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Phosphorus-31 NMR Spectra of Cobaloximes: Influence of Electronic and Steric Effects of Axial Ligands

JOSEPH A. KARGOL, ROGER W. CRECELY, JOHN L. BURMEISTER*
Department of Chemistry, University of Delaware, Newark, Del. 19711

and PAUL J. TOSCANO and LUIGI G. MARZILLI*
Department of Chemistry, The Johns Hopkins University, Baltimore, Md. 21218, U.S.A.

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The ^{31}*P NMR spectra of a large number of cobaloxime compounds having the general formula* trans-*Co(DH)*$_2$*(L)X (where DH = the monoanion of dimethylglyoxime) have been measured. Series examined include those where L = tri-*n*-butylphosphine or trimethylphosphite, X = various ligands and L = various phosphorus donors, X =* Cl^- *or* CH_3^-*. Several factors were found to influence the* ^{31}*P coordination chemical shifts (Δ's) such as ligand cone angle, hybridization of the phosphorus donor orbital, substituent groups on the phosphorus, and the* trans-*influence (or -effect) of the X groups. The data are discussed in the context of other NMR and structural studies of cobaloximes. The results lend support to a common* trans-*effect/influence series for octahedral complexes [1, 2].*

Introduction

Cobaloxime complexes, species which contain the $Co(DH)_2^+$ unit, where DH = the monoanion of dimethylglyoxime, have been of considerable interest because of their behavioral similarities to vitamin B_{12} coenzymes [3]. This appears to be due to the strong ligand field produced by the glyoximates, which is comparable to that of the corrin ring system. The surprisingly inert cobalt-carbon σ bond in organo-cobaloximes underlines this analogy [4].

Although cobalt(III) has generally been acknowledged to be a class a or hard metal center, some evidence has been presented which supports class b behavior in some cobaloximes [5]. Experiments designed to quantify these observations have shown the bonding characteristics of the metal center to be quite sensitive to the nature of the axial ligands. The bonding of axial ligands has been described using electrostatic and covalent considerations [6].

Nuclear magnetic resonance spectroscopy, which has been utilized to examine the hydrogen-1 [7, 8], carbon-13 [9], and cobalt-59 [10] nuclei in a number of cobaloxime complexes, has demonstrated the sensitivity of the shifts of these nuclei to variation of the axial ligands. An extensive study has led to the formulation of a ^{1}H NMR spectrochemical series [11]. Recently, the chemical shifts of the oxime methyl carbons were shown to be related to the rates of reaction of axial ligands (in this case trimethylphosphite), giving a direct measure of the *trans*-effect for an octahedral system [12].

A large number of cobaloxime complexes containing phosphine and phosphite ligands have now been reported, but in only one limited case [13] have their ^{31}P NMR signals been measured. Most studies on P-donor cobaloxime complexes have tended to emphasize the effects of the phosphorus ligand on the $Co(DH)_2^+$ moiety or the *trans* ligand, rather than the effects which coordination produces on the phosphorus ligand. One exception to this assessment is Trogler and Marzilli's determination of phosphorus ligand cone angles [14].

The present work was initiated with several objectives in mind. We wished to determine whether coordination chemical shifts (Δ's) for ^{31}P in cobaloximes were (a) sensitive to variation in axial ligands, (b) related to variations in rates of reactions and in NMR chemical shifts, as found in other studies on cobaloximes and (c) comparable to ^{31}P shift trends found for other metal complexes.

Experimental

The preparative methods for many of the complexes used have been reported previously [8b, 9a, 11, 12, 14–16]. Methyltriphenylphosphine cobaloxime was prepared from *trans*-$Co(DH)_2(S(CH_3)_2)(CH_3)$ [17] by metathesis in ethanol. Similarly, *trans*-$Co(DH)_2(PBu_3^n)X$ (where X = C_2H_5, *n*-Pr, *i*-Pr) and *trans*-$Co(DH)_2(P(OCH_3)_3)X$ (where X = C_2H_5,

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*Authors to whom correspondence should be addressed.

TABLE I. ^{31}P Chemical Shifts for *trans*-$Co(DH)_2(X)L$ Complexes.[a]

X	δ, L = PBu^n_3, ppm	δ, L = $P(OCH_3)_3$, ppm
H_2O/ClO_4^-	+41.0	–
NO_3^- (1)	+35.6	+89.0
CN^- (2)	+34.6	+102.9
Br^- (3)	+33.9	+100.9
I^- (4)	+33.8	+101.8
Cl^- (5)	+30.9	+97.3
SCN^- (6)	+29.8	–
N_3^- (7)	+25.8	–
$Sn(C_6H_5)_3^-$	+24.9	–
$PBu^n_3/B(C_6H_5)_4^-$	+24.0	–
NCS^- (8)	+24.0	–
NO_2^- (9)	+22.3	+103.2
$SO_2C_6H_4CH_3$ (10)	+19.0	+112.7
$CHBr_2$ (11)	+9.5	+110.1
$P(O)(OCH_3)_2$ (12)	–	+121.0
CH_2Br (13)	+5.5	+126.3
C_6H_5 (14)	+3.2	+127.3
$CH(CH_3)_2$ (15)	+3.1	+131.9
CH_2CH_3 (16)	+2.3	+131.1
CH_3 (17)	+1.9	+128.2
$(CH_2)_2CH_3$ (18)	+1.9	+130.5

[a] Measurements made in $CDCl_3$ solution, with all values relative to external H_3PO_4. Numbers in parentheses correspond to the labeling of points on all subsequent graphs.

