sponding relationships within each series are maintained.[11] It is noteworthy that the paired compounds in Table I have similar absorption spectra; a similarity such as that between the two sets of absorption spectra in Figure 1 may therefore be deceptive and cannot be taken as *prima facie* evidence for the comparability of Cotton effects. The special role of the substituent is under further investigation.[13]

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[11] Thus, in the spectroscopically accessible region, **1** has two CD bands, one at 254 mμ (−3.5) and another at 217 mμ (+5.0),[10] while **2** only has one, at 215 mμ (−1.3),[10] and three effects in the region 250–270 mμ of low intensity ($\Delta\epsilon < 0.3$). However, the CD of menthyl (*R*)-methylphenylphosphinate[2] is at 215 mμ (+1.9),[10] along with three low-intensity effects in the region 250–270 mμ ($\Delta\epsilon < 0.3$), confirming the conclusions of an earlier independent ORD study.[12]

[12] R. A. Lewis, O. Korpiun, and K. Mislow, *J. Am. Chem. Soc.*, **89**, 4786 (1967).

[13] The nearest Cotton effects of (*R*)-benzylmethylphenylphosphine oxide (Table I) and of (*R*)-methylphenylpropylphosphine oxide,[2] 216 mμ (+0.9),[10] have the same sign; this observation is in accord with similar conclusions based on the sign of the tails of the corresponding ORD curves in methanol.[14]

[14] W. D. Balzer, *Tetrahedron Letters*, 1189 (1968).

[15] Public Health Service Postdoctoral Fellow, 1967–1968.

[16] Public Health Service Predoctoral Fellow, 1966–1967.

Franklin D. Saeva,[15] Dennis R. Rayner,[16] Kurt Mislow
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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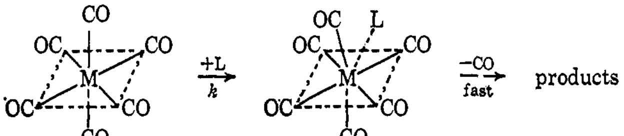
Octahedral Metal Carbonyls. IX.[1] Kinetics of the Reaction of N,N,N′,N′-Tetramethylethylenediaminechromium Tetracarbonyl with Triethyl Phosphite

Sir:

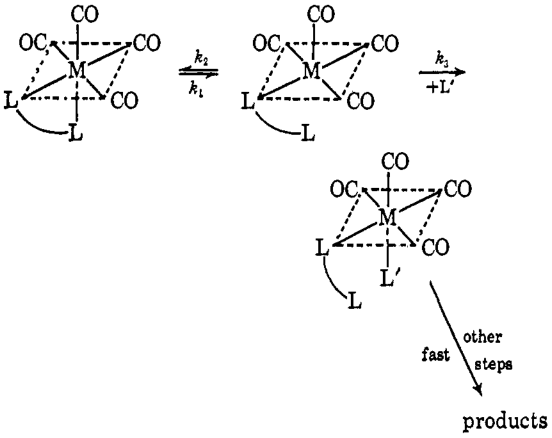
Ligand substitution reactions of octahedral metal carbonyls and their derivatives commonly proceed according to rate laws which are first order in the carbonyl, and zero or first order in the ligand (L). Often, both first- and second-order terms are observed in the rate expression. Dependence of rate on ligand concentration has, in general, been attributed to SN2 nucleophilic attack of the ligand on the substrate, with formation of a seven-coordinate activated complex or intermediate, *e.g.*



(I)

$$\text{rate} = k[\text{substrate}][\text{L}] \qquad (1)$$

and is more common for complexes of second and third transition series metals (Mo, W, Re) than for the first transition series metals Cr and Mn. This trend has been related to the smaller sizes of Cr and Mn, which inhibit formation of seven-coordinate species.[2] Further, with the exception of a small second-order term at high ligand concentration in the rate expression for replacement of CO by L from $Cr(CO)_6$,[3] all Cr and Mn systems which have been found to exhibit rate dependence on ligand concentration, $(DTH)Cr(CO)_4$,[4] $(DTH)Mn(CO)_3Br$[5] (DTH = 2,5-dithiahexane), and $[Mn(CO)_4X]_2$[6] (X = Cl, Br, I), possess a chelating group as a common structural feature. In such systems a second mechanism has been proposed,[4,6,7] also consistent with the kinetic data, which involves reversible dissociation of one end of the bidentate group, followed by attack by L on the resulting five-coordinate species.



