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Phosphorus Ligand Size. Synthesis and Spectral Characterization of Cobaloxime Complexes Containing Phosphorus Ligands Which Are Systematically Varied Both Sterically and Electronically

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The methods involved in obtaining the ^{1}H NMR spectra of 21 complexes of the type $LCo(DH)_2CH_3OH^+$ are described (DH = monoanion of dimethylglyoxime and L = phosphorus ligands of varying size and electronic properties). The chemical shift of the methanol methyl resonance is sensitive to the steric bulk of L. The use of the spectral data to obtain a measure of the size of the phosphorus ligands is described. The "mechanism" whereby the size of the ligand influences shift is probed by a calculation based on the magnetic anisotropy of the C=N bonds of the DH ligand. Although the calculation gives reasonable steric sizes (calculated cone angles, CCA), a high anisotropy or a large geometric distortion is required. An alternative explanation, that the changes in shifts result from changes in the magnetic anisotropy of cobalt, accounts for the data, but current theory is inadequate to test this mechanism with a calculation. The methanol methyl resonance is split by the phosphorus in the trans position. The dependence of this splitting on the electronic properties of L is discussed briefly.

The assessment of the importance of ligand steric properties in influencing (1) the conformation of other ligands in the coordination sphere, (2) reaction rates, (3) the electronic properties and geometry of the metal center, (4) complex stability, (5) the reaction of coordinated ligands, (6) stereoselectivity, etc., has not, with a few notable exceptions,[1,2] been very successful. This general lack of progress results in large measure from the difficulty involved in determining the bulk dynamic steric properties of ligands, separately from electronic influences. By bulk dynamic steric properties, we mean the steric effects averaged over all rotational, vibrational, etc., conformations of the ligand, weighted by the percentage of each conformer.

Molecular models have served chemists as a useful albeit qualitative guide to steric interactions. More recently, computer-assisted calculation of the conformation of polyaminecobalt(III) complexes has led to some quantitatively accurate predictions of both geometry and the relative stability of isomers.[1] These studies have not been used to generate a steric scale which may readily be transferred to other systems.

Tolman's concept of the cone angle,[2,3] which is based on measurements of molecular models, is probably the most successful general application of steric considerations to transition metal solution chemistry. The cone angle refers to the size of phosphorus ligands and was defined as "the apex angle of a minimum cone, centered 2.28 Å away from P and just touching the outermost atoms of the ligand at their van der Waals radii". Applications of this steric parameter have been summarized previously.[3,4]

The study to be reported here details a steric phenomenon which appears to be unaccompanied by any appreciable electronic effects. This study developed from our finding that the methanol methyl resonance in the complex, $(n\text{-}C_4H_9)_3PCo(DH)_2(CH_3OH)^+$ (DH = monoanion of dimethylglyoxime), was observable upfield to that of CH_3OH solvent. At the time this observation was made, the difference in chemical shifts between coordinated and free ligands in axial positions of cobaloxime complexes (e.g., those with the $Co(DH)_2$ moiety) had been attributed to the magnetic anisotropy of the DH moiety.[5] Also Cotton and Norman had shown that in related Rh complexes the DH moieties could be distorted out of the plane away from bulky ligands such as triphenylphosphine.[6] It seemed realistic to hope that the shift of the methanol methyl resonance might be a measure of the size of the ligand, L, in $LCo(DH)_2(CH_3OH)^+$ complexes.

Current evidence[7] suggests that the shift trends in cobaloxime complexes result from electronically induced changes in the magnetic anisotropy of cobalt, *not* changes in the proximity of the axial ligand hydrogens to the anisotropic DH ligands. We believe that the large upfield shift of the methanol resonance is caused by the magnetic anisotropy of cobalt.[4] In this paper, factors which may be responsible for the *changes* in the shift of the upfield resonance as L is changed are considered and synthetic procedures, which should be useful in assessing steric properties of new ligands, are given.

Results

In some cases, dissolution of $LCo(DH)_2Cl$ complexes in methanol will generate small amounts of the solvolyzed complex $LCo(DH)_2(CH_3OH)^+$. However, we found that high percentages of the methanol complexes could be achieved only in the absence of chloride. Our initial plan was to prepare the aquo complex, as the perchlorate or nitrate salts, but these salts would not always crystallize. Recognizing that many phosphorus ligands would be available in small quantities or would be expensive, we compared the results of using isolated salts with results obtained by formation of the solvolyzed complex in methanol. This species was generated by treatment of the chloro complex with $AgNO_3$. The shifts obtained in both cases were identical.

Problems may be expected in the synthesis of complexes of ligands with small size[2-4] and good electron donor ability.[8-10] Such ligands, like $(CH_3)_3P$, tend to form disubstituted products, $[L_2Co(DH)_2]Cl$. These products have characteristic triplet oxime methyl ^{1}H NMR signals, and their formation can be minimized by the slow addition of 1 mol of the ligand/mol of cobalt in the synthetic reaction (such as the substitution of $(C_6H_5)_3P$ in $(C_6H_5)_3PCo(DH)_2Cl$). However, if the presence of the disubstituted product cannot be avoided, the characteristic triplet does not interfere in the measurement of the coordinated methanol resonance.

Obviously, sterically hindered ligands also created problems, since these coordinated only with difficulty. Complexes of such ligands tend to decompose readily and should be stored in the cold. None of the complexes are air sensitive. Attempts to prepare complexes of tri-*o*-tolylphosphine and of trineopentylphosphine (a generous gift of Dr. R. B. King) were not successful.

Complete details of the ^{1}H NMR spectra of the methanol complexes (examples of which are given in Figure 1) were presented in an earlier report except for the complexes of a
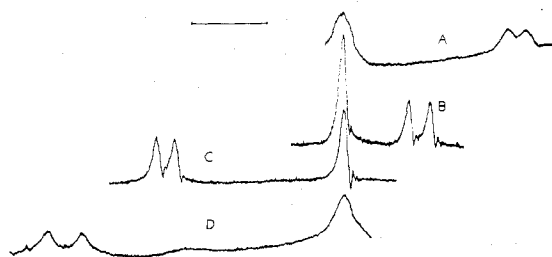
Figure 1. The ^{1}H NMR signal (doublet) of the methyl group of coordinated methanol of $LCo(DH)_2(CH_3OH)$, where L = $(C_6H_{11})_3P$ (A), $(C_6H_5)_3P$ (B), $(n\text{-}C_4H_9)_3P$ (C), and $(C_2H_5O)_3P$ (D). The spectra were recorded on a Varian HA-100 instrument at scale expansion of 1 Hz/cm. The bar in the figure is 5 Hz long. The singlet resonance is caused by the ^{13}C satellite of the solvent.