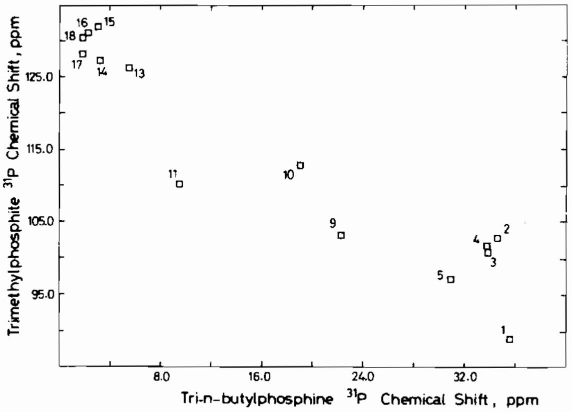

Fig. 1. Phosphine *versus* Phosphite ^{31}P Chemical Shifts for *trans*-$Co(DH)_2(X)L$ Complexes.

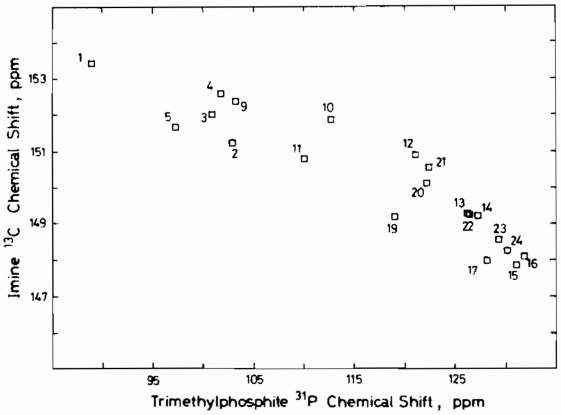

Fig. 2. Trimethylphosphite ^{31}P Chemical Shifts *versus* Imine ^{13}C Chemical Shifts for *trans*-$Co(DH)_2(X)P(OCH_3)_3$ Complexes.

n-Pr) were generated *in situ* by addition of the phosphorus ligand to a deuterochloroform solution of the appropriate alkyl dimethylsulfide complex; the triphenyltin complex was generated *in situ* by addition of tri-*n*-butylphosphine to a solution of *trans*-$Co(DH)_2(Py)(Sn(C_6H_5)_3)$ [18] (Py = pyridine). Some phosphine and phosphite complexes were prepared *in situ* by the addition of the appropriate ligand to a $DCCl_3$ suspension of $[Co(DH)_2CH_3]_2$ [17, 19]. Exceptions to this were the PBu^3_n, $P(C_6H_5)_3$, $P(C_6H_5)_2OCH_3$, $P(C_6H_5)(OCH_3)_2$, and $P(OCH_3)_3$ complexes. In all cases where complexes were generated *in situ*, the addition of excess phosphorus ligand did not produce an effect upon the ^{31}P resonance of the complex. The rate of exchange of the phosphorus ligands is slow enough so that sepa-

TABLE II. $^{13}C^{a}$ and ^{31}P NMR Data for *trans*-Co(DH)$_2$(X)P(OCH$_3$)$_3$ Complexes.

X		$^{31}P(OCH_3)_3$ δ, ppm^{b}	Imine ^{13}C δ, ppm^{c}	$^{13}CH_3$(oxime) δ, ppm^{c}	$P(O^{13}CH_3)_3$ δ, ppm^{c}	$^{2}J_{P-O-C}$ Hz
NO_3^-	(1)	89.0	153.41	12.77	55.80	9.2
Cl^-	(5)	97.3	151.70	12.77	55.19	8.7
Br^-	(3)	100.9	152.03	12.86	55.07	9.0
I^-	(4)	101.8	152.60	12.94	54.93	8.7
CN^-	(2)	102.9	151.25	12.55	54.45	8.6
NO_2^-	(9)	103.2	152.37	12.65	54.37	8.4
$CHBr_2$	(11)	110.1	150.80	12.54	53.68	7.8
$SO_2C_6H_5CH_3$	(10)	112.7	151.88	12.41	54.13	8.0
CH_2I	(19)	119.1	149.18	12.53	52.95	6.8
$P(O)(OCH_3)_2$	(12)^{d}	121.0	150.90	12.24	53.29	6.8
CH_2CN	(20)	122.2	150.11	12.55	53.40	7.6
$CHCl_2$	(21)	122.4	150.56	12.37	53.41	7.9
CH_2Br	(13)	126.3	149.27	12.26	52.87	6.7
CH_2Cl	(22)	126.5	149.23	12.10	52.77	6.8
C_6H_5	(14)	127.3	149.21	12.09	52.67	6.9
CH_3	(17)	128.2	147.96	11.96	52.24	5.9
$(CH_2)_3CN$	(23)	129.4	148.56	12.04	52.51	6.6
$(CH_2)_2C_6H_5$	(24)	130.3	148.27	11.98	52.32	6.0
CH_2CH_3	(16)	131.1	147.87	11.89	52.95	6.8
$CH(CH_3)_2$	(15)	131.9	148.11	11.97	52.18	6.4

^{a}References 9a, 12. ^{b}Relative to H_3PO_4 (ext). ^{c}Relative to TMS. ^{d} ^{31}P NMR chemical shift of $P(O)(OCH_3)_2$ is 59.3 ppm. The J_{P-P} is ~626 Hz.

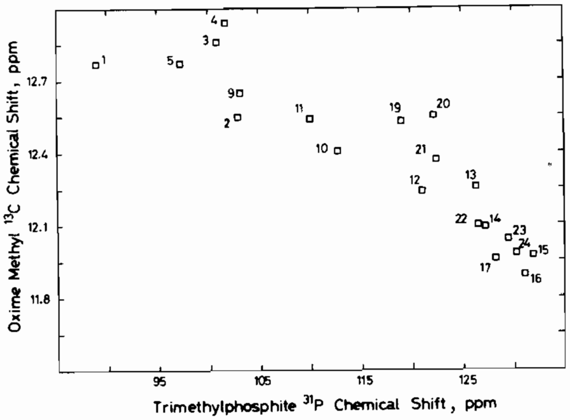

Fig. 3. Trimethylphosphite ^{31}P Chemical Shifts *versus* Oxime Methyl ^{13}C Chemical Shifts for *trans*-Co(DH)$_2$(X)P(OCH$_3$)$_3$ Complexes.