(II)

Using a steady-state approximation

$$\text{rate} = \frac{k_1k_3[\text{substrate}][\text{L}]}{k_2 + k_3[\text{L}]} \qquad (2)$$

When $k_3 \ll k_2$, this reduces to a second-order rate expression.

We wish to report kinetic results for the reaction

$$(\text{tmen})Cr(CO)_4 + 2P(OC_2H_5)_3 \longrightarrow [P(OC_2H_5)_3]_2Cr(CO)_4 + \text{tmen}^8 \qquad (3)$$

in methylcyclohexane, which shows rate dependence on ligand concentration and permits an unequivocal choice between mechanisms I and II to be made. Data were obtained by monitoring the decay of an absorption characteristic of $(\text{tmen})Cr(CO)_4$ (425 mμ) under pseudo-first-order reaction conditions (>20-fold excess of triethyl phosphite).

It is to be expected that the bulky tmen should strongly inhibit nucleophilic attack on Cr. Further, linear plots of k_{obsd} *vs.* [L], to be expected for mechanism I, are not obtained (Figure 1). Rather, such plots show a complex dependence of rate upon concentration, the degree of dependence decreasing at higher ligand concentrations, as might be expected for mechanism II if $k_3 \sim k_2$. Rearrangement of eq 2 gives

$$1/k_{\text{obsd}} = 1/k_1 + k_2/k_1k_3[\text{L}] \qquad (4)$$

and thus plots of $1/k_{\text{obsd}}$ *vs.* 1/[L] should be linear, with intercept equal to $1/k_1$ and slope/intercept equal to k_2/k_3 should the data be consistent with the mechanism. Plots of $1/k_{\text{obsd}}$ *vs.* 1/[L] at four different temperatures are shown in Figure 2. From the data, activation parameters have been calculated to be (one standard deviation error limits): $\Delta H_1^{\ddagger} = 24.1 \pm 1.0$ kcal/mole; $\Delta S_1^{\ddagger} = 2.6 \pm 2.5$ eu; $\Delta H_2^{\ddagger} - \Delta H_3^{\ddagger} = -5.8 \pm 5.5$ kcal/mole;

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[1] Part VIII: E. P. Ross and G. R. Dobson, *J. Inorg. Nucl. Chem.*, in press.

[2] For a recent review of the kinetics and mechanism of substitution reactions of metal carbonyls, see R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

[3] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 2082 (1967).

[4] G. C. Faber and G. R. Dobson, *ibid.*, **7**, 584 (1968).

[5] G. C. Faber and G. R. Dobson, unpublished results.

[6] F. Zingales and U. Sartorelli, *Inorg. Chem.*, **6**, 1243 (1967).

[7] J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **87**, 5590 (1965).

[8] tmen = N,N,N′,N′-tetramethylethylenediamine, $(CH_3)_2NC_2H_4N(CH_3)_2$.

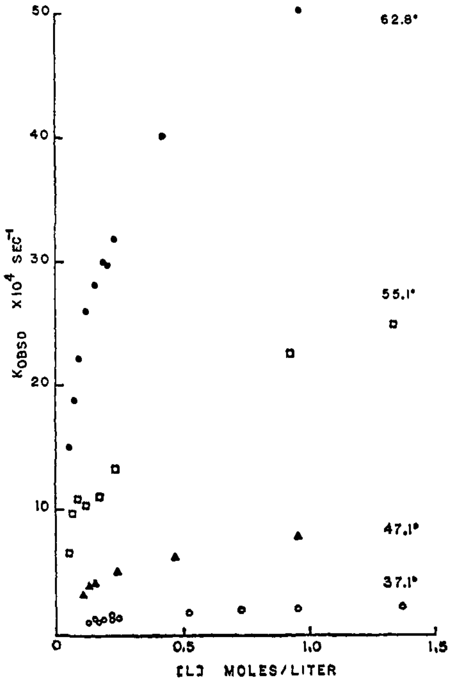

Figure 1. Plots of K_{obsd} *vs.* [L] at various temperatures for the reaction of (tmen)Cr(CO)$_4$ with triethyl phosphite in methylcyclohexane.