Table I. H^1 Spectral Data for $[LCo(DH)_2(CH_3OH)]^+$ Complexes[a]

|	RR'$_2$P	CH$_3$OH shift, τ (J_{PH}, Hz)	Oxime methyl shift, τ (J_{PH}, Hz)	pK_a[9]	$\Sigma\chi$[8]
1	(c-C$_6$H$_{11}$)$_3$P*	7.460 (1.1)	7.51 (0.5)	9.70	0.3
2	(i-C$_3$H$_7$)$_3$P*	7.420 (0.9)	7.52 (0.5)	7.97	3.0
3	(C$_6$H$_5$)$_3$P*	7.395 (1.5)	7.83 (0.8)	2.73	12.9
4	(n-C$_4$H$_9$)(C$_6$H$_5$)$_2$P	7.310 (1.3)	7.89 (0.7)		10.0
5	(C$_2$H$_5$)(C$_6$H$_5$)$_2$P	7.310 (1.3)	7.90 (0.7)		10.4
6	(CH$_3$)(C$_6$H$_5$)$_2$P	7.265 (1.4)	7.95 (0.7)	4.6	11.2
7	(C$_6$H$_5$CH$_2$)$_3$P	7.255 (1.3)	7.71 (0.6)		10.1
8	(CH$_3$O)(C$_6$H$_5$)$_2$P	7.250 (1.6)	7.90 (0.7)		16.3
9	(2-(CN)C$_2$H$_4$)$_3$P*	7.245 (1.5)	7.47 (0.8)	1.36	21.9
10	(o-CH$_3$C$_6$H$_4$O)$_3$P	7.240 (2.7)	7.90 (0.6)		28.2
11	(o-i-C$_3$H$_7$C$_6$H$_4$O)$_3$P	7.240 (2.7)	7.89 (0.6)		
12	(n-C$_4$H$_9$)$_3$P*	7.230 (1.2)	7.56 (0.8)	8.43	4.2
13	(CH$_3$)$_2$(C$_6$H$_5$)P	7.200 (1.3)	7.81 (0.7)	6.50	9.5
14	(CH$_3$O)$_2$(C$_6$H$_5$)P	7.200 (2.0)	7.79 (0.5)		19.7
15	(i-C$_3$H$_7$O)$_3$P*	7.180 (2.2)	7.59 (0.5)	3.4	18.9
16	(C$_6$H$_5$O)$_3$P*	7.170 (2.8)	7.78 (0.5)		29.1
17	(CH$_3$)$_3$P	7.145 (1.0)	7.59 (0.6)	8.65	7.8
18	C$_2$H$_5$(CH$_2$O)$_3$P	7.155 (2.7)	7.59 (0.5)		30.6
19	(CH$_3$O)$_3$P	7.150 (2.3)	7.58 (0.5)		23.1
20	(C$_2$H$_5$O)$_3$P	7.150 (2.2)	7.59 (0.5)		20.4
21	(ClC$_2$H$_4$O)$_3$P	7.150 (2.6)	7.56 (0.4)		27.9

[a] See ref 4 for additional details. J_{PH} values reported earlier[4] were remeasured in view of the correlation observed in Figure 3.

few ligands which had spectral properties identical or nearly identical with the spectral properties of other ligands. These spectral properties are now detailed completely in Table I, except for the resonances of the coordinated phosphorus ligands. These resonances did not differ greatly from those of the parent chloro complexes and details concerning all the resonances of these chloro complexes are given in the Experimental Section.

Tolman has investigated the influence of an extensive number of phosphorus ligands on the ν(CO) of LNi(CO)$_3$ (A mode, cm^{-1}).[8] A value, $\Sigma\chi$, can be assigned to each ligand, L, which reflects the difference between ν(CO) of (t-Bu)$_3$PNi(CO)$_3$ and LNi(CO)$_3$. The factors which determine the $\Sigma\chi$ value are not completely understood, but electron-withdrawing substituents on P lead to increased values of $\Sigma\chi$. We have used these values to compare the methanol methyl chemical shift (Figure 2) and the coupling of this resonance to the trans phosphorus (Figure 3).

Discussion

The conclusion[4] that the methanol chemical shift depends on trans ligand steric properties relies on two important aspects of the influence, in this case, of the phosphorus ligand on the cobaloxime methanol moiety: (1) the inability of the electronically different but sterically similar phosphorus ligands to induce significant differences in shifts and (2) the ability of some phosphorus ligands to distort the geometry of the complex. It is also of importance that a "mechanism" exists
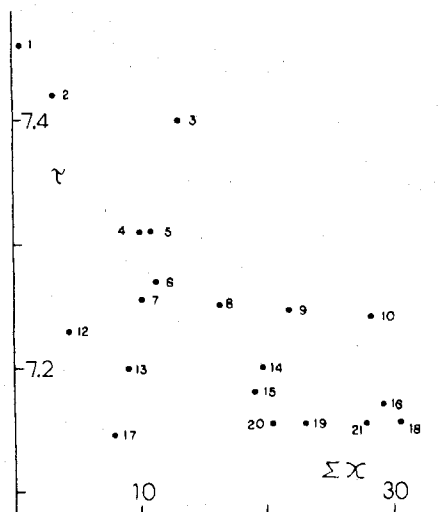
Figure 2. Plot of the chemical shift of the methyl resonance of the coordinated methanol in $[LCo(DH)_2CH_3OH]^+$ vs. Tolman's $\Sigma\chi$[8] (cm^{-1}). Numbers correspond to ligands in Table I and II. No value for $\Sigma\chi$ is available for 11.
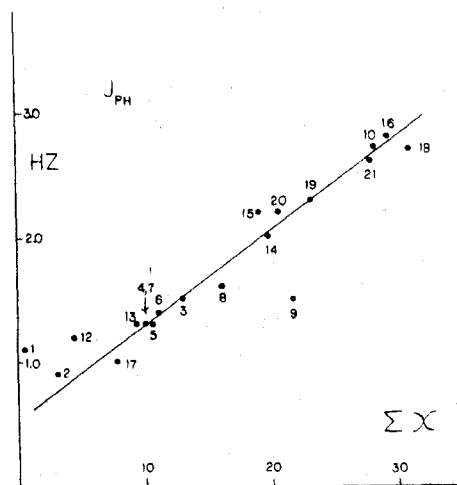
Figure 3. Plot of the PH coupling (Hz) of the methyl resonance of the coordinated methanol in $[LCo(DH)_2OH_3OH]^+$ vs. Tolman's $\Sigma\chi$[8] (cm^{-1}). Numbers correspond to ligands in Table I and II. No value for $\Sigma\chi$ is available for 11.

which allows this geometric distortion to influence shifts.

The Importance of the Electronic Effects of L. Several aspects of our ^{1}H NMR data, in addition to the complete lack of correlation between shift and electronic properties,[4] lead us to believe that electronic effects are negligible (see Figure 2). For ligands which have small cone angles (Table II) and therefore have little steric influence on geometry, all of the shifts of the coordinated methanol occur at essentially the same τ value (Table I). However, the electronic properties of these ligands vary as widely as any we have studied. Not only are these small cone angle ligands different in several common scales of electronic properties ($\Sigma\chi^8$ and pK_a,[9] Table I), but (CH$_3$)$_3$P is the best coordinating ligand toward cobaloximes and CH$_3$CH$_2$C(CH$_2$O)$_3$P among the worst of the ligands we have studied. Ligands of similar electronic properties but widely different size, such as trimethylphosphine and tricyclohexylphosphine, induce shifts at the opposite extremes of our series. Finally, ligands which have similar sizes but which are electronically different—tri-2-cyanoethylphosphine and tri-n-butylphosphine—induce similar methanol shifts (Table I).