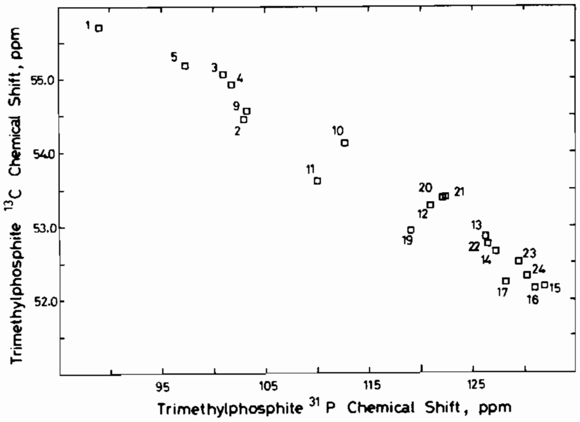

Fig. 4. Trimethylphosphite ^{31}P Chemical Shifts *versus* Trimethylphosphite ^{13}C Chemical Shifts for *trans*-Co(DH)$_2$-(X)P(OCH$_3$)$_3$ Complexes.

rate signals for the free ligand and complex can be obtained. Trace amounts of free ligand, when present, are readily apparent because of the sharpness of these signals, relative to the broad signals for the complexes.

The ^{31}P NMR shifts of the free ligands have previously been determined; however, a complete series in the same medium was not available. Therefore, these values were remeasured in solutions made by adding 5 or 6 drops (or a few crystals for solids) of ligand to 2 mL of $DCCl_3$. The values obtained compare favorably with those reported previously [20, 21], with minor changes due to solvent effects.

Phosphorus-31 measurements were made on a pulsed Bruker HFX-90 spectrometer, with a $DCCl_3$ lock. All chemical shifts given are relative to external

TABLE III. ^{13}C and ^{31}P NMR Data for *trans*-$Co(DH)_2(X)PBu^n_3$ Complexes.

X		$^{31}PBu^n_3$ ^{b} δ, ppm	$^{13}CH_3$(oxime)^{a,c} δ, ppm	^{13}C-1^{a,c} δ, ppm	$^1J_{P-C}$ ^{a} Hz
CN^-	(2)	34.6	12.52	18.98	21.8
Br^-	(3)	33.9	12.86	20.08	23.2
I^-	(4)	33.8	12.95	19.22	22.4
Cl^-	(5)	30.9	12.77	20.44	23.6
SCN^-	(6)	29.8	13.05	–	–
N_3^-	(7)	25.8	12.62	20.79	23.2
NCS^-	(8)	24.0	12.74	20.37	24.6
NO_2^-	(9)	22.3	12.61	20.47	22.0
$SO_2C_4H_5CH_3$	(10)	19.0	12.35	20.13	20.0
CH_2Br	(13)	5.5	12.16	19.78	17.2
C_6H_5	(14)	3.2	11.99	19.51	15.4
CH_3	(17)	1.9	11.81	19.50	15.0

^{a}Reference 9a. ^{b}Relative to H_3PO_4 (ext). ^{c}Relative to TMS.

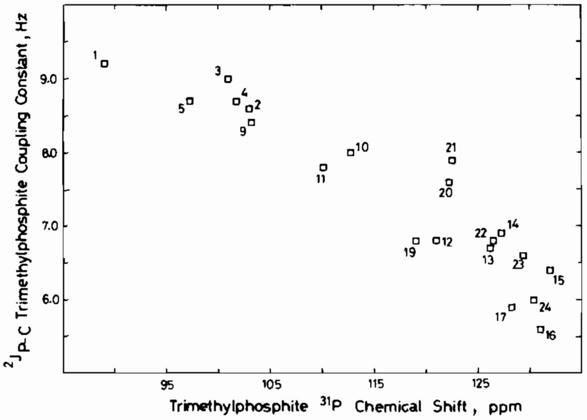

Fig. 5. Trimethylphosphite ^{31}P Chemical Shifts *versus* Trimethylphosphite Coupling Constants ($^2J_{P-C}$) for *trans*-$Co(DH)_2(X)P(OCH_3)_3$ Complexes.

H_3PO_4. Solutions containing phosphine complexes were approximately 0.1 *M* in concentration. Solutions of complexes with P–O bonds were made twice this concentration, due to the larger line broadening caused by cobalt–phosphorus coupling.

Results and Discussion

We shall first consider the influence of the variation in X on ^{31}P shifts of both coordinated phosphine and phosphite ligands. The results will be compared with the effects of X variation on reaction rates and previously observed spectroscopic results. Next, we will consider variations in P-donor ligands, while keeping X fixed.

The phosphorus-31 chemical shifts for some *trans*-$Co(DH)_2(L)X$ (X = various ligands, L = PBu^n_3 or $P(OCH_3)_3$) complexes are given in Table I. These results form two series for which the chemical shifts vary in opposite directions. Although there is not an exact one-to-one relationship between the ordering of the X groups in both series, a plot of the resonances does give a fairly good linear correlation (Fig. 1). This opposition in trends has not been found previously.

