Table III. Electronic Spectral Data for *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]X$ and *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$

complexes		λ_{max}, nm $(\epsilon)^a$		
no.	L or R	in CH_2Cl_2	in $(CH_3)_2CO$	ref
	CN	356 (829)		5
	CO	363 (sh)^b		5
	COOMe	340 (sh)		5
1a	CNMe	352 (1606)	352 (1593)	this work
1b	CNMe	353 (1613)		this work
1c	CNMe	353 (1616)		this work
2a	$C(NMeH)_2$	351 (798)	350 (806)	this work
2b	$C(NMeH)NMe_2$	355 (757)		this work
3	C(OMe)=NMe	353 (sh)		this work
4a	C(OMe)NMeH	347 (974)	348 (1006)	this work
4b	C(OEt)NMeH	347 (927)		this work
4c	$C(OMe)NMe_2$	352 (903)		this work
5	$C(OMe)_2$	343 (1614)	343 (sh)	this work
	C(OMe)Me	332 (sh)		7, 19
	C(OEt)Me	332 (sh)		7, 19
	C(O-*n*-Pr)Me	335 (sh)		7, 19

[a] The spectra exhibited very intense bands in the ultraviolet region tailing toward the visible region. The total ϵ values are shown here. [b] Measured for Nujol mull.

can be explained only by assuming the presence of Ni–C-(carbene) π bonding (or resonance D), which becomes stronger as the carbene ligand becomes electron poorer.

The above conclusion agrees well with the results reported by a number of workers studying with different physical methods that diaminocarbene[20–22] and amino(alkoxy)-carbene[22,23] ligands are weak π acceptors, that the dialkoxycarbene ligand is a stronger π acceptor than diaminocarbene,[16a] that alkyl(alkoxy)carbene ligands are either weak π acceptors[24–26] or moderate to strong π acceptors,[27,28] and that methylene,[29] CHR,[29] and diphenylcarbene[30] are strong π acceptors.

Although the results in Table III indicate that the carbene ligands are apparently at a higher position in the spectrochemical series than CN^- and CO, it is difficult to compare from these data the total amount of Ni–C π-bond character. This is so not only because of the difference in the σ-orbital hybridization (sp^2 or sp) which effects the $d_{x^2-y^2}$ (σ^*) orbital but also because of the cylindrical property of the latter ligands, i.e., that the two nickel d_π orbitals can participate in the π bonding.

Registry No. 1a, 68550-26-5; **1b**, 68550-27-6; **1c**, 68568-34-3; **2a**, 68550-29-8; **2b**, 68550-31-2; **3**, 68550-32-3; **4a**, 68550-34-5; **4b**, 68550-36-7; **4c**, 68550-38-9; **5**, 68550-40-3; [Ni]-CN, 59991-83-2; [Ni]-Cl, 15526-04-2; [Ni]-COOMe, 59982-61-5.

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An Extensive Trans-Effect Series: The Reaction of Coordinated Trimethyl Phosphite

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The rate of reaction of Br^- with $(CH_3O)_3PCo(DH)_2X$ to form $(CH_3O)_2P(O)Co(DH)_2X$ (where DH = monoanion of dimethylglyoxime) varies by a factor of 10^5 as X is varied from NO_3 to C_2H_5. The log of the observed rate constant for this reaction correlates very well with the ^{13}C chemical shift of the phosphite carbon. Comparisons are made between the effects of the X group on ligand substitution reaction and on the reaction of the coordinated phosphite. A hypothesis is presented proposing that the steric bulk of X may influence the ability of X to act as an electron donor to the metal center. In contrast to some studies on ligand substitution reactions, our results do not correlate well with the Hammett substituent constants σ_p and σ_p^-.

Recently, there has been great interest in the study of how the variation of both neutral (L) and negative (X) ligands affects structural, spectroscopic, and rate parameters of both transition- and non-transition-metal complexes.[1–3] It now appears that the influence of either L or X ligands is frequently roughly transferable, i.e., is independent of the metal moiety.[1–3]

However, the ordering of ligands in terms of their effects has relied heavily on the overlapping of data from several series.[1-3] Such overlapping is necessary because few series are known in which X or L can be varied over a very wide range. It would be desirable to have at least one series in which structural, spectroscopic, and rate information is available for a wide variety of ligands.