$\Delta S_2^{\ddagger} - \Delta S_3^{\ddagger} = -33.4 \pm 17.2$ eu. The positive entropy of activation for the dissociation of one end of the chelating tmen is consistent with the indicated mechanism. The results strongly suggest that mechanism II may be important for other reactions involving octahedral metal carbonyl derivatives containing chelating groups and which exhibit rate dependence on ligand concentration. This should be especially true for the smaller metal atoms of the first transition series for which an associative mechanism is less plausible.

These results may also be contrasted with those reported by Angelici and Graham for the reaction of (dmp)Cr(CO)$_4$ (dmp = 1,2-diamino-2-methylpropane) with phosphites, for which a ligand-independent rate law was found, and for which replacement of CO to give (dmp)(L)Cr(CO)$_3$ rather than replacement of the chelating group was observed.[9] Reaction of (tmen)Cr(CO)$_4$ with triethyl phosphite in refluxing *n*-heptane results in the formation of *trans*-[P(OC$_2$H$_5$)$_3$]$_2$Cr(CO)$_4$, as shown by infrared spectrum and chemical analysis; no carbonyl replacement was noted.

The difference in behavior of (dmp)Cr(CO)$_4$ and (tmen)Cr(CO)$_4$ in their reactions with phosphites may arise as a consequence of the more stringent steric requirements of tmen. For reactions of (tmen)Mo(CO)$_4$ with Lewis bases, bulky triphenylphosphine and triphenyl phosphite replace tmen without CO loss, while trimethyl phosphite replaces CO to give *cis*-(tmen)-[P(OCH$_3$)$_3$]$_3$Mo(CO)$_3$.[10] These observations suggest that the equilibrium

$$\text{(bidentate)Cr(CO)}_4 + \text{P(OC}_2\text{H}_5\text{)}_3 \rightleftharpoons \text{(bidentate)[P(OC}_2\text{H}_5\text{)}_3\text{]Cr(CO)}_3 + \text{CO} \quad (5)$$

may be shifted further to the left for tmen than for dmp. On the other hand, the correlation between a ligand's "hardness"[11] and its ability to labilize carbonyls[9] has been attributed to inhibition of carbonyl-to-metal σ-bond formation by strongly basic substituents.[10] The steric demands of tmen may diminish its basicity toward the chromium carbonyl moiety, thus strengthening carbonyl-to-metal σ bonds in (tmen)-Cr(CO)$_4$ relative to those in (dmp)Cr(CO)$_4$.

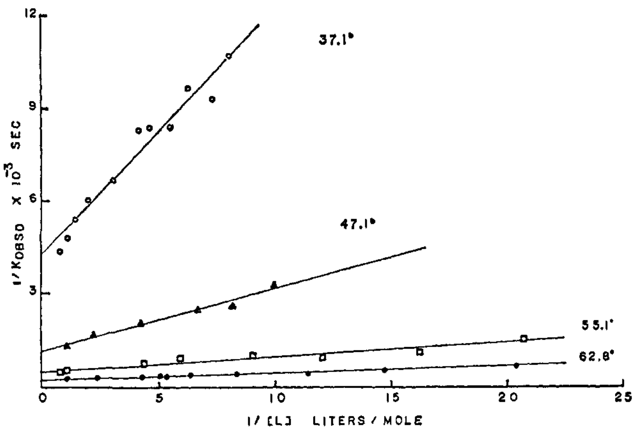

Figure 2. Plots of $1/k_{\text{obsd}}$ *vs.* 1/[L] at various temperatures for the reaction of (tmen)Cr(CO)$_4$ with triethyl phosphite in methylcyclohexane.

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[12] NDEA Predoctoral Fellow, 1967–1969.

Gary C. Faber,[12] Thomas D. Walsh, Gerard R. Dobson
Department of Chemistry, University of South Dakota
Vermillion, South Dakota 57069
Received May 17, 1968

A Revised Structure for Ceanothine-B

Sir:

Peptide alkaloids have been found in a number of plants of the family Rhamnaceae.[1-11] Among these

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(8) R. Tschesche, H. Last, and H. W. Fehlhaber, *ibid.*, **100**, 323 (1967).

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(10) H. Saltzman, Ph.D. Thesis, New York University, New York, N. Y., 1965.

(11) F. K. Klein and H. Rapoport, *J. Am. Chem. Soc.*, **90**, 2388 (1968).