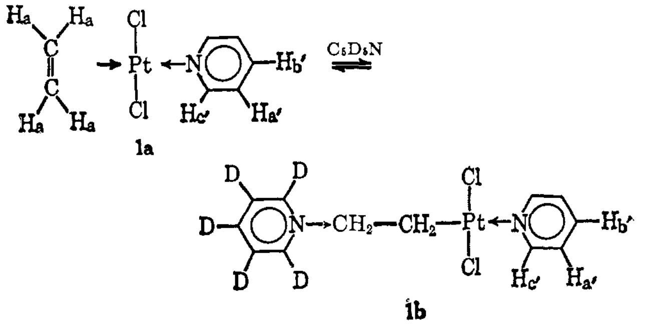
fully varying the temperature to change its chemical shift. The values given here, δ_{CH_2-Pt} = 2.44 ppm and J_{Pt-CH_2} = 83.4 cps, J_{H-H} = 7.1 cps, compare favorably with those for $(CH_3CH_2)_3PtI$, δ_{CH_2-Pt} = 2.23 ppm, J_{Pt-CH_2} = 86.0 cps, J_{H-H} = 7.5 cps;[4] and for those of $Pt(C_3H_5)_2$ at −20°, where δ_{CH_2-Pt} = 2.26 ppm and J_{Pt-CH_2} = 83 cps.[5] Both our triplets display a small deviation from symmetry in the spectra determined over the temperature range −35 to −50°; the spacing between adjacent peak maxima differs by about 0.5 cps. This asymmetry is considered to indicate an AA′XX′ system rather than an A_2X_2 system,[6] possibly because bulky groups on the carbons hinder rotation about the methylene–methylene bond at these low temperatures.

Table I. Chemical Shifts[a] and Coupling Constants[b] (−40°)



Nmr spectrum of **1a**	π complex[c]	Complex plus base[c]	Free base[c]
δ_{H_a}	4.87	4.81	
$\delta_{H_{a'}}$	7.525	7.89	7.36
$\delta_{H_{b'}}$	7.96	7.775	7.76
$\delta_{H_{c'}}$	8.855	8.69	8.69
$J_{Pt^{195}-H^1_a}$	60.6	60.5	
$J_{Pt^{195}-H^1_{c'}}$	35.6	None	
δ_{CH_2-Pt}		2.44	
$J_{Pt^{195}-H^1}$		83.4	
δ_{CH_2-N}		4.55	
$J_{H_1-H_2}$		7.1[d]	

[a] All chemical shifts are given in parts per million from tetramethylsilane (TMS) as an external reference; coupling constants are given in cycles per second. The internal reference was $CHCl_3$. [b] The coupling constants are given in cycles per second. [c] The solutions were prepared in a 10% w/w solute:solvent ratio. The D_5-pyridine was added in approximately a 4:1 ratio of base to complex. [d] The coupling constant between vicinal hydrogens is an average value, since there is some variation in magnitude with temperature.

The π complex was converted to the σ derivative in at least a 30% yield when the pyridine was added to a 10% w/w solution in deuteriochloroform in the temperature range −35 to −50°. The relative concentration of the σ complex was highly dependent on the amount of base used as well as the temperature. Thus, a 1:1 ratio of base to complex produces very little σ complex, although some of the undeuterated pyridine is replaced from the π complex, while a 4:1 ratio of base to complex yielded 30–40% new species. In our experiments the optimum temperature for σ-bond formation appears to be around −50°. At −20 to −30° the new species rapidly disappears, and at −10° the ethylene peak of the π complex broadens, presumably because of an exchange process involving the excess pyridine. Eventually all the ethylene is displaced by pyridine. Whether the normal room-temperature displacement of ethylene by pyridine proceeds by prior π → σ rearrangement remains a provocative but unanswered question.

The chemical shifts of the aromatic protons in the undeuterated pyridine molecule in the solution to which C_5D_5N was added indicate that the major portion of originally complexed C_5H_5N has been replaced by the deuterated species and is present, free, in solution. There are at least two additional pyridine species which, as yet, have not been categorized, owing to the somewhat complex absorption pattern observed in the aromatic region. Further work is in progress.

Synthesis. The ethylene–pyridine complex was prepared by the reaction of pyridine with an aqueous solution of Zeise's salt. The compound was then reprecipitated from chloroform–pentane.

Deuterated pyridine was added to a precooled, 10% w/w, deuteriochloroform solution of the ethylene complex.

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Direct Configurational Correlation of Sulfoxides and Phosphine Oxides by Intersystem Matching of Cotton Effects[1]

Sir:

In the course of studies on the circular dichroism (CD) of phosphine oxides prepared by the Grignard synthesis,[2] we have come upon a remarkable finding which we wish to communicate at this time.

