_3} Cr(CO)_3[P(OCH_2)_3CCH_3](\text{chelate})$$

That the product of these reactions (eq 1) is the *cis* isomer suggests that the CO groups *trans* to the *o*-phenanthroline in $Cr(CO)_4$(X-*o*-phen) are more strongly bonded to Cr than are the CO groups which are *trans* to each other. Approximate force constant calculations[5] support this conclusion. These bond strength considerations would then imply that in the above mechanism one of the CO groups which are *trans* to each other would be most likely to dissociate from $Cr(CO)_4$-(X-*o*-phen) in the rate-determining step, although there is no kinetic evidence to confirm this supposition.

Table I

Rates of Reaction of $Cr(CO)_4$(X-*o*-phen) and $Cr(CO)_4$(1,2-diamino-2-methylpropane) with $P(OCH_2)_3CCH_3$ in 1,2-Dichloroethane at 47.9°

| X-*o*-phen no. | X | $[P(OCH_2)_3CCH_3]$, *M* | $10^4k_{obsd}$, $sec^{-1}$ |
|---|---|---|---|
| 1 | 5,6-Dichloro | 0.0662 | 1.34 |
| | 3.47[a] | 0.543 | 1.36 |
| | | 1.16 | 1.33 |
| 2 | 5-Nitro | 0.0284 | 1.08 |
| | 3.57 | 0.284 | 1.10 |
| | | 0.800 | 1.13 |
| 3 | 4,7-Diphenyl | 0.0284 | 2.62 |
| | 4.84 | 0.284 | 2.66 |
| | | 0.800 | 2.67 |
| 4 | Unsubstituted | 0.00783 | 0.593[b] |
| | 4.86 | 0.0365 | 0.590[b] |
| | | 0.0662 | 0.570[b] |
| | | 0.543 | 0.590[b] |
| | | 0.903 | 0.582[b] |
| | | 0.0662 | 1.63[c] |
| | | 0.543 | 1.63[c] |
| | | 0.903 | 1.62[c] |
| | | 0.0662 | 2.73 |
| | | 0.543 | 2.68 |
| | | 1.16 | 2.72 |
| | | 0.0662 | 4.56[d] |
| | | 0.543 | 4.63[d] |
| | | 0.903 | 4.60[d] |
| | | 0.0662 | 9.27[e] |
| | | 0.302 | 9.27[e] |
| | | 0.543 | 9.29[e] |
| 5 | 3-Methyl | 0.0662 | 2.80 |
| | 5.00 | 0.543 | 2.79 |
| | | 1.16 | 2.76 |
| 6 | 3,5,7-Trimethyl | 0.0662 | 4.84 |
| | 5.90 | 0.543 | 4.82 |
| | | 1.16 | 4.83 |
| 7 | 3,4,7,8-Tetramethyl | 0.0662 | 1.66[b] |
| | 6.31 | 0.543 | 1.66[b] |
| | | 0.903 | 1.65[b] |
| | | 0.0662 | 3.26[c] |
| | | 0.543 | 3.29[c] |
| | | 0.903 | 3.30[c] |
| | | 0.0662 | 6.14 |
| | | 0.543 | 6.11 |
| | | 0.903 | 6.10 |
| | | 0.0662 | 11.6[d] |
| | | 0.302 | 11.7[d] |
| | | 0.543 | 11.6[d] |
| | | 0.0662 | 21.5[e] |
| | | 0.302 | 21.5[e] |
| | | 0.543 | 21.6[e] |
| 8 | 3,4,6,7-Tetramethyl | 0.0662 | 7.17 |
| | 6.45 | 0.543 | 7.18 |
| | | 1.16 | 7.17 |
| $Cr(CO)_4$(1,2-diamino-2-methylpropane) | | 0.0126 | 48.0 |
| | | 0.0247 | 50.0 |
| | | 0.0884 | 45.0 |
| | | 0.139 | 44.0 |
| | | 1.09 | 43.0 |
| | | 1.41 | 47.0 |

[a] Numbers below names are $pK_a$ values of the respective *o*-phenanthrolines. See ref 10. [b] At 37.8°. [c] At 42.9°. [d] At 53.0°. [e] At 58.0°.

