and follows the order Cl > $CH_3O$ > $NH_2$ > $CH_3$ > COOMe. Although the total range is very small (0.18 ppm), it appears that the largest effects are now produced by substituent groups possessing *available lone pairs*. This might suggest that the change in behavior could be due to the strong demand of electrons from the chromium carbonyl moiety. The electrons are coming from the $\pi$ orbitals of the benzene ring, ultimately from substituent lone pairs, if available. This decrease in electron density in the $\pi$ orbital of the substituent will then be compensated by an inductive back donation from the $\sigma$ system of the ring to the substituent. It thus leads to positive charges mainly in the *meta* position but should also affect the *ortho* position. As a matter of fact, an effect of that kind appears and the signal for *ortho* protons is also shifted by complex formation to negative values for all substituents possessing an available lone pair (Table VI)

$$\begin{array}{lccccc} & NH_2 & > & CH_3O & > & Cl \\ \text{shift } (=\delta_{\text{complex}} - \delta_{\text{free ligand}}) & -0.30 & & -0.23 & & -0.10 \end{array}$$

This is compared to a positive shift for the other substituents $COOCH_3$ (+0.10) and $CH_3$ (+0.04).

Although this conclusion seems to be supported by experimental facts, it is surprising that such a redistribution of charge density does not affect the reactivity of the ester group as shown by the very good correlation which exists between the rate of saponification of the complexes and their corresponding parent compounds.[2b] This might however be due, as already noted, to the fact that the *meta* effects appear to be rather small.

Theoretical calculations which take into proper account the effect of the chromium tricarbonyl moiety might clarify these points. Such calculations are now in progress and will be reported in a forthcoming paper.

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# Octahedral Metal Carbonyls: Reactions and Bonding. VII. Kinetics of the Substitution Reactions of 2,5-Dithiahexane Complexes of Chromium Hexacarbonyl and Molybdenum Hexacarbonyl[1]

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The complexes $(DTH)Cr(CO)_4$ and $(DTH)Mo(CO)_4$ (DTH = 2,5-dithiahexane) react with phosphites with the replacement of the bidentate ligand to yield *cis*- and *trans*-$(\text{phosphite})_2M(CO)_4$ complexes according to a second-order rate law. Activation parameters and previous results suggest, however, that the reactions of the two complexes occur substantially through different mechanisms, the Cr reaction proceeding through a preequilibrium step involving the dissociation of one end of the bidentate ligand followed by attack on the resulting five-coordinate species, with the Mo reaction proceeding through the formation of a seven-coordinate intermediate. Reaction rates vary according to the steric nature of the various phosphite ligands employed; the results obtained are compared to those previously obtained for similar systems and are discussed in terms of $\sigma$- and $\pi$-bonding properties of the bidentate ligands.

## Introduction

Recently the emphasis in the study of bonding in octahedral metal carbonyls has shifted from almost exclusive consideration of infrared spectral data to kinetic and mechanistic investigation of their reactions.[3] Of particular interest in their implications as to the nature of steric and bonding effects have been the investigations of the kinetics of the reaction of (bidentate)-$M(CO)_4$ molecules [bidentate = 2,2′-dipyridyl (dipy),[4] *o*-phenanthroline (phen) and various substituted phenanthrolines,[5] and 1,2-diamino-2-methylpropane (dmp);[5] M = Cr, Mo, W] with various phosphites (L). It was found that derivatives of Cr react according to a first-order rate law

$$\text{rate} = k[(\text{bidentate})Cr(CO)_4] \qquad (1)$$

to give $(L)(\text{bidentate})Cr(CO)_4$ complexes; the reaction evidently involves dissociation of a carbonyl in the rate-determining step. Mo and W complexes, on the other hand, obey a mixed-order rate law

$$\text{rate} = k_1[(\text{bidentate})M(CO)_4] + k_2[(\text{bidentate})M(CO)_4][L] \qquad (2)$$

with the formation of several products for the dipy and dmp derivatives. The exclusive first-order rate de-

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[1] Part VI: G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967); presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

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[3] For a brief review of work in this field, see M. Graziani, F. Zingales, and U. Belluco, *Inorg. Chem.*, **6**, 1582 (1967).