A comparison of the ^{31}P results with previously reported ^{13}C NMR data [9a, 12] would seem to be appropriate, in view of the dependence of both nuclei upon paramagnetic electronic shielding contributions. Such data are given in Table II for a number of cobaloxime complexes with trimethylphosphite. Fairly good correlations appear to exist between the ^{31}P resonances of trimethylphosphite and the ^{13}C resonances (Figs. 2–4). A similar correlation can be made with the ^{31}P resonances and the coupling constants for phosphite carbon to phosphorus, although this graph exhibits greater scatter (Fig. 5). The best correlation appears to be that between the ^{31}P resonances and the ^{13}C resonances of the methoxy carbon of the phosphite (Fig. 4). When the analogous comparisons are made for the tri-*n*-butylphosphine complexes, poorer correlations and greater scatter are obtained (Table III and Figs. 6–8) than for trimethylphosphite. Based on the ^{13}C data reported [9a], it is also evident that the trimethylphosphite oxygen is much better at transmitting electronic changes due to variations in the *trans*-ligand than the α-carbon of tri-*n*-butylphosphine. The β-carbon resonances of tri-*n*-butylphosphine are only

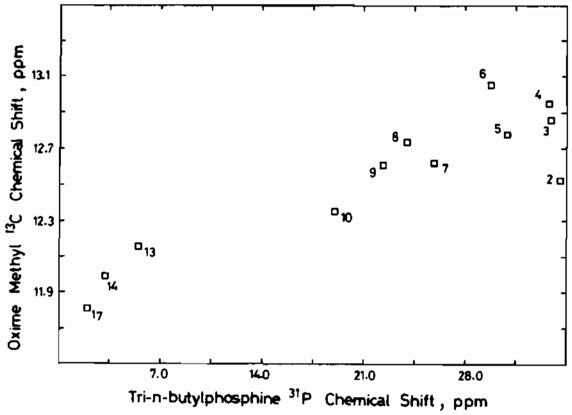

Fig. 6. Tri-*n*-butylphosphine ^{31}P Chemical Shifts *versus* Oxime Methyl ^{13}C Chemical Shifts for *trans*-$Co(DH)_2(X)PBu^n_3$ Complexes.

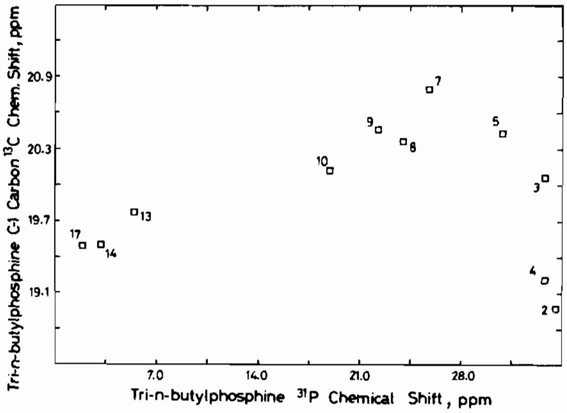

Fig. 7. Tri-*n*-butylphosphine ^{31}P Chemical Shifts *versus* Tri-*n*-butylphosphine C-1 Carbon ^{13}C Chemical Shifts for *trans*-$Co(DH)_2(X)PBu^n_3$ Complexes.

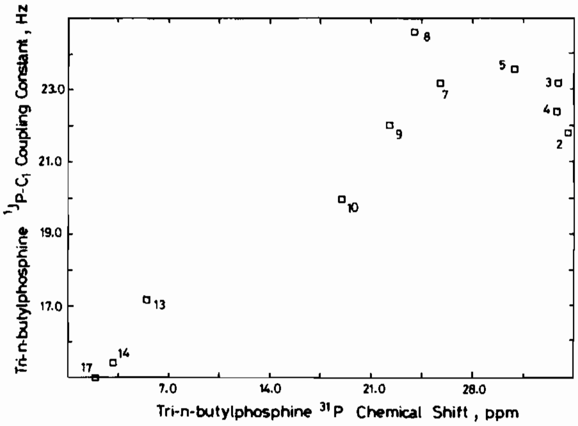

Fig. 8. Tri-*n*-butylphosphine ^{31}P Chemical Shifts *versus* Tri-*n*-butylphosphine $^1J_{P-C_1}$ Coupling Constants for *trans*-$Co(DH)_2(X)PBu^n_3$ Complexes.

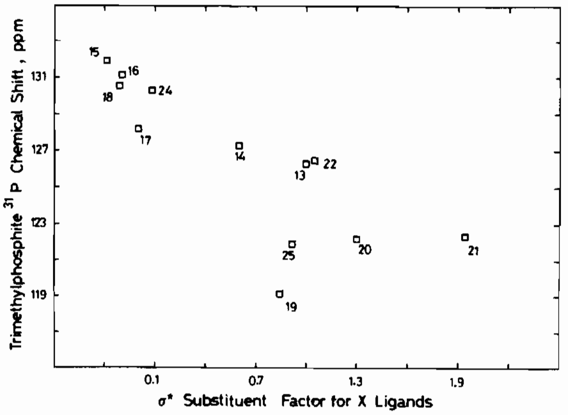

Fig. 9. σ^* Substituent Factors *versus* Trimethylphosphite ^{31}P Chemical Shifts for *trans*-$Co(DH)_2(X)P(OCH_3)_3$ Complexes.

slightly affected by changes in the *trans*-ligand. The α-carbon resonances themselves are anomalous [9a].

It is presently believed that, because of the absence of π-bonding in the transition state of ligand substitution reactions of octahedral complexes, the *trans* effect and *trans* influence series should be related [22].

Efforts to derive a *trans*-influence series for octahedral complexes have been hindered by a general lack of data [23]. The correlation between ^{31}P resonances and the ^{13}C resonances of the methoxy carbon in the trimethylphosphite series is significant because the ^{13}C shifts are linearly related to the log k for the reaction of coordinated phosphite with Br^- [12]. From the experimentally determined rates of ligation for cobaloximes [24, 25], the following ordering of decreasing *trans*-effect can be made:

$$CH_3 > C_6H_5 > (CH_3O)_2P(O) >$$
$$CH_3C_6H_4SO_2 > NO_2.$$

This order agrees with both the ^{31}P NMR shifts found here and with the ^{13}C NMR shifts as found earlier [24]. These findings support a common *trans* effect/influence series for octahedral complexes.