We believe that the *electronic* influence of ligands on the ^{1}H NMR spectra of LCo(DH)$_2$X complexes results from

Table II. Comparison of Derived Cone Angles with Input Cone Angles

	RR'$_2$P	ECA^a	CCA	Input
1	(c-C$_6$H$_{11}$)$_3$P*	173	171	179
2	(i-C$_3$H$_7$)$_3$P*	164	164	160
3	(C$_6$H$_5$)$_3$P*	159	160	155
4	(n-C$_4$H$_9$)(C$_6$H$_5$)$_2$P	140	145	140
5	(C$_2$H$_5$)(C$_6$H$_5$)$_2$P	140	145	141
6	(CH$_3$)(C$_6$H$_5$)$_2$P	132	137	136
7	(C$_6$H$_5$CH$_2$)$_3$P	130	136	165
8	(CH$_3$O)(C$_6$H$_5$)$_2$P	129	134	132
9	(2-(CN)C$_2$H$_4$)$_3$P*	129	134	130
10	(o-CH$_3$C$_6$H$_4$O)$_3$P	128	133	133
11	(o-i-C$_3$H$_7$C$_6$H$_4$O)$_3$P	128	132	148
12	(n-C$_4$H$_9$)$_3$P*	127	131	130
13	(CH$_3$)$_2$(C$_6$H$_5$)P	125	125	127
14	(CH$_3$O)$_2$(C$_6$H$_5$)P	125	125	120
15	(i-C$_3$H$_7$O)$_3$P*	124	121	122
16	(C$_6$H$_5$O)$_3$P*	123	119	121
17	(CH$_3$)$_3$P	<117	<115	118
18	C$_2$H$_5$(CH$_2$O)$_3$P	<117	<115	101
19	(CH$_3$O)$_3$P	<117	<115	107
20	(C$_2$H$_5$O)$_3$P	<117	<115	109
21	(ClC$_2$H$_4$O)$_3$P	<117	<115	110

^{a} C. E. Weatherburn, "Mathematical Statistics", Cambridge University Press, New York, N.Y., 1968, pp 99–105.

changes in the magnetic anisotropy of cobalt.[7] The most important feature of X which influenced the anisotropy was the donor atom.[7] For ligands with the same donor atom rather drastic changes must be made in the nature of X in order to make an appreciable difference in the proton shifts of the LCo(DH)$_2$ moiety. Such disparate ligands as cyano and methyl led to differences in shift of the oxime methyl resonance of only 0.14 ppm (trans ligand, 4-*tert*-butylpyridine). Therefore, little difference in shifts between electronically similar phosphines can be expected. The difference between the oxime methyl resonance shifts of the trimethylphosphine and tricyclohexylphosphine complexes is −0.08 ppm. This difference is much too large and is of the wrong direction to be attributed to the electronic influence of these ligands on the anisotropy of cobalt.

That the magnetic anisotropy of cobalt can be the dominant factor in causing differences in proton shifts rests on some theoretical foundation.[11–13] A comparison of the data for cobaloxime complexes with data for platinum complexes[14] led us to conclude[7] that electronically different ligands required different states of rehybridization of the cobalt in order to achieve maximum bonding efficiency. Such rehybridization would in turn change the magnetic anisotropy of cobalt. This aspect of our interpretation does have some theoretical basis but the analogy to other systems[14] is quite close. Thus, variation in the coupling constant between the coordinated phosphorus and the oxime methyl hydrogens in (n-C$_4$H$_9$)$_3$PCo(DH)$_2$X complexes could be taken as a measure of the rehybridization of cobalt. Ordinarily coupling between so many bonds (five) would not be interpretable. The similarity of the coupling constants to those of phosphorus of the methanol methyl hydrogens of the trialkylphosphine–methanol complexes (1.1 ± 0.2 Hz) and the analogous similarity in coupling of P with the oxime methyl hydrogens (0.6 ± 0.2 Hz) suggest that little rehybridization is taking place throughout the series. This view is in keeping with the absence of an electronic effect of the P donor ligand. Furthermore, LaRossa and Brown[15] have found that phosphite and phosphine ligands have rather similar influences on the NQR and NMR spectra of [59]Co in alkylcobaloximes. Also, the bonding mode of SCN in cobaloximes is similarly influenced by phosphines and by phosphites.[16]

As opposed to the complete lack of correlation of the shift of the methanol resonance with $\sum\chi$[8] (Figure 2), a remarkably

good correlation is found between coupling constant for this resonance with phosphorus and the $\sum\chi$ for L (Figure 3). It is our belief that there is no appreciable rehybridization at cobalt in this series and we believe that the variation in the coupling constant reflects primarily the hybridization of the phosphorus in L(PR$_3$).[17] Structural evidence suggests that the hybridization at phosphorus is not very dependent on the nature of the trans ligand.[18] The phosphorus hybridization is influenced primarily by the nature and hybridization of the atom in R which is attached directly to P. The inductive effect of R will also be important. Tolman[8] noted that $\sum\chi$ correlated well with the inductive effect of R on proton acidities (Kabachnik's σ parameters).[19] It is not clear whether such inductive effects will exactly parallel the ability of the R groups to rehybridize phosphorus. Close examination of our data in fact suggests to us that such a relationship may not hold. For example, tris(2-cyanoethyl)phosphine falls well to the right of the line drawn in Figure 3, and tricyclohexylphosphine falls to the left of the line. The coupling constants for simple trialkylphosphine complexes do not vary much, but $\sum\chi$ for these ligands varies appreciably. A less pronounced trend can be observed for the trialkyl phosphite complexes. We would like to suggest that perhaps the $\sum\chi$ values are rather sensitive to the overall inductive effect of L, measuring, perhaps, the flow of electron density toward the metal and hence into the carbonyl π orbitals. The coupling constants measured here are then a less sensitive function of such inductive effects and are more reflective of the nature of the atom on R which is attached to phosphorus.

The division of ligand effects into two such categories is crude but agrees with more general conclusions reached by Appleton, Clark, and Manzer.[14] Furthermore, it is implied in their analysis that vibrational frequencies would depend on both effects whereas coupling constants would depend primarily on orbital hybridization. The results presented here would, then, tend to support the proposals of these authors. Additionally, Bodner[20] has shown that, in LNi(CO)$_3$ compounds, a good correlation exists between ^{13}C chemical shifts and Kabachnik's σ parameter.

Steric Effect of L. We believe that the variation in chemical shifts of the methanol resonances of these complexes reflects primarily a steric effect of L.[4] Three approaches can be used to establish a steric scale. These are (1) use the shift values, (2) empirically correlate the shifts to a physical or molecular model, and (3) determine the "mechanism" of the shifts and set up the appropriate equations to calculate a steric parameter. The first approach requires no further elaboration except to say that it is probably the best approach and suffers only from the inability to rank small ligands. Such small ligands, however, are usually expected to be sterically least important. We have considered both the second and third approach. These approaches overcome the problem of ranking small ligands and the third approach provides some insight into the origins of the shift phenomenon. These approaches both require input cone angles.

Input Cone Angles. Input parameters were derived from Tolman's published values.[2,3] During the course of our studies, Tolman[3] reported that the cone angles in the original paper were measured on models in a strained configuration. Our early studies had tended to adjust the cone angles away from these strained values. Tolman reported a set of unstrained values. These were now larger than our early results. Therefore, we chose cone angles which were intermediate between the strained and unstrained configurations, when the two angles were given or could be estimated from ref 3.

These intermediate values or Tolman's original values are given in Table II and are referred to here as TCA. It is important to note that, in the calculations to be described, the
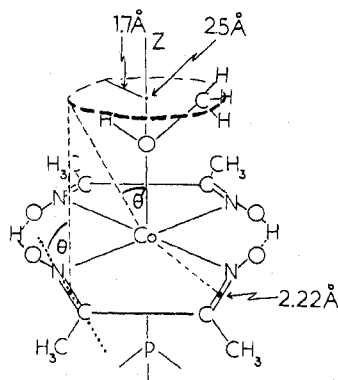
Figure 4. Figure depicting the pertinent angles and distances used in calculations and referred to in the Discussion. The two different θ values represent placement of the point dipole in the C=N bond, θ, and placement of the point dipole at cobalt, θ'.

calculated cone angle for a ligand is only indirectly related to the TCA of that ligand. Rather, the TCA of all ligands used in the scaling calculations (ligands used are starred) influenced the values of the calculated cone angles of *all* ligands. However, this influence is greatest for ligands of similar size. Tris(2-cyanoethyl)phosphine was not studied by Tolman and we estimated the cone angle as similar to that of tri-*n*-butylphosphine. The values for triphenylphosphine found early in our studies were not in agreement with TCA = 145° and the input value we used was 155°.