In Figure 1 are displayed the CD curves of three isomeric anisyl *p*-tolyl sulfoxides and anisylmethylphenylphosphine oxides in isooctane. All six compounds were prepared by the Grignard displacement reaction, the sulfoxides from menthyl (*S*)-*p*-toluenesulfinate (**1**),[3] the phosphine oxides from menthyl (*S*)-methylphenylphosphinate (**2**);[2] the sulfoxides and phosphine oxides therefore[2,4] have the *S* configuration at sulfur and phosphorus, respectively.

Because of the richness of their features, the over-all correspondence between the two sets of spectra is apparent upon inspection and is a spectacular confirmation of the *independently* arrived at absolute configurational assignments.[2–4] This intersystem matching of Cotton effects,[5] which we believe to be unprecedented in kind, also provides striking evidence that the lone pair on sulfur in the anisyl *p*-tolyl sulfoxides is not significantly implicated in the generation of the optically

[1] This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67.

[2] O. Korpiun and K. Mislow, *J. Am. Chem. Soc.*, **89**, 4784 (1967).

[3] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965).

[4] P. Bickart, M. Axelrod, J. Jacobus, and K. Mislow, *ibid.*, **89**, 697 (1967).

[5] The "matching" refers to sign, shape, position, and relative intensity of the major Cotton effects; the rotational strengths of the sulfoxides are approximately twice those of the corresponding phosphine oxides.

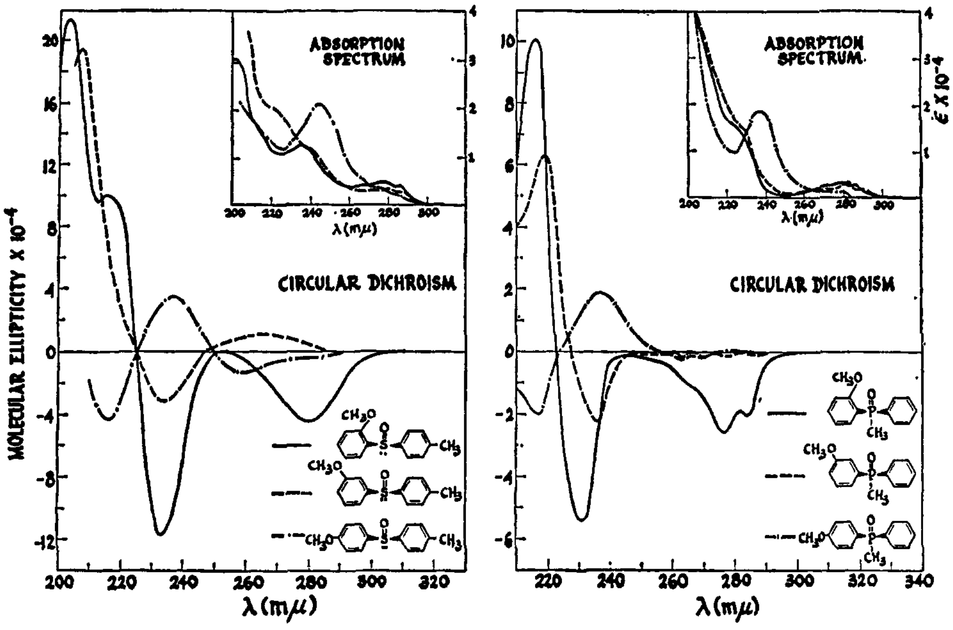

Figure 1.

active transitions, since the transition energy of the P–CH$_3$ σ-bond pair in the analogous phosphine oxides is expected to be quite high compared to that of n or π electrons in the molecule.

The similarity in the dichroism of the two systems suggests the possibility of a displacement rule embracing sulfoxides and phosphine oxides.[6] At a wavelength λ far from the center of the optically active transitions, the molecular rotation ([Φ]) is proportional to the sum over all transitions of $\lambda_i^2R_i/(\lambda^2 - \lambda_i^2)$, where λ_i and R_i are the position of the band center and the rotational strength of the *i*th transition, respectively.[7] From the data in Figure 1, the calculated *relative* ratios of the contribution to molecular rotations at 589 mμ, using *p*-anisyl *p*-tolyl sulfoxide as −1.0, of *o*-, *p*-, and *m*-anisyl *p*-tolyl sulfoxides are −5.5, −1.0, and +6.8, respectively, and of *o*-, *p*-, and *m*-anisylmethylphenylphosphine oxides are −2.1, +0.45, and +1.3, respectively; the observed [Φ] values for the corresponding compounds (in methanol) are −538, −82, and +129° (sulfoxides) and −53, −21, and +25° (phosphine oxides). A displacement rule clearly obtains and, considering the approximate nature of the calculation, is accounted for satisfactorily by the data in Figure 1, both as to sign trend and to relative magnitudes of rotation.