Previous reports [8a, 25, 26] have discussed correlations between substituent parameters (σ^*) [27] and experimental data for cobaloxime complexes. A similar comparison can be made for the ^{31}P NMR chemical shifts and σ^* values (Table IV and Fig. 9). While there does not appear to be a correlation with the ^{31}P values of PBu^n_3, it appears that there is one with $P(OCH_3)_3$. Deviations from this correlation very likely arise because the σ^* values were derived for

TABLE IV. Comparison of ^{31}P Chemical Shifts with σ^* Values for *trans*-$Co(DH)_2(L)X$ Complexes.

X		σ^* [41]	δ, L = $P(OCH_3)_3$, ppm	δ, L = PBu_3^n, ppm
$CHCl_2$	(21)	1.94	122.4	
CH_2CN	(20)	1.30	122.2	
CH_2Cl	(22)	1.05	126.5	
CH_2Br	(13)	1.00	126.3	5.5
CH_2CF_3	(25)	0.92	121.9	
CH_2I	(19)	0.85	119.1	
C_6H_5	(14)	0.60	127.3	3.2
$(CH_2)_2C_6H_5$	(24)	0.08	130.3	
CH_3	(17)	0.00	128.2	1.9
CH_2CH_3	(16)	–0.1	131.1	2.3
$(CH_2)_2CH_3$	(18)	–0.115	130.5	1.9
$CH(CH_3)_2$	(15)	–0.19	131.9	3.2

TABLE V. ^{31}P Chemical Shifts of *trans*-$Co(DH)_2(L)Cl$ Complexes.

L		δ (ppm), Free Ligand	δ (ppm), Complex	Δ(ppm)[a]
PPr_3^i	(31)	20.8	35.0	14.2
$P(cy\text{-}Hex)_3$	(32)	14.0	23.9	9.9
$P(C_6H_5)_3$	(33)	–5.2	24.9	30.1
$P(C_6H_5)_2C_2H_5$	(34)	–11.4	34.8	46.2
$P(C_6H_5)_2Bu^n$	(35)	–16.0	32.3	48.3
$P(C_2H_5)_3$	(36)	–18.6	36.0	44.6
$P(C_6H_5)_2CH_3$	(37)	–26.8	21.4	48.2
PBu_3^n	(38)	–30.9	30.9	61.8
$P(CH_3)_3$	(39)	–60.9	26.8	87.7
$P(C_6H_5)_2OCH_3$	(50)	115.6	124.3	8.7
$P(C_6H_5)(OCH_3)_2$	(51)	159.0	140.3	–18.7
$P(OC_6H_5)_3$	(40)	128.0	81.6	–46.4
$P(OCH_2CCl_3)_3$	(41)	137.6	101.5	–36.1
$P(OCH_2CH_2Cl)_3$	(42)	138.6	96.7	–41.9
$P(OBu^n)_3$	(43)	139.1	92.0	–47.1
$P(OPr^i)_3$	(44)	139.1	86.1	–53.2
$P(OC_2H_5)_3$	(45)	139.2	90.9	–48.3
$P(Oallyl)_3$	(46)	139.3	94.5	–44.8
$P(OCH_3)_3$	(47)	141.0	97.3	–43.7

[a] $\Delta = \delta_{complex} - \delta_{free}$.

organic systems. Based upon data such as those presented here and elsewhere [24], it would appear that substituent constants derived from organic systems are not readily applied to inorganic systems.

Recently, a ^{13}C NMR study [28] of a number of *trans*-$H_3^{13}CRh(DH)_2X$ complexes revealed, for the ligands investigated in the present study, that the methyl resonance becomes deshielded in the following order: $NO_2^- > N_3^- > Cl^- > SCN^- > Br^- > CN^-$, OH_2. This generally follows the ordering of these ligands in the phosphine ^{31}P series.

The ^{19}F NMR spectra for a series of complexes with the general formula *trans*-3 or 4-$FC_6H_4M(DH)_2X$ (where M = Co, Rh and X = various ligands) have been reported and the data used to discuss the *trans*-influence of the X groups [28, 29]. The

TABLE VI. Phosphine Coordination Chemical Shifts (Δ) Related to Other Physical Properties.

Ligand		Δ^a (ppm)	Cone Angle^b (degrees)	$\Sigma_X{}^c$	$pK_a{}^e$
$P(cy\text{-}Hex)_3$	(32)	9.9	179	0.3	9.70
PPr^i_3	(31)	14.2	160	3.0	7.97
$P(C_6H_5)_3$	(33)	30.1	155	12.9	2.73
$P(C_2H_5)_3$	(36)	44.6	132	5.4	8.69
$P(C_6H_5)_2C_2H_5$	(34)	46.2	141	10.4	4.91^f
$P(C_6H_5)_2CH_3$	(37)	48.2	132^d	11.2	4.6
$P(C_6H_5)_2Bu^n$	(35)	48.3	140	10.0	4.99^f
PBu^n_3	(38)	61.8	130	4.2	8.43
$P(CH_3)_3$	(39)	87.7	118	7.8	8.65

[a] For *trans*-Co(DH)$_2$(L)Cl complexes. [b] Reference 14. [c] Reference 36. [d] C. A. Tolman, *Chem. Rev.*, *77*, 313 (1977). [e] L. Maier, Ch. 1, in 'Organic Phosphorus Compounds', vol. 1 (G. M. Kosolapoff and L. Maier, Eds.), Wiley–Interscience, New York, 1972. [f] Calculated using $pK_a = 7.85 - 2.67\ \Sigma\sigma^*$, as in W. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc.*, *82*, 5791 (1960).

ordering which was arrived at does not agree with that determined here. Other comparisons which were poor included those with Jϕrgensen's f values [30] and with the ^1H NMR spectrochemical series for cobaloximes [11].