On the basis of π-bonding arguments one might anticipate that the rate of CO dissociation would depend on the basicity of the chelate. Presumably an increase in chelate basicity would introduce a greater negative charge on the Cr which in turn would enhance π-bonding to the CO groups thus making them more tightly bonded to the Cr. That this is probably true is suggested by the infrared frequencies in Table II which show that the higher the $pK_a$ of the chelate the lower the C–O stretching frequencies become. Assuming that the C–O stretching frequencies do indicate that the Cr–CO bond is stronger in molecules bearing the

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(10) A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956).

TABLE II

C–O STRETCHING FREQUENCIES ($cm^{-1}$) OF $M(CO)_4$(X-o-phen) AND $Cr(CO)_3[P(OCH_2)_3CCH_3]$(X-o-phen) COMPLEXES IN $CHCl_3$

| X-o-phen | | $Cr(CO)_4$(X-o-phen) | | | |
|---|---|---|---|---|---|
| no. | $pK_a$ | m | vs | s | s |
| 1 | 3.47 | 2010 | 1910.5 | 1889 | 1837 |
| 2 | 3.57 | 2010 | 1912 | 1891 | 1838 |
| 3 | 4.84 | 2007 | 1905 | 1881 | 1829 |
| 4 | 4.86 | 2008 | 1907 | 1883 | 1831 |
| 5 | 5.00 | 2007.5 | 1905 | 1881 | 1829 |
| 6 | 5.90 | 2006.5 | 1903 | 1878 | 1825 |
| 7 | 6.31 | 2006 | 1901 | 1874 | 1822 |
| 8 | 6.45 | 2006 | 1901 | 1874 | 1822 |
| | | $Mo(CO)_4$(X-o-phen) | | | |
| | | m | vs | s | s |
| 1 | 3.47 | 2016 | 1913 | 1885 | 1838 |
| 2 | 3.57 | 2016.5 | 1915.5 | 1888 | 1840 |
| 3 | 4.84 | 2013 | 1909 | 1879 | 1831 |
| 4 | 4.86 | 2014 | 1910 | 1881 | 1833 |
| 5 | 5.00 | 2014 | 1909 | 1878 | 1829 |
| 6 | 5.90 | 2013 | 1906 | 1875 | 1826 |
| 7 | 6.31 | 2012 | 1905 | 1873 | 1824 |
| 8 | 6.45 | 2012 | 1905 | 1873 | 1824 |
| | | $W(CO)_4$(X-o-phen) | | | |
| | | m | vs | s | s |
| 2 | 3.57 | 2013 | 1907 | 1886 | 1840 |
| 4 | 4.86 | 2010 | 1901 | 1877 | 1831 |
| 7 | 6.31 | 2008 | 1895 | 1871 | 1822 |
| | | $Cr(CO)_3[P(OCH_2)_3CCH_3]$(X-o-phen) | | | |
| | | s | s | s | |
| 3 | 4.84 | 1936 | 1845 | 1803 | |
| 7 | 6.31 | 1933 | 1839 | 1796 | |

more basic chelating groups, one would expect the rate of CO dissociation to be slower in these latter complexes.

Clearly from Table I, the opposite is true–the more basic the chelating group, the faster the CO group dissociates. A free energy plot (Figure 1) of log $k_1$ vs. the $pK_a$ of X-o-phen shows an excellent correlation between these parameters. Since 1,2-diamino-2-methylpropane has the expected two $pK_a$ values (10.00 and 6.79),[11] it is difficult to include it in the plot with the unusual o-phenanthrolines which are diprotonated only under rather drastic conditions.[10] If one, however, naïvely and arbitrarily assumes that the first $pK_a$ (10.00) of 1,2-diamino-2-methylpropane will determine the rate of CO dissociation from $Cr(CO)_4$(1,2-diamino-2-methylpropane), an extrapolation of Figure 1 to $pK_a$ = 10.00 yields a rate constant of $5.0 \times 10^{-3}$ $sec^{-1}$, in incredibly good agreement with the observed value of $4.6 \times 10^{-3}$ $sec^{-1}$. On the other hand, the values of $k_1$ for $Cr(CO)_4$(dipy) and $Cr(CO)_4$(4,4′-dimethyldipy) definitely do not fall on the line established by the o-phenanthrolines, as shown in Figure 1.