[4] (a) R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **87**, 5586 (1965); (b) J. R. Graham and R. J. Angelici, *ibid.*, **87**, 5590 (1965).

[5] (a) R. J. Angelici and J. R. Graham, *Inorg. Chem.*, **6**, 988 (1967); (b) J. R. Graham and R. J. Angelici, *ibid.*, **6**, 992 (1967).

pendence for Cr was attributed to steric factors which prevent the formation of a seven-coordinate intermediate for this metal; the second-order term observed for Mo and W undoubtedly arises from the formation of such an intermediate for these metals, at least for phen. Moreover, an anomalous labilization of carbonyl groups, an effect inexplicable in terms of commonly advanced $\pi$-bonding arguments, is observed for these systems. Accordingly, it is of interest to ascertain the effect on reaction mechanism of bidentate ligands possessing differing donor–acceptor properties from dipy, phen, and dmp, all of which coordinate through nitrogen donor atoms. It has recently been shown that $(DTH)M(CO)_4$ (DTH = 2,5-dithiahexane, $CH_3SCH_2CH_2SCH_3$; M = Cr, Mo) reacts with monodentate Lewis bases with the exclusive replacement of the bidentate group to give, for phosphites, *cis*-$L_2M(CO)_4$ and/or *trans*-$L_2M(CO)_4$ products;[1] herein is reported an investigation of the kinetics of this reaction.

## Experimental Section

$(DTH)Cr(CO)_4$ and $(DTH)Mo(CO)_4$ were prepared through a standard procedure[6] and were twice recrystallized from chloroform. The ligands $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P[OCH(CH_3)_2]_3$, and $P(OC_6H_5)_3$ were obtained from commercial sources and were fractionally distilled at reduced pressure under nitrogen. Reagent grade 1,2-dichloroethane was used as obtained.

Kinetic runs were carried out in 100-ml foil-wrapped volumetric flasks fitted with adapters which permitted withdrawal of reaction solutions through a rubber septum, but which prevented contact of the solution with the septum. A weighed amount of phosphite was diluted to volume with 1,2-dichloroethane at the reaction temperature, and 60 mg of the substrate was then added. After the solution reequilibrated, small volumes of nitrogen were injected into the reaction vessel, and samples were withdrawn. The absorbances of these samples were immediately measured in a 1-cm quartz cell on a Beckman DU spectrophotometer. The decay of a band in the visible spectrum, characteristic of the substrate, was monitored (for Cr the wavelength was 4250 Å; for Mo, 4000 Å). The absorbance at $t = \infty$ was less than 1% of the absorbance at $t = 0$ for all runs. Plots of concentration *vs.* absorbance were found to obey Beer's law throughout the concentration ranges employed. In all cases at least a 20-fold excess of ligand was employed so that pseudo-first-order conditions obtained. Plots of $\ln [(A_0 - A_\infty)/(A_t - A_\infty)]$ *vs.* $t$ were linear to at least 90% of completion of the reactions. Blank runs containing no ligand showed no substrate decomposition during the longer reaction periods. The absorbances of blanks containing ligand and solvent only were subtracted from all measurements.

The reactions of $(DTH)M(CO)_4$ (M = Cr, Mo) with various monodentate Lewis bases have been shown to involve replacement of the DTH ligand.[1] For phosphites and phosphines the reactions proceed through the steps[1]

$$(DTH)M(CO)_4 + 2L \longrightarrow cis\text{-}L_2M(CO)_4 + DTH \qquad (3)$$

$$cis\text{-}L_2M(CO)_4 \rightleftarrows trans\text{-}L_2M(CO)_4 \qquad (4)$$

Carbonyl stretching data for the observed products, several of which have previously been reported in the literature, are given in Table I. Since band broadening is often observed in solvents such as 1,2-dichloroethane, frequencies are reported in hydrocarbon solvent. 1,2-Dichloroethane was removed *in vacuo* from reaction solutions after 8–9 half-lives, the residues were dissolved in *n*-hexane, and the infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer.