Some of the differences which exist between phosphines and phosphites when X is held constant are demonstrated in the ^{31}P chemical shifts for some *trans*-[Co(DH)$_2$(Cl)(L)], Table V. From these results, it can be seen that the phosphines all experience positive coordination chemical shifts (Δs) whereas all of the phosphites have negative Δ's. Based on current theory [31], this corresponds to a decrease in electron density for phosphines and an apparent increase in p or d electron density for phosphites.

It would be expected that, upon coordination, the strongest interaction results from the formation of the metal–phosphorus σ-bond. Such bonding would have a deshielding effect upon the phosphorus for both phosphines and phosphites. Because of the greater amount of p character [32] in the donor atom of phosphines (relative to phosphites), it would be expected that a greater degree of deshielding will occur.

The greater shielding of coordinated phosphites relative to the free ligands may not be indicative of π-bonding, although such arguments were once suggested [33]. A more recent study tends to discount the importance of π-bonding of phosphites [34]. More likely the results are due to a change in the ligand cone angle (*vide infra*) which causes a change in the hybridization of the donor orbital and results in the observed increase in electronic shielding [35]. These chemical shift changes can also be accommodated if an increase in the mean electron excitation energy (ΔE) for phosphites occurs upon coordination [36].

The difference in the amount of s character in the donor orbital also affects the degree of cobalt–phosphorus coupling. Phosphites, having greater s electron density, are expected to have a much larger Fermi contact contribution. Cobalt-phosphorus coupling was evident in line-broadening of the ^{31}P resonances, with the resonances for the phosphites indeed being much broader. Further coupling to *trans* ligands such as -NO$_2$ and -NCS was apparent, from the additional line broadening. Although phosphorus-proton coupling is observed in the ^1H NMR signals for the methyl groups of the glyoximates [7c, 8a], the converse is not apparent in the ^{31}P spectrum, due to the extreme broadening caused by interaction with the quadrupolar cobalt-59 nucleus.

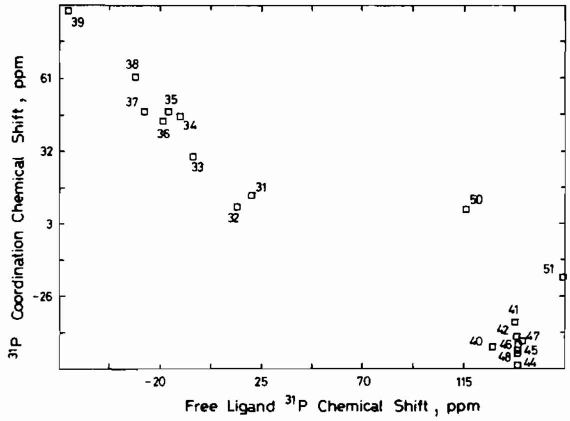

Fig. 10. Free Ligand ^{31}P Chemical Shifts *versus* ^{31}P Coordination Chemical Shifts of Phosphorus Donors for Chlorocobaloximes.

A plot of the phosphine Δ values *versus* the ^{31}P resonances for the uncomplexed ligands yields the expected linear correlation [37]. A similar plot for the phosphites would not be very meaningful, due to the small changes which occur for the free ligand

TABLE VII. Phosphite Coordination Chemical Shifts (Δ) Related to Other Physical Properties.

Ligand		Δ^a (ppm)	Cone Angle^b (degrees)	$\Sigma_X{}^c$
$P(OCH_2CCl_3)_3$	(41)	−36.1	131^c	35.7
$P(OCH_2CH_2Cl)_3$	(42)	−41.9	110	27.9
P(Oallyl)$_3$	(46)	−44.8		23.1
$P(OCH_3)_3$	(47)	−43.7	107	23.1
$P(OC_6H_5)_3$	(40)	−46.4	121	29.1
$P(OBu^n)_3$	(43)	−47.1		19.5
$P(OC_2H_5)_3$	(45)	−48.3	109	20.4
$P(OPr^i)_3$	(44)	−53.2	114^d	18.9

^{a}For *trans*-Co(DH)$_2$(L)Cl complexes. ^{b}Reference 14. ^{c}Reference 36. ^{d}C. A. Tolman, *Chem. Rev.*, *77*, 313 (1977).

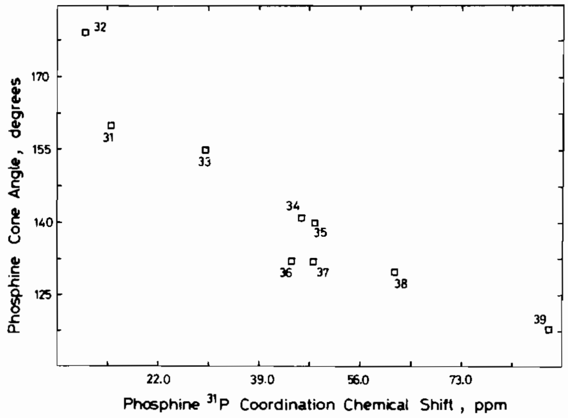

Fig. 11. Phosphine Coordination Chemical Shifts *versus* Phosphine Cone Angles.