We have carried out extensive NMR spectroscopic studies on cobaloxime complexes (species containing the $Co(DH)_2$ unit, where DH = monoanion of dimethylglyoxime).[3-8] Cobaloxime complexes can be prepared with a diversity of X ligands varying from the hard NO_3 to the soft CH_3 ligand.[4] Spectroscopic trends we have observed for cobaloximes closely parallel trends for other metal systems.[2,3] Thus, a deeper knowledge of the trends and bonding in cobaloxime complexes could provide insight into bonding in other metal systems as well.

Most spectroscopic and structural studies of ligand effects have been obtained on Pt(II) complexes.[1,2] However, ligand substitution reactions for Pt(II) compounds are associative. Cobaloximes undergo ligand substitution reaction (1) via the

$$LCo(DH)_2X + L' \rightleftharpoons L'Co(DH)_2X + L \qquad (1)$$

simpler dissociative mechanism.[9-12] It is very likely that a highly reactive five-coordinate intermediate is formed during the reaction.[11,12] The steric effect of X may play a role in this reaction, and we have had only moderate success in comparing NMR spectroscopic trends with rate parameters for reaction 1.[12] Additionally, the leaving group changes from L to X as X becomes hard.

We now wish to report a rate study on the first extensive series of complexes in which no changes are made except in the X ligand, and, therefore, no assumptions are needed to establish a complete kinetic trans-effect series. Studies from this laboratory have previously demonstrated that the ester carbon of trialkyl phosphites coordinated to a cobaloxime center shows increased reactivity toward nucleophiles as compared to the free phospite.[11,13] Reaction 2, where Nuc is

$$(RO)_3PCo(DH)_2X + Nuc^- \rightarrow (RO)_2(O)(P)Co(DH)_2X^- + CH_3Nuc \qquad (2)$$

a nucleophile, was found to involve essentially a bimolecular nucleophilic attack of the Nuc at the ester carbon of the coordinated phosphite when X = Cl. In the present study we have determined the relationship between X and the rate of reaction 2 when $Nuc^- = Br^-$. In contrast to most previous kinetic studies of the trans effect, which involve ligand substitution reactions, reaction 2 takes place at a center three atoms removed from the cobalt. The steric effects associated with changing X are minimized. We have found a *direct* linear relationship between the logarithm of the pseudo-first-order rate constant of reaction 2 (Br^- is in large excess) and the ^{13}C chemical shift of the ester carbon of the coordinated $P(OCH_3)_3$.

Results

NMR Spectra. Assignments of ^{13}C chemical shifts of new trimethyl phosphite–cobaloxime complexes were easily and unambiguously made by comparison with those of known compounds.[4,5] For these $(CH_3O)_3P$ compounds, the dioxime ^1H NMR methyl resonances are found at $\delta \sim 2.0$–2.2 and are doublets (J = 1–4 Hz) since the protons are coupled to ^{31}P. Complete spectral data can be found in the supplementary material.

Reaction Stoichiometry. When $P(OCH_3)_3Co(DH)_2Cl$ is treated with $(CH_3(C_6H_5)_3)PBr$, CH_3Br is observed, and the phosphonate salt $[CH_3(C_6H_5)_3P][P(O)(OCH_3)_2Co(DH)_2Cl]$ is formed. The dioxime methyl resonance of this salt is also split into a doublet by ^{31}P and occurs approximately 0.1–0.2 ppm upfield with a smaller coupling constant than the corresponding resonance of the starting complex.