Mechanistic Approach. We have considered two mechanisms by which the methanol methyl resonance is dependent on the size of the phosphorus ligand. Both explanations involve anisotropic effects and changes in the planarity of the Co(DH)$_2$ moiety, Figure 4. The first assumes that the changes in the influence of the anisotropic DH groups on the shift are responsible for the trends observed. The second assumes that sterically induced *changes* in the anisotropy of cobalt are responsible for the changes in shift. Note that *even without steric distortion* of the Co(DH)$_2$ moiety, we believe that the upfield position of the methanol resonances is caused by the magnetic anisotropy of cobalt.[7]

Our initial hypothesis for the mechanism of the shift centered on the possibility that the DH ligands, which are anisotropic, approached the methanol methyl group as the complex geometry was distorted. The principal evidence for this shift mechanism is that a semiempirical calculation of the dependence of shift on cone angle gives remarkably good agreement. The four C=N bonds (Figure 4) were assumed anisotropic in magnetic susceptibility. These were treated as point dipoles placed at a distance (R_D) of 2.22 Å from cobalt using crystallographic data (direction given by the unit vector 0.5422, 0.8402, and 0.0 in a right-handed orthogonal coordinate system centered at cobalt). When appropriate, allowance was made for the presence of four such dipoles. For a Co–O bond length of 1.95 Å, the average position of the hydrogens of the methyl group rotates in a circle 1.7 Å in the *xy* plane with $z = 2.5$ Å. The geometric factor $(1 - 3\cos^2\theta)/R^3$ for a point dipole was averaged over this circle by numerical integration and a value of 1.822×10^{-2} Å^{-3} was obtained. Two solutions with $R_0 = 3.79$ and 2.80 Å corresponded to this average shielding factor. These radii were used in a least-squares fit of eq 1. Implicit in this equation is the

$$\tau_{CH_3} = \text{slope} \times \frac{1 - 3\cos^2\theta_0}{[R_0 - k\phi R_D]^3} + \text{intercept} \quad (1)$$

assumption that the distance R_0 between the methyl hydrogens and the point dipole at the C=N bond decreases linearly with increasing ϕ, the difference between TCA and 118° (the angle at which steric effects are no longer observed). The angle θ

has its usual significance and k is a scaling constant. The denominator is of the approximate form[21] for the expected decrease in R induced by a folding of the Co(DH)$_2$ moiety, since the approximation $k\phi = \sin k\phi$ holds well ($k\phi < 0.25$ radian).

A value of $k = 0.079$ was used since this value corresponds to the 6° angle between the planes of the DH ligands for the (C$_6$H$_5$)$_3$P complex. This angle was found crystallographically for (C$_6$H$_5$)$_3$PCo(DH)$_2$Cl.[22] Calculated cone angles, however, were not very sensitive to k, nor for that matter to R.[21] The least-squares fit gave correlation coefficients of 0.977 and 0.979 for $R = 2.80$ and 3.79 Å, respectively. The calculated cone angles, CCA, are given in Table II and agree to within ±1° for the two R_0 values.

The slopes of the lines allowed calculation of the magnetic anisotropy of a single C=N group. For $R_0 = 2.80$ and 3.79 Å, the values obtained were $(1.27 \pm 0.25) \times 10^{-27}$ and $(3.66 \pm 0.75) \times 10^{-26}$ cm^3/molecule, respectively. These values are several orders of magnitude greater than accepted anisotropies for other double bonds such as C=O[23] and are even larger than that for benzene.[13] No value for C=N is available.[24] This calculation is only approximate, but it suggests that the anisotropy of the DH ligand is not an important contributor to the chemical shift trend, unless large distortions in the planar moiety can occur.

As noted above, good correlations were observed between shift and TCA for a wide range of k and R values. This observation suggests that the functional form of the equation may reflect physical reality or, at the least, that the equation is a good functional empirical expression. In any case, the cone angles derived by either this or the empirical procedure to be described below are quite similar (Table II).

We believe it is likely that the anisotropy at cobalt will change as the Co(DH)$_2$ geometry is distorted. There is at present no theoretical model to test this point. We feel it is possible that the entire variation in the methanol shifts reflects a change in the anisotropy of the central cobalt. The main experimental support for this mechanism is the concomitant decrease in shift of the oxime methyl resonance with increase in shift of the methanol resonance. This change is consistent with the location of the point dipole at cobalt. The oxime methyl group is less likely to change its position relative to the point dipole centered at the C=N of the DH ligand. Neither model can be entirely ruled out at this time nor can a combination of effects be ruled out. We therefore decided to explore an empirical expression which assumes no mechanism.

Empirical Approach. The method used was to fit expression 2 with the left-hand side of the equation equal to the TCA

$$\text{ECA} = \sum_{i=1}^{4} C_i \left(1.0 - \frac{0.15}{(\tau - 7.0)}\right)^{i-1} \quad (2)$$

of the starred ligands by the method of least squares. This yields values of the constants C_1 to C_4 equal to 116.7, 81.6, -310.9, and 465.4, respectively. By substitution of the shift values determined experimentally into eq 2 and using these constants, one can calculate the ECA for all ligands, not only the ones employed in the original fit. Again the values of all the starred ligands influence the ECA of every ligand.

It is interesting to note that both the empirical fit and the fit based on the DH anisotropy model suggest that the angle of 145° for triphenylphosphine is too low. If in either method of calculation, the values of TCA were to change, then new values would be obtained by our approaches. In particular, if the input value of 179 for tricyclohexylphosphine were to be lowered, then the discrepancy noted for triphenylphosphine would decrease. For complexes with methanol shifts close to τ 7.15, the empirical expression must be used with caution since small errors in shift measurements can be very important.

Comparison of Methods Used to Obtain Steric Parameters. The cone angles reported by Tolman reflect a dynamic (rotational) situation in that a solid cone is defined. The major uncertainty is in the definition of the conformation of the phosphorus ligand. Also Tolman's method does not allow for the geometry of the metal and the other ligands or for the effect of interligand interactions on the conformation. Other applicable techniques such as X-ray crystallography and conformational analysis could, in principle, overcome this problem and yield atomic parameters for (usually) the most stable conformer. From such data a cone could be calculated. During rotation about the M–P bond, the conformation of the ligand is likely to change. Insofar as our method yields an average value, these problems are not a limitation.

There are no topologically unusual features in the planar cobaloxime moiety which should limit the generality of these steric parameters. There are, unfortunately, very few quantitative data in the literature with which to test our angles. We noted earlier[4] that the parameters obtained can be used to explain the dependence on L of NiL_4 stability constants.[3] Most other applications of cone angles have dealt with qualitative observations or have involved phenomena in which electronic effects of the phosphine ligand were also very important. We believe that inorganic chemical phenomena will usually be dominated by electronic effects of ligands and that observations such as those reported here and by Tolman[2,3] will continue to be uncommon. Nevertheless, several applications of cone angles or observations of the importance of phosphorus ligand size have been published since the writing of our previous report,[25] and, additionally, steric factors are most likely to be important in inorganic systems where usually large groups are attached to the central atoms and where bond energies tend to be smaller than in more "covalent" compounds. It is conceivable that careful investigation of the variation in coupling constants and stretching frequencies in large series of phosphorus ligand complexes may provide further insight into the relative importance of σ and π bonding in the M–P bond.

Experimental Section

Warning! Some of these phosphorus ligands are toxic and/or pyrophoric and caution should be exercised! Perchlorate salts may be explosive and detonate on heating.