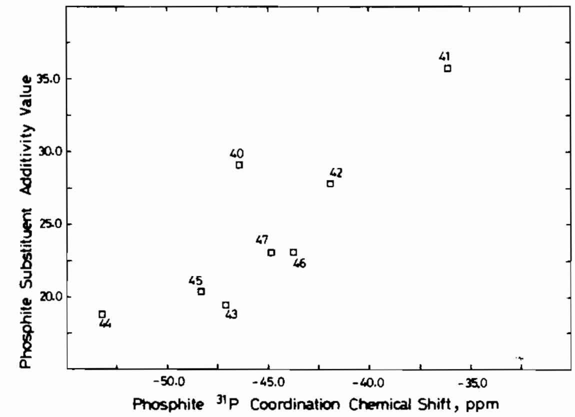

Fig. 13. Phosphite Coordination Chemical Shifts *versus* Phosphite Substituent Additivity Values.

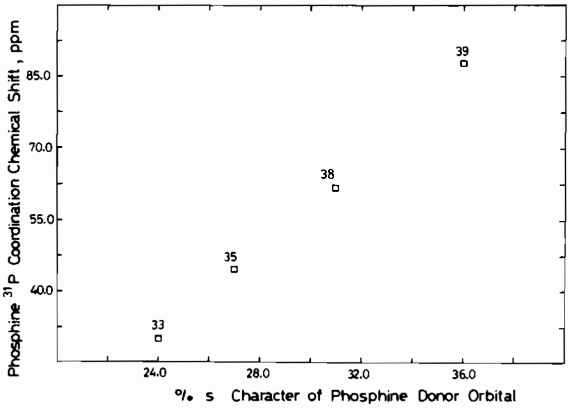

Fig. 12. % s Character of Phosphine Donor Orbitals *versus* Phosphine Coordination Chemical Shifts.

resonances; however, if the line for the phosphines is extended, one sees that the phosphites would fall as a cluster on or near the line (Fig. 10). The two phosphorus ligands of mixed phosphine and phosphite character [$P(C_6H_5)(OCH_3)_2$ and $P(C_6H_5)_2OCH_3$] do not fall on this line.

A comparison of the Δ's for the phosphine series with phosphine pK_a values and substituent additivity values (Σ_X) [38] does not produce any apparent correlation (Table VI). The ordering is also not related to their *trans*-effect/influence. Tricyclohexylphosphine, which has a high *trans*-effect in cobaloximes [39], is at the low end of this series. When Δ is compared to the ligand cone angle, however, the expected linear correlation [40] is observed (Fig. 11). The amount of s character of the phosphine lone pair and ligand bond angles (C–P–C) have been shown to be linearly related [31].

It is therefore not surprising that Δ, being dependent upon θ, is also related to the % s character [32] of the phosphine donor orbital (Fig. 12). This correlation is the inverse of what would be predicted solely on electronic grounds, *i.e.*, greater s character should give smaller positive Δ values [31, 35].

The values of the coordination chemical shifts for phosphites can also be compared with θ and Σ_X

TABLE VIII. ^{31}P NMR of *trans*-$Co(DH)_2(L)CH_3$ Complexes.

L		δ (ppm), Free ligand	δ (ppm), Complex	Δ (ppm)
$P(cy\text{-}Hex)_3$	(32)	14.0	3.3	−10.7
$P(C_6H_5)_3$	(33)	−5.2	19.8	25.0
$P(C_6H_5)_2C_2H_5$	(34)	−11.4	19.8	31.2
$P(C_6H_5)_2Bu^n$	(35)	−16.0	16.6	32.6
$P(C_2H_5)_3$	(36)	−18.6	5.7	24.3
$P(C_6H_5)_2CH_3$	(37)	−26.8	8.0	34.8
PBu^n_3	(38)	−30.9	1.9	32.8
$P(C_6H_5)_2OCH_3$	(50)	115.6	126.4	10.8
$P(C_6H_5)(OCH_3)_2$	(51)	159.0	158.3	−0.7
$P(OC_6H_5)_3$	(40)	128.0	112.1	−12.9
$P(Oallyl)_3$	(46)	139.3	124.2	−15.1
$P(OBu^n)_3$	(43)	139.1	127.5	−11.6
$P(OCH_3)_3$	(47)	141.0	128.2	−12.8
$P(OPr^i)_3$	(44)	139.1	118.2	−19.9
$P(OCH_2CH_2Cl)_3$	(42)	138.6	127.3	−11.3

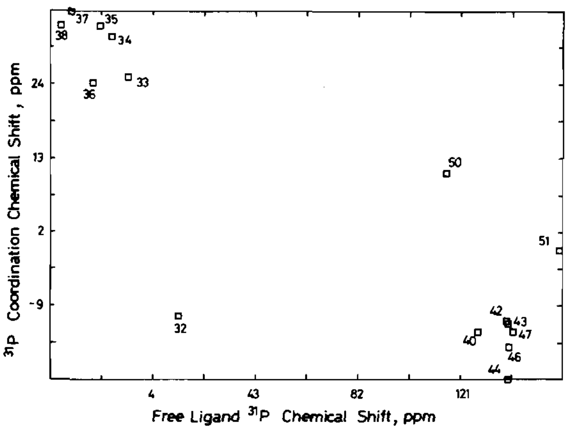

Fig. 14. Free Ligand ^{31}P Chemical Shifts *versus* ^{31}P Coordination Chemical Shifts of Phosphorus Donors in Methyl Cobaloximes.

(Table VII). Cone angles (θ) for phosphites are dominated by the O–P–O bond angles. These are much more similar within the phosphite series than are the C–P–C bond angles within the phosphine series. Therefore, there is a narrower range of values for θ in phosphites and this does not produce a good correlation with the Δ values. Similarly, there does not appear to be a correlation between Δ and the % s character of the phosphite donor orbitals. When Δ is compared to Σ_X, a general trend does appear to exist between these values, with the exception of $P(OC_6H_5)_3$ (Fig. 13).