Least-squares analyses were performed on all data. The enthalpies and entropies of activation were also determined using a least-squares computer program. Limits of error were determined through standard procedures.[7]

Proton nmr spectra for $(DTH)Cr(CO)_4$ and DTH were obtained in $CDCl_3$ and in acetone-$d_6$ over a temperature range of +40 to −75° on a Varian Associates Model HA-100 spectrometer.

## Results

The reactions of $(DTH)Cr(CO)_4$ and $(DTH)Mo(CO)_4$ with phosphites obey a second-order rate law

$$\text{rate} = k_2[(DTH)M(CO)_4][L] \qquad (5)$$

according to the reaction scheme given in eq 3 and 4. In only one instance, for the reaction of trimethyl phosphite with $(DTH)Cr(CO)_4$, was a band perhaps attributable to the presence of a trisubstituted reaction product observed (Table I). With this possible exception, there was no evidence for carbonyl replacement or for the formation of products other than those resulting from the replacement of dithiahexane by phosphites. In no case was the presence of a $(DTH)(L)M(CO)_3$ species detected.

TABLE I

CARBONYL STRETCHING FREQUENCIES FOR OBSERVED REACTION PRODUCTS, $(DTH)Cr(CO)_4$ AND $(DTH)Mo(CO)_4$ PLUS PHOSPHITES

| Product | Carbonyl str freq,[a] $cm^{-1}$ |
|---|---|
| *trans*-$[P(OCH_3)_3]_2Cr(CO)_4$ | 1967 w, 1918 vs |
| *cis*-$[P(OCH_3)_3]_3Cr(CO)_3$ | 1881? |
| *trans*-$[P(OC_2H_5)_3]_2Cr(CO)_4$[b] | 1966 w, 1909 vs |
| *cis*-$[P(OC_2H_5)_3]_2Cr(CO)_4$ | 2032 w, 1939 m?, 1909 vs |
| *trans*-$\{P[OCH(CH_3)_2]_3\}_2Cr(CO)_4$ | 2030 w, 1961 w, 1903 vs |
| *trans*-$[P(OC_6H_5)_3]_2Cr(CO)_4$[c] | 2060 w?, 1973 w, 1932 vs |
| *cis*-$[P(OCH_3)_3]_2Mo(CO)_4$[d] | 2043 m, 1950 ms, 1924 vs |
| *trans*-$[P(OCH_3)_3]_2Mo(CO)_4$ | 1957 sh |
| *cis*-$[P(OC_2H_5)_3]_2Mo(CO)_4$ | 2041 m, 1933 m, 1921 vs |
| *trans*-$[P(OC_2H_5)_3]_2Mo(CO)_4$ | 1957? |
| *cis*-$\{P[OCH(CH_3)_2]_3\}_2Mo(CO)_4$ | 2037 m, 1940 m, 1922 vs |
| *trans*-$\{P[OCH(CH_3)_2]_3\}_2Mo(CO)_4$ | 1950?, 1912 vs? |
| *cis*-$[P(OC_6H_5)_3]_2Mo(CO)_4$ | 2058 m, 1965 ms, 1945 vs |

[a] Hydrocarbon solvent, unless otherwise noted; relative band intensities: s, strong; m, medium; w, weak; v, very. [b] Previously reported by G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967). [c] Previously reported by T. D. Magee, C. N. Mathews, and T. S. Wang, *J. Am. Chem. Soc.*, **83**, 3200 (1961). Spectrum obtained in $CH_2Cl_2$. [d] Previously reported by R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

The relative amounts of *trans*- and *cis*-$L_2M(CO)_4$ products obtained were found to be a function of the reaction temperature, the metal, and the ligand employed. Formation of the *trans* isomer was favored by the use of a bulky ligand or $(DTH)Cr(CO)_4$ containing the smaller Cr atom and by higher reaction temperatures which facilitated isomerization. Thus, for example, for the reaction of $P(OCH_3)_3$ with $(DTH)Mo(CO)_4$ almost pure *cis*-$[P(OCH_3)_3]_2Mo(CO)_4$ was obtained whereas only *trans*-$\{P[OCH(CH_3)_2]_3\}_2Cr(CO)_4$ was obtained from the reaction of $(DTH)Cr(CO)_4$ and triisopropyl phosphite.