Materials. Solvents acetone, methanol, toluene, chloroform, and methylene chloride were reagent grade and used without further purification. Phosphorus ligands purchased were as follows: P-(n-C_4H_9)$_3$, P(2-(CN)-C_2H_4)$_3$, P(OCH$_3$)$_3$, P(OC$_2H_5$)$_3$, P(O-i-C_3H_7)$_3$, P(OC$_6H_5$)$_3$, and P(O-2-Cl-C_2H_4)$_3$ (Aldrich); P(OCH$_2$)$_3$CC$_2H_5$, P(c-C_6H_{11})$_3$, P(C_6H_5)$_3$, P(i-C_3H_7)$_3$, P(n-C_4H_9)(C_6H_5)$_2$, P(C-H$_3$)$_2$(C_6H_5), P(C_2H_5)(C_6H_5)$_2$, P(OCH$_3$)$_2$(C_6H_5), and P(OC-H$_3$)(C_6H_5)$_2$ (Strem); P(CH$_3$)(C_6H_5)$_2$ (Research Organic/Inorganic). The ligands P(CH$_3$)$_3$, P(O-o-(CH$_3$)C_6H_4)$_3$, P(O-o-(i-C_3H_7)C_6H_4)$_3$, and P(CH$_2C_6H_5$)$_3$ were generous gifts of Dr. C. A. Tolman. Preparations with the phosphorus donors P(CH$_3$)$_3$, P(i-C_3H_7)$_3$, P(CH$_3$)$_2$(C_6H_5)$_3$, P(CH$_3$)(C_6H_5)$_2$, P(OCH$_3$)(C_6H_5)$_2$, and P(OC-H$_3$)$_2$(C_6H_5) were done with degassed solvents under a dry N$_2$ atmosphere. The other phosphorus donors could withstand limited exposure to the atmosphere with no deleterious effects on the preparations.

Spectral Measurements. Ir spectra were recorded as KBr disks on a PE 457 grating instrument with polystyrene (1028 and 1601 cm^{-1}) calibrant. ^{1}H NMR spectra of PRR'$_2$Co(DH)$_2$Cl compounds were recorded on a Varian A-60 spectrometer (28°C), in CH$_2$Cl$_2$ relative to TMS. ^{1}H NMR spectral data for the methanol complexes PRR'$_2$Co(DH)$_2$O(H)CH$_3^+$, in reagent grade methanol, were taken on a Varian HA-100 spectrometer (23°C, 8% TMS reference, and internal lock signal) in the frequency sweep mode. Chemical shifts were insensitive to both concentration (0.02–0.1 M) and traces of water and acid (but not base) and reproducible (±0.01) with a JEOL MH-100 or Varian A-60 instrument (the latter was used to ensure that no complex resonance was obscured by the ^{13}C-induced satellite of the solvent CH$_3$OH). Coupling constants for the methanol

complexes, determined at expanded scale, are reproducible to ±0.2 Hz. Methanol complexes were generated either by dissolving [PRR'$_2$Co(DH)$_2$(H$_2$O)]NO$_3$ in methanol or by treating 0.2 mmol of PRR'$_2$Co(DH)$_2$Cl with 0.24 mmol of AgNO$_3$ in 10 ml of methanol and stirring for 1–2 hr in a warm water bath. After filtration, the solvent was removed and 1.7 ml of absolute methanol added. This solution (1 ml) was transferred to an NMR tube and TMS was added (8% solution). At this point, traces of silver salts precipitated. After 1 hr, the clear solution was decanted into another NMR tube and the ^{1}H NMR spectrum was recorded. The second procedure produced an ^{1}H NMR spectrum identical with that obtained by dissolving the corresponding aquonitrate salt in methanol, when such comparisons were possible.

Preparations. **P(OC$_6H_5$)$_3$Co(DH)$_2$Cl.** A mixture of tri-n-butylamine (6.6 ml, 28 mmol) and Co(DH)(DH$_2$)Cl$_2$ (10.0 g, 28 mmol) in 400 ml of CHCl$_3$ was stirred (5 min) and P(OC$_6H_5$)$_3$ (11.1 ml, 35 mmol) was added. After continued stirring (1 hr) the solution was filtered and extracted with four 100-ml portions of distilled water. (Note: the first two water washings were intensely dark and separation of the two liquid phases was difficult.) The CHCl$_3$ was evaporated (vacuum) and the oily residue was dissolved in the minimum amount of CH$_2$Cl$_2$. After filtration, CH$_2$Cl$_2$ was added (final volume 150 ml) and then toluene (150 ml) was added. Evaporation of the solution (to ca. 125 ml) afforded orange crystals; yield 76%. The crystals were washed with toluene and ether. Ir: 358 cm^{-1} (Co—Cl), 1560 cm^{-1} (C=N), 1243 and 1093 cm^{-1} (N—O stretch and bend). ^{1}H NMR (CH$_2$Cl$_2$): τ 7.96 (d, 4, J_{P-H} = 1.8 Hz, (DH)$_2$), τ 2.99 (m, 3, (OC$_6H_5$)), τ 3.11 (m, 2, (o-OC$_6H_5$)). Anal. Calcd for C$_{26}$H$_{29}$CoClN$_4$O$_7$P: C, 49.19; H, 4.60; Co, 9.28. Found: C, 49.5; H, 4.58; Co, 9.2.

P(O-o-(CH$_3$)C_6H_4)$_3$Co(DH)$_2$Cl. This complex was prepared in the same manner as the corresponding P(OC$_6H_5$)$_3$ derivative except for the isolation procedure. After the water washings the CHCl$_3$ layer was taken to dryness (reduced pressure) and the residue was dissolved in methanol (ca. 35 ml). After filtration, water was added slowly, and the golden powder, which separated, was collected (55% yield), washed with ether, and dried in vacuo. ^{1}H NMR: τ 8.05 (d, 12, J_{P-H} = 1.7 Hz, (DH)$_2$), τ 7.80 (s, 9, o-CH$_3$), τ 2.90–3.06 (m, 12, C$_6H_4$). Anal. Calcd for C$_{29}$H$_{35}$CoClN$_4$O$_7$P: C, 51.45; H, 5.21; Co, 8.70. Found: C, 51.4; H, 5.21; Co, 9.11.

P(O-o-(i-C_3H_7)C_6H_4)$_3$Co(DH)$_2$Cl. This preparation was the same as that for the corresponding P(O-o-(CH$_3$)C_6H_4)$_3$ complex. ^{1}H NMR: τ 8.06 (d, 12, J_{P-H} = 1.8 Hz, (DH)$_2$), τ 8.87 (d, 18, J = 7 Hz, o-(i-C_3H_7)). Anal. Calcd for C$_{35}$H$_{47}$CoClN$_4$O$_7$P: C, 55.23; H, 6.22; Co, 7.74. Found: C, 55.2; H, 6.65; Co, 7.69.

P(c-C_6H_{11})$_3$Co(DH)$_2$Cl. Tricyclohexylphospine (3.0 g, 10.7 mmol) was added to a suspension of Co(DH)(DH$_2$)Cl$_2$ (1.91 g, 5.3 mmol) in 200 ml of CHCl$_3$. After refluxing the stirred solution (1.5 hr), the volume was reduced (to 100 ml). After filtration the CHCl$_3$ solution was extracted (with three 50-ml portions of distilled water) and ethanol (100 ml of 95%) was added. The solution volume was reduced (vacuum) until a brown powder formed. The product was sometimes contaminated with [HP(c-C_6H_{11})$_3$][Co(DH)$_2$Cl$_2$] and it must be recrystallized from toluene. Yields also varied from 25 to 75%. Anal. Calcd for C$_{26}$H$_{47}$CoClN$_4$O$_4$P: C, 51.61; H, 7.83; Co, 9.74. Found: C, 51.6; H, 7.66; Co, 9.48. ^{1}H NMR: τ 7.69 (d, 12, J_{P-H} = 1.3 Hz, (DH)$_2$), τ 8.11–9.05 (m, 33, (C$_6H_{11}$)$_3$). Ir: 340 cm^{-1} (Co-Cl), 1548 cm^{-1} (C=N), 1235 and 1085 cm^{-1} (N—O stretch and bend).