Table I. Rates of Reaction 2[a] and Ester Carbon Chemical Shift

X	k_{obsd}, s^{-1} [b]	correln coeff[b]	$\delta(O^{13}CH_3)$[c]
NO_3	$(2.16 \pm 0.06) \times 10^{-2}$	0.999	55.70
Cl	$(5.73 \pm 0.25) \times 10^{-3}$	0.997	55.19
Br	$(5.67 \pm 0.20) \times 10^{-3}$	0.998	55.07
I	$(3.98 \pm 0.31) \times 10^{-3}$	0.992	54.93
N_3	$(1.89 \pm 0.09) \times 10^{-3}$	0.996	54.64
NO_2	$(2.50 \pm 0.13) \times 10^{-3}$	0.996	54.57
CN	$(6.98 \pm 0.39) \times 10^{-4}$	0.994	54.45
SO_2PhCH_3	$(4.89 \pm 0.30) \times 10^{-4}$	0.996	54.13
$CHBr_2$	$(4.55 \pm 0.23) \times 10^{-5}$	0.996	53.62
$CHCl_2$	$(1.80 \pm 0.13) \times 10^{-5}$	0.991	53.41
CH_2CN	$(1.80 \pm 0.07) \times 10^{-5}$	0.998	53.40
$P(O)(OCH_3)_2$	$(1.81 \pm 0.13) \times 10^{-5}$	0.993	53.29
CH_2I	*d*	*d*	52.95
CH_2Br	$(4.16 \pm 0.21) \times 10^{-6}$	0.997	52.87
CH_2Cl	*d*	*d*	52.77
C_6H_5	$(1.77 \pm 0.09) \times 10^{-6}$	0.996	52.67
$(CH_2)_3CN$	*d*	*d*	52.51
$C_6H_5(CH_2)_2$	*d*	*d*	52.32
CH_3	$(4.75 \pm 0.66) \times 10^{-7}$	0.967	52.24
i-C_3H_7	$(5.63 \pm 0.61) \times 10^{-7}$	0.983	52.18
C_2H_5	$(2.20 \pm 0.11) \times 10^{-7}$	0.996	52.16

[a] At 31.5 ± 0.5 °C, CH_2Cl_2 (reagent grade), 0.6 M $[CH_3(C_6H_5)_3P]Br$, and [Co] = 0.05 M. [b] Average of three trials. [c] Ppm, measured from Me_4Si. [d] Rates not measured.

We have now found that the reaction of coordinated trimethyl phosphite occurs for such diverse trans ligands as NO_3 and CH_3. In all cases, a product was observed to form having oxime methyl resonances upfield from the starting complex. The formation of CH_3Br was confirmed for all reactions which had a half-life of less than 1 day. For some of the slower reactions ($t_{1/2}$ > 4 days) the initial phosphonate product was unstable.

The complex with X = i-C_3H_7 deserves special mention here. This compound was found to be unstable in solution relative to the time scale required to measure the rate of the nucleophilic reaction (on the order of a month). Furthermore, in the presence of $[CH_3(C_6H_5)_3P]Br$, an alternative reaction occurs in which CH_3OH and $HP(O)(OCH_3)_2$ form (as indicated by the ^1H NMR spectral changes). This reaction was not observed for any other complex, and it was not investigated in detail. The same products are known to form from uncoordinated trimethyl phosphite under acid conditions.[14] We found that we could satisfactorily observe reaction 2 in the presence of an excess of $P(OCH_3)_3$ and 2,6-lutidine, a noncoordinating base in this system. To demonstrate that these added reagents did not alter the reaction rate, we repeated our rate measurements on the X = CH_2Br complex and found the results in the presence of these other reagents to be comparable to those obtained in the absence of these added reagents.

Treatment of the Rate Data. The spectral change in the ^1H NMR spectrum of the dioxime methyl resonance was used to monitor the reactions as described previously.[13] Pseudo-first-order conditions were employed, and k_{obsd} was determined by linear least-squares analyses of semilog plots. As can be seen from the data in Table I, good first-order kinetic behavior was realized for 2–3 half-lives for nearly all of the complexes. Reproducibility was ca. 10% and often better, and the values reported in Table I are the averages for three determinations. In some cases, secondary products formed from the initial phosphonate products; inclusion of these products in the total amount of products formed resulted in good first-order kinetics.