Pseudo-first-order rate constants ($k_{obsd}$) as obtained

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(6) R. B. King, *Organometal. Syn.*, **1**, 179 (1965).

(7) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 86–92.

TABLE II

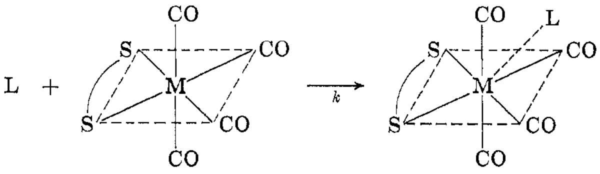
RATES OF REACTION OF (a) (DTH)Cr(CO)$_4$ AND (b) (DTH)Mo(CO)$_4$ WITH PHOSPHITE LIGANDS IN 1,2-DICHLOROETHANE

| Ligand concn, $M$ (a) | Ligand concn, $M$ (b) | $10^4k_{\text{obsd}}$, sec$^{-1}$ at various temperatures (a) | $10^4k_{\text{obsd}}$, sec$^{-1}$ at various temperatures (b) |
|---|---|---|---|
| L = P(OC$_2$H$_5$)$_3$ | | 65.0° | 64.9° |
| 0.300 | 0.200 | 14.3 | 42.6 |
| 0.249 | 0.149 | 12.0 | 33.1 |
| 0.199 | 0.099 | 9.63 | 22.6 |
| 0.149 | 0.075 | 7.25 | 16.3 |
| 0.100 | 0.049 | 4.64 | 10.7 |
| | | 55.5° | 55.5° |
| 0.608 | 0.400 | 8.86 | 43.6 |
| 0.600 | 0.300 | 8.71 | 31.9 |
| 0.515 | 0.300 | 7.59 | 31.7 |
| 0.450 | 0.240 | 6.48 | 26.3 |
| 0.375 | 0.200 | 5.41 | 21.3 |
| 0.300 | 0.101 | 4.87 | 11.0 |
| 0.250 | 0.051 | 3.79 | 5.01 |
| 0.150 | | 2.41 | |
| 0.100 | | 1.53 | |
| | | 46.0° | 45.1° |
| 0.600 | 0.370 | 2.76 | 16.1 |
| 0.450 | 0.300 | 2.14 | 13.4 |
| 0.349 | 0.200 | 1.65 | 8.48 |
| 0.249 | 0.099 | 1.22 | 4.14 |
| 0.149 | 0.050 | 0.730 | 1.88 |
| L = P(OCH$_3$)$_3$ | | 55.5° | 55.5° |
| 0.499 | 0.415 | 9.13 | 42.6 |
| 0.402 | 0.298 | 7.71 | 31.4 |
| 0.302 | 0.167 | 5.75 | 17.4 |
| 0.200 | 0.099 | 4.02 | 10.8 |
| 0.149 | 0.051 | 2.95 | 4.26 |
| 0.101 | | 2.18 | |
| L = P(OC$_6$H$_5$)$_3$ | | 64.7° | 64.5° |
| 0.800 | 0.200 | 15.7 | 17.3 |
| 0.600 | 0.150 | 11.0 | 12.5 |
| 0.400 | 0.100 | 7.94 | 8.67 |
| 0.199 | 0.050 | 3.79 | 4.29 |
| 0.100 | | 1.99 | |
| | | 55.5° | 55.5° |
| 0.699 | 0.399 | 5.02 | 17.5 |
| 0.500 | 0.288 | 3.10 | 13.0 |
| 0.350 | 0.193 | 2.53 | 8.78 |
| 0.250 | 0.097 | 1.93 | 4.26 |
| 0.149 | | 1.15 | |
| | | 45.7° | 43.6° |
| 1.002 | 0.500 | 1.99 | 7.75 |
| 0.800 | 0.400 | 1.65 | 6.21 |
| 0.600 | 0.300 | 1.26 | 4.91 |
| 0.400 | 0.199 | 0.842 | 3.33 |
| 0.200 | | 0.344 | |
| L = P[OCH(CH$_3$)$_2$]$_3$ | | 63.9° | 64.5° |
| 0.600 | 0.300 | 15.1 | 34.4 |
| 0.500 | 0.200 | 13.1 | 23.8 |
| 0.401 | 0.150 | 10.7 | 18.0 |
| 0.300 | 0.104 | 8.13 | 12.2 |
| 0.200 | 0.050 | 5.64 | 5.56 |
| | | 55.5° | 55.5° |
| 0.599 | 0.400 | 6.48 | 23.2 |
| 0.400 | 0.300 | 4.14 | 18.6 |
| 0.192 | 0.200 | 2.11 | 11.1 |
| 0.150 | 0.150 | 1.72 | 8.32 |
| | 0.050 | | 2.60 |
| | | 44.3° | 44.3° |
| 0.800 | 0.400 | 1.99 | 9.40 |
| 0.700 | 0.350 | 1.76 | 8.17 |
| 0.598 | 0.300 | 1.49 | 6.98 |
| 0.400 | 0.199 | 0.993 | 4.56 |
| 0.200 | | 0.495 | |