P(i-C_3H_7)$_3$Co(DH)$_2$Cl. The complex (2.0 g, 5.6 mmol), (CH$_3$-OH)Co(DH)$_2$Cl (prepared by the method of Ablov), was suspended in degassed 50:50 CH$_2$Cl$_2$–CH$_3$OH (20 ml) and P(i-C_3H_7)$_3$ (0.4 ml, ca. 3.0 mmol) added. The mixture was stirred in a nitrogen atmosphere for 1–2 hr. After filtration, the solution was reduced in volume (to 5 ml). Ether (ca. 150 ml) was added. The deep purple precipitate (33% yield), which was formed, was collected, washed with ether, and dried in vacuo. ^{1}H NMR: τ 7.68 (d, 12, J_{P-H} = 1.1 Hz, (DH)$_2$) τ 8.65–9.18 (m, 7, i-C_3H_7). Anal. Calcd for C$_{17}$H$_{35}$CoClN$_4$O$_4$P: C, 42.11; H, 7.23; Co, 12.16. Found: C, 41.8; H, 6.8; Co, 12.4.

PRR'$_2$Co(DH)$_2$Cl. Many complexes were most readily synthesized by the Co^{II}-catalyzed displacement of P(C_6H_5)$_3$ from P(C_6H_5)$_3$-Co(DH)$_2$Cl (samples of this complex have a sufficient amount of Co^{II} catalyst). The ligand-exchange reaction normally proceeds readily since P(C_6H_5)$_3$ is a good leaving ligand. To a solution of P(C$_6$-H$_5$)$_3$Co(DH)$_2$Cl (8.0 g, 13.6 mmol) in 50 ml of CH$_2$Cl$_2$ 16 mmol of PRR'$_2$ is added when PRR'$_2$ = P(OCH$_3$)$_3$, P(OC$_2H_5$)$_3$, P(O-

i-C₃H₇)₃, P(O-2-Cl-C₂H₄)₃, P(CH₂C₆H₅)₃, P(OCH₂)₃CC₂H₅, and P(OCH₃)₂(C₆H₅); however, when PRR'₂ = P(CH₃)(C₆H₅)₂, P-(n-C₄H₉)(C₆H₅)₂, P(C₂H₅)(C₆H₅)₂, and P(OCH₃)(C₆H₅)₂, only 13.6 mmol of PRR'₂ should be added, dropwise, or the disubstituted products (PRR'₂)₂Co(DH)₂⁺ are obtained. After 15 min, the solution was filtered to remove any solids and ether (50–250 ml) was slowly added. The precipitated product was collected and recrystallized from the minimum amount of CH₂Cl₂ (filtered) by adding ether (vide infra). Relevant data for each reaction are given below.

P(OCH₃)₃: yellow powder; 74% yield; ir 365 cm⁻¹ (Co–Cl), 1562 cm⁻¹ (C=N), 1242 and 1095 cm⁻¹ (N–O stretch and bend). ¹H NMR τ 7.72 (d, 4, J_{P-H} = 1.5 Hz, (DH)₂), τ 6.39 (d, 3, J_{P-H} = 11.0 Hz, (OCH₃)₃). Anal. Calcd for C₁₁H₂₃CoClN₄O₇P: C, 29.43; H, 5.17; Co, 13.14. Found: C, 29.5; H, 5.14; Co, 13.2.

P(OC₂H₅)₃: yellow-orange; yield 89%; ¹H NMR τ 7.76 (d, 4, J_{P-H} = 1.5 Hz, (DH)₂), τ 6.12 (m, 2, CH₂), τ 8.85 (t, 3, J = 7 Hz, OCCH₃). Anal. Calcd for C₁₄H₂₉CoClN₄O₇P: C, 34.26; H, 5.95; Co, 12.01. Found: C, 34.3; H, 6.20; Co, 12.1.

P(O-i-C₃H₇)₃: orange; 88% yield; ir 361 cm⁻¹ (Co–Cl), 1380 cm⁻¹ (i-Pr split), 1562 cm⁻¹ (C=N), 1245 and 1095 cm⁻¹ (N–O stretch and bend); ¹H NMR τ 7.75 (d, 4, J_{P-H} = 1.5 Hz, (DH)₂), τ 5.52 (m, 1, CH), τ 8.82 (d, 6, J = 6 Hz, OC(CH₃)₂). Anal. Calcd for C₁₇H₃₅CoClN₄O₇P: C, 38.32; H, 6.62; Co, 11.06. Found: C, 38.2; H, 6.44; Co, 11.35.

P(O-2-Cl-C₂H₄)₃: yellow; 58% yield; ir 361 cm⁻¹ (Co–Cl), 1548 cm⁻¹ (C=N), 1242 cm⁻¹ (N–O stretch); ¹H NMR τ 7.70 (d, 2, J = 1.3 Hz, (DH)₂), τ 5.90 (m, 1, OCH₂ or CH₂Cl), τ 6.48 (m, 1, OCH₂ or CH₂Cl). Anal. Calcd for C₁₄H₂₆CoCl₄N₄O₇P: C, 28.16; H, 4.89; Co, 9.87. Found: C, 28.6; H, 4.88; Co, 10.1.

P(CH₂C₆H₅)₃: orange; 86% yield; ¹H NMR τ 7.77 (d, 12, J_{P-H} = 1.3 Hz, (DH)₂), τ 7.15 (d, 6, J_{P-H} = 10 Hz, PCH₂–), τ 2.81 (m, 15, C₆H₅). Anal. Calcd for C₂₉H₃₅CoClN₄O₄P: C, 55.38; H, 5.61; Co, 9.37. Found: C, 55.0; H, 5.37; Co, 9.30.

P(OCH₂)₃CC₂H₅: orange; 79% yield; ir 372 cm⁻¹ (Co–Cl), 1565 cm⁻¹ (C=N), 1246 and 1097 cm⁻¹ (N–O stretch and bend); ¹H NMR τ 7.77 (d, 12, J_{P-H} = 1.8 Hz, (DH)₂), τ 5.77 (d, 6, J_{P-H} = 5 Hz, OCH₂), τ 8.76–9.30 (m, 5, C₂H₅). Anal. Calcd for C₁₄H₂₅CoClN₄O₇P: C, 34.58; H, 5.18; Co, 12.11. Found: C, 34.9; H, 4.97; Co, 12.2.

P(OCH₃)₂(C₆H₅): brown; 58% yield; ir 352 or 362 cm⁻¹ (Co–Cl), 1561 cm⁻¹ (C=N), 1246 and 1094 cm⁻¹ (N–O stretch and bend); ¹H NMR τ 7.93 (d, 12, J_{P-H} = 1.5 Hz, (DH)₂), τ 6.37 (d, 6, J_{P-H} = 11 Hz, POCH₃), τ 2.57 (m, 5, C₆H₅). Anal. Calcd for C₁₆H₂₅CoClN₄O₆P: C, 38.84; H, 5.09; Co, 11.91. Found: C, 38.6; H, 5.06; Co, 11.5.

P(CH₃)(C₆H₅)₂: beige; 53% yield; ir 343 cm⁻¹ (Co–Cl), 1559 cm⁻¹ (C=N), 1241 and 1091 cm⁻¹ (N–O stretch and bend); ¹H NMR 8.13 (d, 12, J_{P-H} = 1.6 Hz, (DH)₂), 8.14 (d, 3, J_{P-H} = 11 Hz, PCH₃), 2.51 (m, 10, (C₆H₅)₂). Anal. Calcd for C₂₁H₂₇CoClN₄O₄P: C, 48.06; H, 5.18; Co, 11.23. Found: C, 48.0; H, 5.3; Co, 11.3.