Not only do the rate constants indicate that a CO group dissociates more rapidly from the complex bearing the more basic o-phenanthroline, but the enthalpy of activation appears to be slightly lower as well. Thus for $Cr(CO)_4$(o-phen), $\Delta H^{\ddagger} = 26.4 \pm 0.8$ kcal/mole and $\Delta S^{\ddagger} = 7.0 \pm 2.6$ eu; for $Cr(CO)_4$(3,4,7,8-tetramethyl-o-phen), $\Delta H^{\ddagger} = 25.2 \pm 0.1$ kcal/mole and $\Delta S^{\ddagger} = 5.2 \pm 0.3$ eu. Since these results cannot be explained in terms of the Cr–CO bond strength as evaluated from C–O stretching frequencies, one must tentatively conclude that the more basic chelates stabilized the transition state to a greater extent than the weaker base.

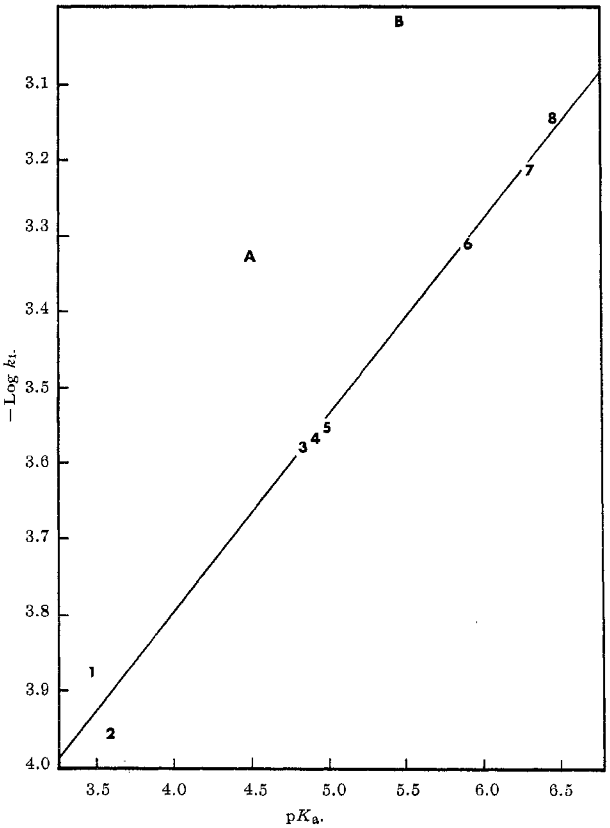

Figure 1.—Free energy plots of $-\log k_1$ vs. $pK_a$ for the reaction of $Cr(CO)_4$(X-o-phen) with $P(OCH_2)_3CCH_3$ in 1,2-dichloroethane at 47.9°. The numbers represent the X-o-phen as listed in Table I. A and B represent the reactions of $Cr(CO)_4$(dipy) and $Cr(CO)_4$(4,4′-dimethyldipy) with $P(OCH_2)_3CCH_3$.

**Labilizing and Nonlabilizing Ligands.**—The o-phenanthrolines and 1,2-diamino-2-methylpropane represent another group of ligands that have greatly labilized the CO groups attached to chromium. Since $Cr(CO)_6$[12] undergoes substitution by an SN1 reaction only at temperatures near 110°, it is far more inert than the molecules presented in this study. In a previous publication,[2] it was shown that some ligands labilize CO groups in Cr(0), Mo(0), and Mn(I) octahedral complexes while others do not. Recent results allow us to extend these observations further. On the basis of qualitative and quantitative substitution studies of $Cr(CO)_6$,[12] $Mo(CO)_6$,[12–14] $Mn(CO)_6^+$,[15] $Mo(CO)_5$(CN-R),[16] $Cr(CO)_5PR_3$, $RO_2SMn(CO)_5$,[17] and $Mn(CO)_4$(L)Br (L = phosphines, phosphites, and $As(C_6H_5)_3$),[18]

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[12] (a) H. Werner and R. Prinz, *Chem. Ber.*, **99**, 3582 (1966); (b) J. R. Graham and R. J. Angelici, to be published.