at various ligand concentrations are given in Table II. Plots of $k_{\text{obsd}}$ *vs.* ligand concentration yielded straight lines, the deviations of the intercepts from zero of which were calculated to be $\pm 0.2 \times 10^{-4}$ sec$^{-1}$; the second-order rate constants (Table III) were calculated from the slopes. Figure 1 shows data obtained for the reaction of (DTH)Cr(CO)$_4$ with various phosphites and at different temperatures. The lines drawn are those obtained from the least-squares fit, and the points are experimental. Activation parameters were evaluated for three of the four ligands employed and are given in Table IV. The proton nmr spectrum of (DTH)Cr(CO)$_4$ in acetone-$d_6$ at 25° showed two resonances at 238 and 286 cps (TMS standard) due to the methyl and ethylene protons, respectively. At −75° the methyl protons also exhibit a sharp resonance, at 235 cps, while the ethylene protons exhibit a complex pattern centered at 306 cps.

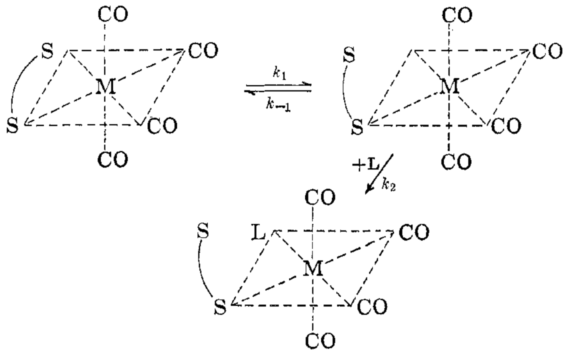
## Discussion

**Mechanism.**—Two possible mechanisms consistent with a second-order rate expression have been discussed by Angelici and Graham.[4b] The first involves nucleophilic attack on the substrate with the formation of a seven-coordinate activated complex or intermediate



(6)

In the second, a preequilibrium in which one end of the bidentate ligand reversibly dissociates is followed by nucleophilic attack on the resulting five-coordinate activated complex or intermediate



(7)