Discussion

Two striking features emerge from the data. First, there is an enormous rate difference between the most reactive

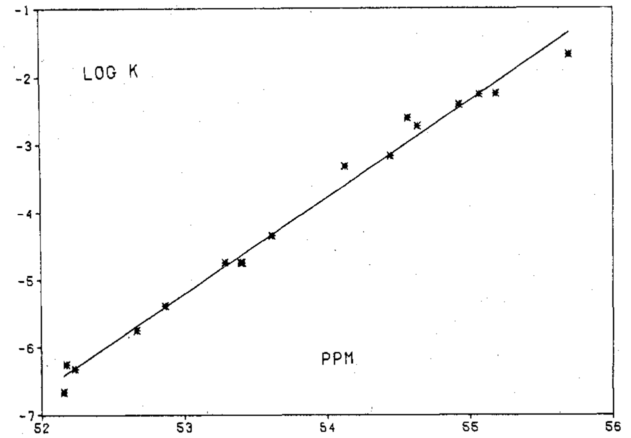

Figure 1. Computer-drawn plot of log k for reaction 2 vs. the ^{13}C chemical shift of the coordinated phosphate in $(CH_3O)_3PCo(DH)_2X$. Points from left to right are C_2H_5 (lower point), i-C_3H_7 (upper point), CH_3, C_6H_5, CH_2Br, $P(O)(OCH_3)_2$, CH_2CN and $CHCl_2$ (superimposed points), $CHBr_2$, $SO_2C_6H_4CH_3$, CN, NO_2, N_3, I, Br, Cl, and NO_3. The least-squares line is included.

Table II. Linear Correlations between the ^{13}C Chemical Shift of Coordinated $P(OCH_3)_3$ and Selected Parameters

	no. of points	correln coeff	Taft f statistic
$\log k_{Br}$[a]	17	0.995	0.038
$\delta\,[\gamma\text{-}^{13}C(4\text{-}t\text{-Bupy})]$[b]	15	0.974	0.001
α_{av}[c]	15	0.970	0.023
σ_p[d]	14	0.693	0.616
σ_p(alkyl, aryl)[d]	8	0.943	0.333
σ_p^-[e]	8	0.299	0.667
σ^*[f]	11	0.959	0.208
P_{trans}[g]	9	−0.959	0.216
$\bar{p}$[g]	9	−0.969	0.202
$\log k_{CNpy}$[h]	9	−0.957	0.158

[a] Logarithm of rate constants for reaction 2, $Nuc^- = Br^-$. [b] ^{13}C chemical shift of the γ carbon of coordinated 4-t-Bupy in 4-t-BupyCo$(DH)_2$X. [c] From ref 3; the chemical shift of the α H in 4-t-BupyCo$(DH)_2$X was used if α_{av} was not available. [d] Hammett substituent constant.[24a] [e] Hammett substituent constant corrected for resonance withdrawal.[24a] [f] Taft substituent constant.[24b] [g] Ligand influence parameters.[2] [h] Logarithm of rate constants for reaction 1, L = 4-CNpy.[12]

complex studied, with X = NO_3, as compared to the least reactive complex, with X = C_2H_5. This rate decreases by approximately 10^5! Second, this decrease in rate is accompanied by an upfield shift in the phosphite ^{13}C NMR resonance of ~3.5 ppm. In Figure 1 we plot the log k_{obsd} vs. the ^{13}C chemical shift. The linear correlation coefficient (LCC) for this plot is 0.995 and the Taft f statistic[15] is 0.038 for 17 points, leaving no doubt that there is a close correlation between the reaction rate and the chemical shift of the NMR signal; see Table II (and Table S-III, supplementary material) for correlations.