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it is clear that the following ligands do not significantly labilize the remaining CO groups when introduced into Cr(0), Mo(0), and Mn(I) octahedral complexes: CO, CN–R, $\mathrm{RO_2S}$–, $\mathrm{PR_3}$, $\mathrm{P(OR)_3}$, and $\mathrm{As(C_6H_5)_3}$. On the other hand, investigations of $[\mathrm{XMo(CO)_5}]^-$[19] (X = Cl, Br, or I), $\mathrm{(py)Mo(CO)_5}$,[3] $\mathrm{Cr(CO)_4(dipy)}$,[2] $\mathrm{Cr(CO)_4}$(*o*-phen), $\mathrm{Cr(CO)_4}$(1,2-diamino-2-methylpropane), $\mathrm{XMn(CO)_5}$ (X = Cl, Br, or I),[20] $\mathrm{HMn(CO)_5}$,[21] and $\mathrm{Mn(CO)_4(hfac)}$, where hfac = hexafluoroacetylacetonate,[22] indicate that the CO groups in these complexes have been substantially labilized as a result of the introduction of the following ligands into the complexes: $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{H^-}$, py, dipy, *o*-phen, 1,2-diamino-2-methylpropane, and hfac. The donor atoms of theses labilizing ligands are either first row elements or halogens. The nonlabilizing ligands, however, exhibit second- and third-row element donor atoms with the exception of CO and CN–R. In general, the labilizing ligands could be classified as class a or "hard" bases, and the nonlabilizing ligands, as class b or "soft" bases.[23] Although it is not clear why these relationships should necessarily be valid, they do provide a useful basis for the synthesis of metal carbonyl complexes containing CO groups of a desired lability.

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# Kinetic Studies of Group VI Metal Carbonyl Complexes. V. Substitution Reactions of *o*-Phenanthroline Complexes of Molybdenum and Tungsten Hexacarbonyls

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Complexes of the type $\mathrm{M(CO)_4}$(X-*o*-phen), where M = Mo and W, undergo substitution reactions with phosphine and phosphite ligands, L, to form *cis*-$\mathrm{M(CO)_3}$(L)(X-*o*-phen) as the reaction product. The rates of reaction follow the two-term rate law: rate = $k_1[\mathrm{M(CO)_4(X\text{-}\mathit{o}\text{-}phen)}] + k_2[\mathrm{M(CO)_4(X\text{-}\mathit{o}\text{-}phen)}][\mathrm{L}]$. The rate constant $k_1$ increases as the $\mathrm{p}K_\mathrm{a}$ of the substituted *o*-phenanthroline is increased in a manner which is predictable from a linear free energy relationship. The second-order rate constant, $k_2$, which also follows a linear free energy relationship surprisingly well, decreases as the $\mathrm{p}K_\mathrm{a}$ of the X-*o*-phen is increased. The magnitude of $k_2$ is determined by such factors as the ligand structure and basicity, the amount of steric hindrance caused by the substituted *o*-phenanthroline, and the basicity of the *o*-phenanthroline. All of these factors are considered in discussing possible reaction mechanisms for the portion of the rate law governed by $k_2$.

## Introduction

Only a relatively small number of octahedral transition metal complexes have been found to undergo reactions with nucleophiles at a rate which is dependent upon the concentration of the nucleophilic reagent. Most of the reactions studied and found to exhibit a ligand-dependent reaction rate involved positively charged metal ions,[1] although a few cases have been reported where the central metal atom was in a zero oxidation state.[2–4] The mechanism for these reactions can be and in some cases has been discussed in terms of a displacement (SN2) mechanism. Since reactions of this type for octahedral complexes are so rare and since alternate mechanisms which do not involve a nucleophilic attack can be proposed for most of the reactions studied, the validity of assigning a displacement mechanism is in some dispute.

A number of reasons have been given[1] for not expecting octahedral complexes to react by displacement mechanisms and these reasons involve factors ranging from steric repulsions resulting from an expanded coordination shell to electrostatic repulsions between the metals with filled or partially filled d orbitals and the attacking nucleophile. Despite this, $\mathrm{Mo(CO)_6}$ has been found[3] to react with phosphines and phosphites at a rate which is dependent on the concentration of the ligand. The most plausible mechanism which explains the second-order character of these reactions is a displacement mechanism at the Mo atom, although an attack at the carbonyl C cannot be ruled out. Since the octahedral group VI metal hexacarbonyls probably react by a displacement mechanism, considerable support is thereby given to the operation of this same type

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