TABLE III

a. Rate Constants for the Reaction of $(DTH)Cr(CO)_4$ with Phosphite Ligands in 1,2-Dichloroethane

| Ligand | Temp, °C | $10^4 K_2$, l./mole sec |
|---|---|---|
| $P(OC_2H_5)_3$ | 65.0 | 48.3 |
| | 55.5 | 14.1 |
| | 46.0 | 4.45 |
| $P(OC_6H_5)_3$ | 64.7 | 19.3 |
| | 55.5 | 6.66 |
| | 45.7 | 2.02 |
| $P[OCH(CH_3)_2]_3$ | 63.9 | 23.9 |
| | 55.5 | 10.4 |
| | 44.3 | 2.52 |
| $P(OCH_3)_3$ | 55.5 | 17.8 |

b. Rate Constants for the Reaction of $(DTH)Mo(CO)_4$ with Phosphite Ligands in 1,2-Dichloroethane

| Ligand | Temp, °C | $10^3 K_2$, l./mole sec |
|---|---|---|
| $P(OC_2H_5)_3$ | 64.9 | 21.3 |
| | 55.5 | 10.9 |
| | 45.1 | 4.45 |
| $P(OC_6H_5)_3$ | 64.5 | 8.50 |
| | 55.5 | 4.34 |
| | 43.6 | 1.45 |
| $P[OCH(CH_3)_2]_3$ | 64.5 | 11.5 |
| | 55.5 | 6.03 |
| | 44.3 | 2.40 |
| $P(OCH_3)_3$ | 55.5 | 10.4 |

TABLE IV

a. Enthalpies and Entropies of Activation for the Reaction of $(DTH)Cr(CO)_4$ with Phosphite Ligands in 1,2-Dichloroethane

| Phosphite | $\Delta H^{\ddagger}$, kcal/mole | $\Delta S^{\ddagger}$, eu |
|---|---|---|
| $P(OC_2H_5)_3$ | $26.2 \pm 0.2$ | $+8.1 \pm 0.3$ |
| $P(OC_6H_5)_3$ | $24.6 \pm 1.0$ | $+1.9 \pm 2.9$ |
| $P[OCH(CH_3)_2]_3$ | $23.8 \pm 0.5$ | $+0.2 \pm 1.5$ |

b. Enthalpies and Entropies of Activation for the Reaction of $(DTH)Mo(CO)_4$ with Phosphite Ligands in 1,2-Dichloroethane

| Phosphite | $\Delta H^{\ddagger}$, kcal/mole | $\Delta S^{\ddagger}$, eu |
|---|---|---|
| $P(OC_2H_5)_3$ | $16.2 \pm 0.2$ | $-18.8 \pm 0.2$ |
| $P(OC_6H_5)_3$ | $16.3 \pm 0.5$ | $-19.9 \pm 1.5$ |
| $P[OCH(CH_3)_2]_3$ | $15.9 \pm 0.3$ | $-20.5 \pm 0.9$ |

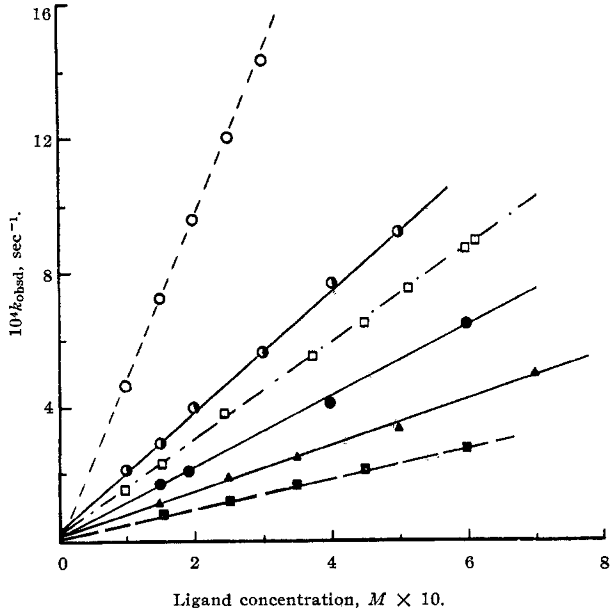


Figure 1.—Kinetics of the reaction of $(DTH)Cr(CO)_4$ with phosphites: ○, $P(OC_2H_5)_3$ at 65.0°; ◑, $P(OCH_3)_3$ at 55.5°; □, $P(OC_2H_5)_3$ at 55.5°; ●, $P[OCH(CH_3)_2]_3$ at 55.5°; ▲, $P(OC_6H_5)_3$ at 55.5°; ■, $P(OC_2H_5)_3$ at 46.0°.