Table I. Circular Dichroism[a] of Sulfoxides (R)(C_7H_7)S(O), **3**, and Phosphine Oxides (R)(CH_3)(C_6H_5)P(O), **4**

R = $C_6H_5CH_2$		R = *p*-ClC_6H_4		R = β-$C_{10}H_7$		R = *p*-$C_6H_5C_6H_4$	
3[b]	**4**[b,c]	**3**[d,e]	**4**[d,f]	**3**[d]	**4**[d,g]	**3**[d]	**4**[d]
258 (+7.7) 223 (−11.7)	230 (+0.5) 218 (+1.9) <210 (<0)	245 (+2.2) 221 (+4.3) <210 (<0)	237 (+1.9) 217 (−2.6)	278 (+0.6) 260 (+1.6) 242 (−7.1) 227 (+5.3) 215 (+8.8) <205 (<0)	232 (+5.1) 220–205 (<0)	282 (−2.2) 245 (+5.2) 233 (+6.0) 218 (−7.0)	223 (−4.3)

[a] Reference 10. [b] *R* configuration. [c] Also three Cotton effects in the region 250–270 mμ with $\Delta\epsilon < 0.3$. [d] *S* configuration. [e] Also three Cotton effects in the region 270–295 mμ with $\Delta\epsilon < 0.6$. [f] Also five Cotton effects in the region 255–285 mμ with $\Delta\epsilon < 0.6$. [g] Also four Cotton effects in the region 250–290 mμ with $\Delta\epsilon < 1.5$.

A description of the chromophore responsible for the pattern in Figure 1 is simplified by the high rotational strength of the transitions[8] through whose dominance the importance of weak asymmetric perturbations is minimized; thus, the contribution of the *p*-tolyl group in the sulfoxides to the optical rotatory power is equivalent to that of the phenyl group in the phosphine oxides.[9] The presence of the methoxy groups appears to be an essential feature for successful intersystem matching. For example, the CD curves of some other aryl *p*-tolyl sulfoxides (**3**) and arylmethylphenylphosphine oxides (**4**) prepared from **1** and **2**, as described above, show no meaningful matching patterns (Table I),[10] albeit corre-

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(6) O. Červinka and O. Bělovský, *Collection Czech. Chem. Commun.*, **30**, 2859 (1965), and O. Červinka and O. Kříž, *ibid.*, **31**, 1910 (1966), have used parallel rotational behavior of phenyldialkylphosphine and phenyldialkylamine oxides at the D line and as manifested in tails of ORD curves to assign relative configurations in the two series.

(7) W. Kauzmann, "Quantum Chemistry," Academic Press Inc., New York, N. Y., 1957, p 710; A. Moscowitz in "Optical Rotatory Dispersion," C. Djerassi, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 166. We thank Professor Kauzmann for helpful discussions of this point.

(8) $\Delta\epsilon$ (= 3.03 ([θ] × 10^{-4})) values as high as 60 were recorded (Figure 1).

(9) For related examples, see ref 3.

(10) CD data refer to isooctane solutions and are given as λ_{max}, mμ, followed by the value for $[\theta]_{max} \times 10^{-4}$ in parentheses.

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]

[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.

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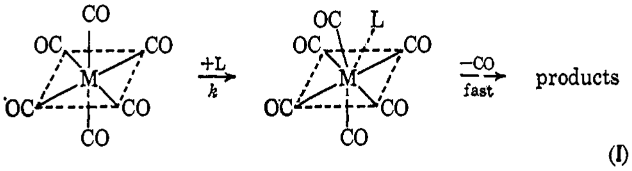
Octahedral Metal Carbonyls. IX.[1] Kinetics of the Reaction of N,N,N′,N′-Tetramethylethylenediaminechromium Tetracarbonyl with Triethyl Phosphite

Sir:

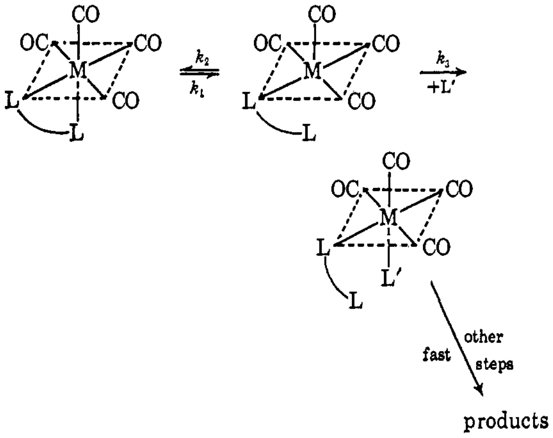
Ligand substitution reactions of octahedral metal carbonyls and their derivatives commonly proceed according to rate laws which are first order in the carbonyl, and zero or first order in the ligand (L). Often, both first- and second-order terms are observed in the rate expression. Dependence of rate 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, $(CH_3)_2NC_2H_4N(CH_3)_2$.