This result is gratifying with regard to two studies reported previously. First, the upfield shift in the ^{13}C resonance was interpreted to suggest that this ^{13}C resonance was responding to the local electron density at the carbon and not to the remote (through-space) effect of the metal.[4,5] The magnetic anisotropy at cobalt changes as X changes in such a way that the ^{13}C shifts of the phosphite C would shift downfield as X is changed from NO_3 to C_2H_5, if remote effects dominated. The electron density at this carbon was suggested to be dependent on the ability of the ligand X to donate electron density to the cobalt center.[5] Second, reaction 2 was previously found to be almost purely S_N2 in character.[13] The rate of reaction 2 should be dependent on the amount of electron density at the carbon center. Thus, both the ^{13}C shifts and the reaction rate should be good measures of the ability of X to donate electron density to the metal center, providing primary steric effects of X on reaction 2 can be shown to be unimportant.

We believe, in fact, that primary steric effects are unimportant in the present study. Consider the complexes with X = $P(O)(OCH_3)_2$, CH_2CN, and $CHCl_2$. These have essentially identical reactivity and very close values for the ^{13}C shift of the phosphite ligand (Table I). However, they differ considerably in steric bulk. Another useful comparison can be made between the CH_3 and i-C_3H_7 compounds. These also have similar rates and similar shifts, although the i-C_3H_7 group may induce steric distortion of the dioxime ligand system (vide infra).

Although there is an emerging modern trend to establish quantitative substituent constants for ligands using data on metal complexes,[2,3] spectroscopic and kinetic trends of transition-metal complexes have been most frequently compared with similar trends reported for organic compounds.[17-23] Often, the number of compounds used in such comparisons is small. We have previously contended that such comparisons are not realistic since the position of CN and NO_2 is usually very different for organic compounds as compared to metal compounds.[3]

Deutsch[17] has found excellent correlations between the log of the rate of ligand substitution reactions and the Hammett substituent parameters σ_p and σ_p^-.[24] However, only three or four points were used, and some of the constants were estimated. The correlation of these parameters with our data, Table II, is very poor (Taft $f > 0.6$), and this suggests that if the ligand substitution reaction could be extended to more and different X groups, the correlation of substitution reaction rates with σ_p and σ_p^- would be poor also. Our correlation with σ_p^-, which takes into account resonance effects,[24] is the poorest we have made. It therefore seems likely that the resonance effects of X in organic compounds and in metal complexes are, in fact, radically different. The excellent correlation with σ_p^- observed earlier[17] is probably fortuitous and most likely results from the sparsity of data (three points). It should be borne in mind that the statistical significance of the correlation coefficient is dependent on the number of data points. If comparisons are made between the log k_{obsd} and σ_p for alkyl/aryl substituents, there is a considerable improvement in the LCC, but the Taft f statistic suggests a relatively poor correlation.

A better fit for alkyl groups is found if σ^* values are used for comparison (Table II). These are restricted, by the nature of their determination, to alkyl/aryl substituents and are believed to reflect the inductive effect of the substituent.[24]

One of the puzzling features which has emerged from studies of the trans effect of halomethyl groups in earlier studies[10] as well as in this study is that electron donation decreases in the order $CH_2F > CH_2Cl > CH_2Br > CH_2I$. This order is opposite to that expected from electronegativity.[10] The size of these groups is such that relief of steric strain in going to a five-coordinate intermediate should parallel decreasing electronegativity, and, thus, primary steric effects cannot explain the trend. Brown[10] has suggested that repulsive interactions between the electrons in the metal d orbitals and the halo group may be greater in the five-coordinate complex, and this effect would account for the trend. However, we see no way to involve such an explanation to account for the trends for reaction 2 or for the ^{13}C shifts.

We postulate that a secondary steric effect may exist in these systems. This secondary steric effect may take one of two forms. First, it is now well established that the Co generally lies away from X out of the plane of the four N's of the two dioxime ligands.[25-27] For bulky X ligands, the Co may be forced into the plane or even into the direction of the X group. The bonding changes which accompany this movement could lead to the observed trends. Second, the binding between X and Co could be weakened by the steric interaction of X with the dioxime ligand system. The X group would then be a poorer electron donor and have a lower trans-labilizing effect. For ligand substitution reactions, a balance would exist between relief of steric strain in the transition state and the lower inductive effect of X. Thus, $i\text{-}C_3H_7$ is a better trans labilizer than expected,[18] and $CHBr_2$ is a poorer trans labilizer than expected.[10] For reaction 2 or for ^{13}C spectra, release of steric strain is less important, and both $i\text{-}C_3H_7$ and $CHBr_2$ have lower inductive effects than expected.