For either mechanism these steps are followed by other, more rapid steps to yield the observed products.

Considering first the $(DTH)Cr(CO)_4$ case, previous investigations of the kinetics of chromium carbonyl systems provide little evidence of second-order rate dependence, often suggestive of an SN2 displacement mechanism. For the $(bidentate)Cr(CO)_4$ systems investigated by Angelici and Graham, of roughly similar steric properties to $(DTH)Cr(CO)_4$, no rate dependence upon ligand concentration was noted, and the only observed product was $(bidentate)(L)Cr(CO)_3$. The failure to observe a second-order term in the rate expression was attributed to crowding about the small Cr atom which would inhibit the formation of a seven-coordinate intermediate. Although a small second-order term has recently been noted for the reaction of $Cr(CO)_6$ with L for which a mixed-order rate expression is obtained ($k_2/k_1 = 0.7$ *vs.* 9.3 and 34.8 for $Mo(CO)_6$ and $W(CO)_6$, respectively), this molecule does not pose comparable steric demands to $(bidentate)Cr(CO)_4$ systems.[5b] The fact that the reactions of $(DTH)Cr(CO)_4$ reported here are second order even with the bulky ligand $P(OC_6H_5)_3$ and that the DTH ligand is replaced strongly suggests that the dissociation of the bidentate ligand plays a role in the mechanism.

There can, however, be no doubt that for the $(phen)Mo(CO)_4$ systems investigated by Angelici and Graham[5b] the second-order term obtained involves formation of a seven-coordinate activated complex or intermediate, since the bidentate is rigid. It is therefore difficult to envision dissociation of one end of phen in a preequilibrium step involving mechanism (7). Further, no replacement of phen is observed for any of its reactions; the situation for dipy and dmp is less clearcut.

Previously reported results for $(bidentate)M(CO)_4$ systems thus indicate that reactions of Cr complexes proceed *via* a dissociative mechanism, while those for Mo proceed, at least in part, *via* a seven-coordinate species. The markedly different entropies of activation observed for the reactions of $(DTH)Cr(CO)_4$ and $(DTH)Mo(CO)_4$ (Table IV) strongly suggest this also to be the case here. The values obtained are in substantial agreement with those found for the $(phen)M(CO)_4$ reactions, the different rate laws observed notwithstanding. It might be expected that for a mechanism involving a seven-coordinate transition state or intermediate for both Cr and Mo a more unfavorable entropy change would be observed for Cr, through the expectation that fewer degrees of freedom would obtain about the smaller Cr atom; yet this is not found to be the case. The large negative entropy of activation observed for the Mo reactions suggests a displacement mechanism, while the positive values observed for Cr are consistent with an activated complex or intermediate in which the coordination number is unchanged; such an activated complex or intermediate would contain DTH only one S of which is coordinated and which therefore might reasonably be expected to be less ordered than (DTH)Cr(CO)$_4$. Thus the evidence strongly indicates that mechanism (6) is dominant for the Cr system, while mechanism (7) is important for Mo.

The relative rate constants of (DTH)M(CO)$_4$ complexes with the various phosphites employed (Table III) vary according to the steric, rather than the basic, nature of the phosphites. The stringency of the steric requirements for Cr may be underscored by comparison of the relative rate constants for trimethyl and triethyl phosphite with (DTH)Cr(CO)$_4$ and (DTH)Mo(CO)$_4$. For Mo, the rate constants for the two ligands are essentially equal, the greater basicity of triethyl phosphite evidently being balanced by its greater size. For Cr, however, the steric factor is dominant, with the rate of reaction for trimethyl phosphite noticeably larger.