P(C₂H₅)(C₆H₅)₂: green-gold; 46% yield; ir 349 cm⁻¹ (Co–Cl), 1552 cm⁻¹ (C=N), 1242 and 1090 cm⁻¹ (N–O stretch and bend); ¹H NMR (CH₂Cl₂) τ 8.08 (d, 12, J_{P-H} = 1.6 Hz, (DH)₂), τ 7.77 (m, 2, PCH₂), τ 9.25 (m, 3, PCCH₃), τ 2.51 (m, 10, (C₆H₅)₂). Anal. Calcd for C₂₂H₂₉CoClN₄O₄P: C, 49.04; H, 5.42; Co, 10.94. Found: C, 49.1; H, 5.10; Co, 10.9.

P(n-C₄H₉)(C₆H₅)₂: gold; 75% yield; ir 347 cm⁻¹ (Co–Cl), 1557 cm⁻¹ (C=N), 1242 and 1090 cm⁻¹ (N–O stretch and bend); ¹H NMR τ 8.05 (d, 12, J_{P-H} = 1.6 Hz, (DH)₂), τ 2.56 (m, 10, (C₆H₅)₂). Anal. Calcd for C₂₄H₃₃CoClN₄O₄P: C, 50.85; H, 5.86; Co, 10.39. Found: C, 51.1; H, 5.57; Co, 10.4.

P(OCH₃)(C₆H₅)₂: brown-green; 53% yield; ir 347 cm⁻¹ (Co–Cl), 1558 cm⁻¹ (C=N), 1245 and 1093 cm⁻¹ (N–O stretch and bend); ¹H NMR τ 8.05 (d, 12, J_{P-H} = 1.5 Hz, (DH)₂), τ 6.56 (d, 3, J_{P-H} = 11 Hz, POCH₃), τ 2.51 (m, 10, (C₆H₅)₂). Anal. Calcd for C₂₁H₂₉CoClN₄O₅P: C, 48.89; H, 5.04; Co, 10.92. Found: C, 48.8; H, 5.80; Co, 10.8.

P(2-(CN)-C₂H₄)₃Co(DH)₂Cl. The ligand, P(2-(CN)-C₂H₄)₃ (3.9 g; 20.0 mmol in 100 ml of CH₂Cl₂), was slowly added with stirring to a filtered solution of P(C₆H₅)₃Co(DH)₂Cl (10.0 g; 17.0 mmol in 500 ml of CH₂Cl₂). After ¹/₂ hr the yellow powder which formed was collected (94% yield) and washed with CH₂Cl₂ and ether and dried in vacuo. The product is extremely insoluble; however, the ¹H NMR spectrum of the corresponding aquonitrate salt is consistent with one phosphine ligand per cobalt. Ir: 2240 cm⁻¹ (C≡N), 343 cm⁻¹ (Co–Cl), 1551 cm⁻¹ (C=N), 1242 and 1094 cm⁻¹ (N–O

stretch and bend). Anal. Calcd for C₁₇H₂₉CoClN₇O₄P: C, 39.43; H, 5.06; Co, 12.31. Found: C, 39.3; H, 5.16; Co, 11.9.

P(CH₃)₃Co(DH)₂Cl. The ligand, P(CH₃)₃, displayed such a great tendency to form the disubstituted product (P(CH₃)₃)₂Co(DH)₂⁺ that analytically pure samples could not be prepared; however, the following procedure allowed preparation of the desired monosubstituted product in 90% purity. Identification of the sample by ¹H NMR spectra is unambiguous since the monosubstituted product has a doublet oxime methyl resonance whereas the disubstituted material has a triplet. Also the disubstituted impurity is innocuous since it is unreactive. To a solution of P(C₆H₅)₃Co(DH)₂Cl (5.1 mmol, 3.0 g) in 150 ml of CH₂Cl₂ (degassed) P(CH₃)₃ (0.42 ml, 4.2 mmol) was slowly added and the solution was stirred under a nitrogen atmosphere (15 min). Then 0.97 g (5.0 mmol) of P(2-(CN)-C₂H₄)₃ was added and stirring was continued (25 min). This procedure converted unreacted P(C₆H₅)₃Co(DH)₂Cl to insoluble P(2-(CN)-C₂H₄)₃Co(DH)₂Cl, which was removed by filtration. The filtrate was evaporated to dryness. The residue was redissolved in CH₂Cl₂ (25 ml) and the solution was filtered. Ether (ca. 5 ml) was slowly added and the initial impure precipitate discarded. The addition of more ether afforded an orange-yellow powder (1.35 g) which was collected and washed with ether and dried in vacuo. ¹H NMR for greater than 90% P(CH₃)₃Co(DH)₂Cl: τ 7.71 (d, J_{P-H} = 1.6 Hz (DH)₂), τ 9.01 (d, J_{P-H} = 1.3 Hz, PCH₃). ¹H NMR of the impurity (P-(CH₃)₃)₂Co(DH)₂Cl: τ 7.67 (t, J_{P-H} = 2.5 Hz, (DH)₂).

P(CH₃)₂(C₆H₅)Co(DH)₂Cl. This complex was synthesized analogously to the P(CH₃)₃ compound and because of its predilection to disubstitute was contaminated with the bis(phosphine) product. ¹H NMR: τ 7.95 (d, J_{P-H} = 1.5 Hz, (DH)₂), τ 8.61 (d, J_{P-H} = 13.5 Hz, PCH₃).

Other Chloro Complexes. These have been reported previously.

[P(2-(CN)-C₂H₄)₃Co(DH)₂OH₂]NO₃. Silver nitrate (3.4 g, 20.2 mmol) was added to a suspension of P(2-(CN)-C₂H₄)₃Co(DH)₂Cl (6.5 g, 12.6 mmol) in 60% H₂O–40% acetone (300 ml). The mixture was boiled (with stirring) until a flocculent precipitate of AgCl formed (1–2 hr). After filtration, the solution was evaporated under vacuum to 75 ml. Ethanol (95%, 75 ml) was added and the solution was filtered again. This solution yielded black crystals when it was allowed to evaporate to 10 ml. These crystals were collected and washed with ethanol and then ether. These were dissolved in a minimum amount of warm methanol. This solution was immediately filtered and rapidly evaporated to 100 ml. Distilled water (50 ml) was added. The solution was allowed to air evaporate (to 20 ml). The large black crystals formed were collected, washed sequentially with water, ethanol, and ether, and dried in vacuo (yield 3.8 g; 58%). Anal. Calcd for C₁₇H₂₈CoN₈O₈P: C, 36.31; H, 5.02; Co, 10.48. Found: C, 37.0; H, 4.93; Co, 10.5.

[LCo(DH)₂H₂O]NO₃ or LCo(DH)₂NO₃. These complexes were synthesized from the reaction of AgNO₃ with LCo(DH)₂Cl as previously described. Recrystallization was from methanol–water.

[P(CH₃)(C₆H₅)₂Co(DH)₂H₂O]NO₃: Anal. Calcd for C₂₁H₂₉CoN₅O₈P: C, 44.30; H, 5.13; Co, 10.35. Found: C, 44.5; H, 5.52; Co, 10.5; yield 90%.

[P(n-C₄H₉)(C₆H₅)₂Co(DH)₂H₂O]NO₃: Anal. Calcd for C₂₄H₃₅CoN₅O₈P: Co, 9.64. Found: Co, 9.4; yield 90%.

[P(OCH₃)(C₆H₅)₂Co(DH)₂H₂O]NO₃·3H₂O: Anal. Calcd for C₂₁H₃₅CoN₅O₁₂P: C, 39.45; H, 6.03; Co, 9.22. Found: C, 39.4; H, 5.64; Co, 9.61; yield 74%.