These hypotheses suggest a steric explanation for the nonlinear relationships which Kallen and Brown have found between the log of the rate constants for ligand substitution reactions or the log of formation constants and σ^*.[18,19] The groups which deviate most from the linear relationship are sterically hindered ($i\text{-}C_3H_7$ and $3\text{-}C_5H_{11}$).[19] We are presently carrying out further spectroscopic, structural, and rate studies to evaluate the validity of these hypotheses.

Experimental Section

Preparation of Complexes. All complexes were prepared by methods similar to those previously outlined.[4,5,7,12,13] Typically, the complex $(4\text{-CNpy})Co(DH)_2X$ was prepared and the 4-cyanopyridine displaced by $(CH_3O)_3P$ to yield the desired product. Analytical data may be found in the supplementary material. *Caution*! Cobaloximes containing the dibromo or ethyl ligands have been found to be shock and temperature sensitive.[28]

NMR Spectra. These were recorded for 0.1 M complex concentrations in $DCCl_3$ with Me_4Si as a standard. The ^{13}C NMR spectra were recorded with a Varian CFT-20 spectrometer (4000-Hz spectral width, ^1H-decoupled, 2000–5000 transients). ^1H NMR spectra for complexes and for rate determinations were obtained with a Varian A-60 ^1H NMR spectrometer at 31.5 ± 0.5 °C. For the rate determinations, the dioxime methyl resonances were scanned repeatedly at a sweep width of 100 Hz. The peaks were integrated by the cut and weigh method. For slower reactions ($t_{1/2} > 1$ h), the ^1H NMR tubes were kept tightly sealed in a constant-temperature bath at 31.5 ± 0.5 °C.

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Registry No. $(CH_3O)_3PCo(DH)_2NO_3$, 61024-82-6; $(CH_3O)_3PCo(DH)_2Cl$, 52654-86-1; $(CH_3O)_3PCo(DH)_2Br$, 61024-81-5; $(CH_3O)_3PCo(DH)_2I$, 68307-58-4; $(CH_3O)_3PCo(DH)_2N_3$, 61024-83-7; $(CH_3O)_3PCo(DH)_2NO_2$, 61024-84-8; $(CH_3O)_3PCo(DH)_2CN$, 61024-85-9; $(CH_3O)_3PCo(DH)_2SO_2PhCH_3$, 61024-86-0; $(CH_3O)_3PCo(DH)_2CHBr_2$, 42934-28-1; $(CH_3O)_3PCo(DH)_2CHCl_2$, 42934-26-9; $(CH_3O)_3PCo(DH)_2CH_2CN$, 68307-59-5; $(CH_3O)_3PCo(DH)_2P(O)(OCH_3)_2$, 61062-61-1; $(CH_3O)_3PCo(DH)_2CH_2I$, 68307-60-8; $(CH_3O)_3PCo(DH)_2CH_2Br$, 42934-27-0; $(CH_3O)_3PCo(DH)_2CH_2Cl$, 42934-25-8; $(CH_3O)_3PCo(DH)_2C_6H_5$, 61024-88-2; $(CH_3O)_3PCo(DH)_2(CH_2)_3CN$, 68307-61-9; $(CH_3O)_3PCo(DH)_2(C_6H_5(CH_2)_2)$, 68307-62-0; $(CH_3O)_3PCo(DH)_2CH_3$, 25586-92-9; $(CH_3O)_3PCo(DH)_2(2\text{-}C_3H_7)$, 68307-63-1; $(CH_3O)_3PCo(DH)_2C_2H_5$, 68307-64-2; Br^-, 24959-67-9.

Supplementary Material Available: Table S-I, additional or new NMR data, Table S-II, summary of analytical data, and Table S-III, least-squares parameters (3 pages). Ordering information is given on any current masthead page.

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