There are very basic differences between the ^{31}P chemical shifts of coordinated phosphines and phosphites. Phosphine chemical shifts are dominated by changes in their cone angles. These cone angle changes are also responsible for changes in both the hybridization of the donor orbital and the Co–P bond length [41, 42]. Ligands with larger cone angles interact more poorly with cobaloximes. This should result in smaller magnitudes for Δ. In contrast to our observation that cone angle differences are by far more important than substituent groups in determining coordination chemical shifts, the converse must be said for phosphites. It is likely, however, that the importance of substituent groups in determining coordination chemical shifts is a result of the small range of cone angles for phosphites. However, the lack of a true linear correlation between Δ and Σ_X illustrates that other factors, among them cone angle changes, contribute to the coordination chemical shifts for phosphites.

The phosphorus-31 chemical shifts and coordination chemical shifts for a number of cobaloxime complexes with phosphorus donors *trans*- to methyl groups are given in Table VIII. When the phosphine Δ values are plotted *versus* the chemical shift values in the manner in which the chloro complexes were treated (Fig. 10), the result is a graph with much more scatter (Fig. 14). Part of this is due to the smaller range of values.

The greater scatter may be the result of differences in bonding for the methyl complexes relative to the

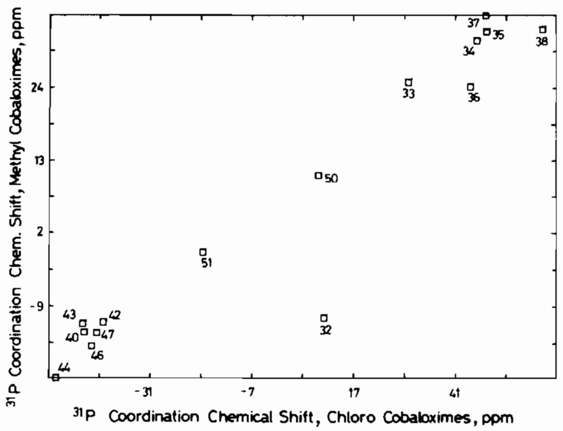

Fig. 15. ^{31}P Coordination Chemical Shifts for Phosphorus Donors in Chloro Cobaloximes *versus* ^{31}P Coordination Chemical Shifts for Phosphorus Donors in Methyl Cobaloximes.

chloro complexes. Courtright *et al.* [6] have described the cobalt–carbon bond as possessing much greater covalent character than would be expected for a cobalt(III) complex. It was suggested that when such strong covalent interactions occur the metal center shifts out of the plane of the glyoximate ligands and moves toward this ligand.

The ligand cone angle also greatly affects Δ for tricyclohexylphosphine. With a cone angle of 179° [14], it has the largest cone angle of the common phosphines [43]. The interaction of this ligand with the cobaloxime moiety produces unfavorable steric interactions, leading to a decrease in the ligand cone angles and an increase in the length of the Co–P bond [41, 42]. The smaller cone angle produces a change in the hybridization of the phosphine, resulting in greater p electron density about the phosphorus. It seems possible that this, coupled with a weaker cobalt–phosphorus σ bond, leads to the negative Δ value. The cobalt–phosphorus bond for the chloro complex is much stronger and might compensate enough for the cone angle reduction to give a positive Δ. In a much less sterically restrictive complex, $(Cyhex)_3PAuBr$, the Δ value for tricyclohexylphosphine has a much larger positive value, clearly indicating the pronounced effect of rehybridization through cone angle changes [44].

Despite the greater *trans*-influence which methyl has relative to chloride, a plot of ΔCH_3 *versus* Δ_{Cl} gives a good linear relationship (Fig. 15). The major exception to this is tricyclohexylphosphine. Recent structural data shows that for a series of cobaloximes with P-donor ligands with different steric sizes the Co–P lengths are elongated for X = alkyl compared to X = Cl about the same amount, regardless of steric size [42]. Consequently, the linear relationship between Δ_{CH_3} and Δ_{Cl} is not surprising. No data is available on an alkyl complex with tricyclohexylphosphine as the neutral ligand, but, when X = Cl, the length is that predicted from the experimental cone angles determined by Trogler and Marzilli [14]. It should be noted that Δ_{CH_3} is smaller than Δ_{Cl}, consistent with the longer and presumably weaker Co–P bond in organo-cobaloximes. or both phosphites and phosphines, a weaker bond is associated with a smaller absolute value of Δ, although as noted earlier, the direction of the shifts as X is changed is opposite for phosphites and phosphines.

Summary

For variation in X:

1) Cobaloximes, *trans*-$Co(DH)_2(L)X$, have ^{31}P NMR spectra in which the ^{31}P shift varies over a wide range as X is changed (up to 40 ppm for L = PBu^n_3).

2) As the *trans* influence of X is increased, the ^{31}P shifts of coordinated phosphines shift upfield whereas those of coordinated phosphites shift downfield.

3) However, the trend in X is similar for both phosphines and phosphites.

4) This trend is the typical *trans* effect/influence series found previously from rate, spectroscopic, and structural studies.

For variation in L:

5) Phosphine coordination chemical shifts appear to be considerably influenced by phosphine steric size.

6) Phosphite coordination chemical shifts appear to be more influenced by the electronic nature of phosphite substituents.

7) The relative shifts of coordinated phosphines and phosphites are the same for both X = Cl and X = CH_3, although the Co–P bond length is longer for X = CH_3.

In general:

8) Since the ^{31}P NMR shifts follow well defined empirical trends, these values will be useful in structural characterization and in the assessment of the *trans* influence of X.

9) Since so many factors appear to influence ^{31}P shifts, and since this study shows that both electronic and steric effects are important, detailed evaluation of the nature of the Co–P bond is not possible from ^{31}P NMR shifts.

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