[P(C₆H₅)₃Co(DH)₂H₂O]NO₃: Anal. Calcd for C₂₆H₃₁CoN₅O₈P: C, 49.45; H, 4.95; Co, 9.33. Found: C, 50.1; H, 4.93; Co, 9.3; yield 56%.

[P(n-C₄H₉)₃Co(DH)₂NO₃], prepared by dehydration (110°C in vacuo) of (P(n-C₄H₉)₃Co(DH)₂H₂O)NO₃: Anal. Calcd for C₂₀H₄₁CoN₅O₇P: C, 43.38; H, 7.47; Co, 10.65. Found: C, 43.5; H, 7.32; Co, 10.8; yield 55%.

[LCo(DH)₂H₂O]ClO₄. Nitrate salts of phosphite complexes would not crystallize; however, the corresponding perchlorate salt often would crystallize. These perchlorate complexes were unstable and decomposed *violently* if heated. Elemental analyses were erratic although spectral characterization (ir and ¹H NMR) were consistent with the proposed formulation. A sample preparation for L = P(O-2-Cl-C₂H₄)₃ is given below.

To a suspension of P(O-2-Cl-C₂H₄)₃Co(DH)₂Cl (4.0 g, 6.7 mmol) in 200 ml of 90% CH₃OH–10% H₂O, AgNO₃ (1.3 g, 7.0 mmol) was added and the mixture was warmed and stirred (1–2 hr). After standing (to cool) for a few hours, the mixture was filtered and a

solution of NaClO₄·H₂O (4.7 g, 33.5 mmol) in water (50 ml) was added. Upon air evaporation under a hood, the red-brown crystals formed were collected and were washed with water and ether. This crude product was dissolved in a small amount of methanol. The solution was filtered to remove some solids and an equal volume of water was added. Crystals formed on air evaporation. The product (39% yield) was washed with water and ether and dried in vacuo. Anal. Calcd for $C_{14}H_{28}CoCl_4N_4O_{12}P$: C, 24.87; H, 4.17; Co, 8.71. Found: C, 25.7; H, 3.5; Co, 8.4.

Registry No. P(OC₆H₅)₃Co(DH)₂Cl, 56629-86-8; P(O-o-(CH₃)C₆H₄)₃Co(DH)₂Cl, 56629-87-9; P(O-o-(i-C₃H₇)C₆H₄)₃Co-(DH)₂Cl, 56629-88-0; P(c-C₆H₁₁)₃Co(DH)₂Cl, 24489-36-9; P(i-C₃H₇)₃Co(DH)₂Cl, 56629-89-1; P(OCH₃)₃Co(DH)₂Cl, 52654-86-1; P(OC₂H₅)₃Co(DH)₂Cl, 56403-89-5; P(O-i-C₃H₇)₃Co(DH)₂Cl, 56403-90-8; P(O-2-Cl-C₂H₄)₃Co(DH)₂Cl, 56629-90-4; P(CH₂C₆H₅)₃Co(DH)₂Cl, 56629-91-5; P(OCH₂)₃CC₂H₅Co(DH)₂Cl, 56629-92-6; P(OCH₃)₂(C₆H₅)Co(DH)₂Cl, 56403-84-0; P(C-H₃)(C₆H₅)₂Co(DH)₂Cl, 56629-93-7; P(C₂H₅)(C₆H₅)₂Co(DH)₂Cl, 24489-34-7; P(n-C₄H₉)(C₆H₅)₂Co(DH)₂Cl, 56629-94-8; P(OC-H₃)(C₆H₅)₂Co(DH)₂Cl, 56403-88-4; P(2-(CN)-C₂H₄)₃Co(DH)₂Cl, 56629-95-9; P(CH₃)₃Co(DH)₂Cl, 23648-10-4; P(CH₃)₂(C₆H₅)-Co(DH)₂Cl, 56629-96-0; [P(2-(CN)-C₂H₄)₃Co(DH)₂OH₂]NO₃, 56629-98-2; [P(CH₃)(C₆H₅)₂Co(DH)₂H₂O]NO₃, 56630-00-3; [P-(n-C₄H₉)(C₆H₅)₂Co(DH)₂H₂O]NO₃, 56630-02-5; [P(OCH₃)(C₆-H₅)₂Co(DH)₂H₂O]NO₃, 56630-04-7; [P(C₆H₅)₃Co(DH)₂H₂O]NO₃, 56630-05-8; [P(n-C₄H₉)₃Co(DH)₂NO₃], 51194-37-7; [P(O-2-Cl-C₂H₄)₃Co(DH)₂H₂O]ClO₄, 56630-13-8; Co(DH)(DH₂)Cl₂, 12107-63-0; (CH₃OH)Co(DH)₂Cl, 28872-22-2; P(C₆H₅)₃Co(DH)₂Cl, 23295-34-3; P(OC₆H₅)₃, 101-02-0; P(OCH₃)₃, 121-45-9; P(OC₂H₅)₃, 122-52-1; P(CH₃)₃, 594-09-2; [(C₂H₅)(C₆H₅)₂PCo(DH)₂-(CH₃OH)]⁺, 56630-06-9; [(C₆H₅CH₂)₃PCo(DH)₂(CH₃OH)]⁺, 56630-07-0; [(o-i-C₃H₇C₆H₄O)₃PCo(DH)₂(CH₃OH)]⁺, 56630-08-1; [(CH₃O)₃PCo(DH)₂(CH₃OH)]⁺, 56630-09-2; [(C₂H₅O)₃PCo-(DH)₂(CH₃OH)]⁺, 56630-10-5; [(ClC₂H₄O)₃PCo(DH)₂(CH₃OH)]⁺, 56630-11-6.

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Resolution of Ethylenediaminetetraacetic Acid-d_2 and Ethylenediaminediacetic-N,N'-di-α-propionic Acid via Resolution of Their Cobalt(III) Complexes

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The sexidentate ligand EDPA, ethylenediaminediacetic-N,N'-di-α-propionic acid, has been resolved via resolution of its cobalt(III) complex. Its coordination to the metal ion is approximately 92% stereospecific. Opposite optical isomers of EDTA-d_2, dideuterated EDTA, can also be generated from enantiomeric forms of [Co(EDTA)]⁻ that have undergone either acidic or basic H–D exchange. The two most labile hydrogen atoms of EDTA and the methyl groups of EDPA seem to occupy the same position on the out-of-plane glycine-like linkages, and the configurations of the two optically active carbon atoms of each ligand are tentatively assigned as RR for the ligands from the (+)₅₄₆ complex with Co(III).

Introduction

Studies into the stereochemistry of cobalt(III) complexes with polyaminopolycarboxylate chelates have undergone steady growth,[1-5] culminating in detailed ¹H NMR work completely assigning the glycinate protons of EDTA and analogous ligands.[6] Carbon-13 NMR data have yielded even more information concerning the stereospecific hydrogen–deuterium exchange of such complexes,[7] an exchange that has been the subject of considerable attention.[8-14] With ligands differing from EDTA by the presence of one or more attached methyl groups, the NMR spectra that result are more complicated but yield more information.[2,3,6,7] Brubaker has summarized

much information regarding the significance of such methyl groups.[15] In this paper we evoke two approaches to elucidate even further the full consequences associated with the stereochemistry of the glycine-like linkages located out of the N–Co–N plane of the [Co(EDTA)]⁻ anion, especially when occupied by a methyl group. We utilize Dwyer's rather classical approach,[16,17] an approach used by Mizukami et al.,[18] whereby ligand stereochemistry is discerned via its influence upon the stereochemistry of the complex. We also use H–D stereospecific exchange techniques[6] to prepare the particular enantiomers of EDTA. This work involved EDTA, an analogous ligand with two methyl groups that we refer to as