The proton nmr spectra for (DTH)Cr(CO)$_4$ in acetone-$d_6$ demonstrate the equivalence of methyl protons through a temperature range of +40 to −75° and thus provide no evidence for the nonequivalence of the two S atoms as is implicit in mechanism (7). However the derived rate expression for (7), obtained through a steady-state approximation, is

$$\text{rate} = \frac{k_1k_2[(\text{DTH})\text{M}(\text{CO})_4][\text{L}]}{k_{-1} + k_2[\text{L}]} \qquad (8)$$

Which reduces to a second-order expression for $k_{-1} \gg k_2$. Thus the concentration of the species in which one end of DTH is dissociated would be small and nmr evidence for its presence is not likely to be observed. A complex pattern for ethylene protons is observed at −75°; this pattern coalesces into a single sharp resonance at room temperature. The equivalence of the ethylene protons at room temperature may be attributed to a time-averaging of ethylenic vibrations. The nmr spectra obtained are consistent with either mechanism.

**Bonding Implications.**—Angelici and Graham[4,5] have noted a correlation between the "hardness"[8] of substituent groups and the labilization of carbonyls in octahedral metal carbonyl complexes, an unexpected trend if metal–carbon bond strengths are to be inferred from carbonyl stretching frequencies or force constants. Although reactions involving carbonyl replacement proceed at least in part through a dissociative mechanism, complexes containing labilizing "hard" base ligands generally have lower carbonyl stretching frequencies and, by inference, stronger metal–carbon bonds relative to complexes of nonlabilizing "soft" base ligands. Thus it was necessary to attribute labilization of carbonyls by "hard" bases to their stabilization of the transition state. More recently, however, metal–carbon stretching data for (bidentate)-Mo(CO)$_4$ complexes have suggested that, in fact, metal–carbon bonds are weaker for hard-base than for soft-base substituents.[1] Arguments were advanced which suggested a dominant influence of σ bonding in the kinetics of these systems.[1]

It has recently been noted for (Xphen)M(CO)$_4$ systems (M = Mo, W) in which X is one or more substituent groups through which the basicity of Xphen can be varied, that with decreased Xphen basicity the rate of carbonyl replacement *via* a dissociative mechanism decreases, while the rate of replacement *via* a displacement mechanism increases.[5b] Through consideration of ligand basicity primarily in terms of its effect on the Lewis acidity of the metal,[1] a strongly basic ligand "neutralizes" a proportionately larger part of the metallic Lewis acidity than a less basic ligand, inhibiting carbonyl-to-metal σ bonding (increasing the lability of carbonyls) and also inhibiting nucleophilic attack on the metal by a prospective displacing ligand.

Data for (DTH)Mo(CO)$_4$ continue this trend. DTH is more weakly basic than were the Xphen ligands investigated, and thus a greater rate by a displacement mechanism and smaller rate by a dissociative mechanism would be predicted. If it is assumed that the second-order rate for (DTH)Mo(CO)$_4$ reflects the rate by the displacement mechanism, the expected trend is followed in that the second-order rate is greater than for (Xphen)Mo(CO)$_4$ molecules and no first-order dissociative term is observed. The lack of a first-order term and failure to observe replacement of CO for (DTH)Mo(CO)$_4$ is consistent with the higher M–C stretching frequencies reported for (DTH)Mo(CO)$_4$ than for (phen)Mo(CO)$_4$.[1] The superior π-accepting ability of the "soft" DTH relative to Xphen, as may be inferred from the carbonyl stretching fequencies for their complexes, also enhances the relative Lewis acidity of the metal, facilitating nucleophilic attack, as the large second-order rate constant would indicate.

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[8] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963). For the purposes of this discussion, a "hard" base will be taken to be a relatively good σ donor and relatively poor π acceptor, a "soft" base a relatively poor σ donor and a relatively good π acceptor.