On the Correlation between Bond Lengths, Chemical Shifts, and Cone Angles in Octahedral Cobaloximes containing P-donor Ligands. Crystal Structure of *trans*-Chlorobis(dimethylglyoximato)(phosphite)cobalt(III) Complexes with Phosphite = $P(OMe)_2Ph$ and $P(OMe)Ph_2$

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The crystal structures of the title compounds, $[CoCl(Hdmg)_2\{P(OMe)_2Ph\}]$ (1) and $[CoCl(Hdmg)_2\{P(OMe)Ph_2\}]$ (2), are reported and discussed. Compound (1) crystallizes in the tetragonal system, space group $I4_1/a$, with unit-cell parameters a = 33.78(1), c = 8.421(6) Å, and Z = 16; (2) crystallizes in the orthorhombic system, space group *Pbca*, with unit-cell parameters a = 18.230(8), b = 15.725(7), c = 17.134(8) Å, and Z = 8. Both structures have been solved by Patterson and Fourier methods and refined by block-diagonal anisotropic least-squares methods to final R values of 0.030 for both compounds, using 1 359 (1) and 1 859 (2) independent reflections. The Co–Cl and Co–P bond lengths are 2.288(2) and 2.213(2) Å in (1) and 2.290(1) and 2.242(1) Å in (2). The equatorial dimethylglyoximate ligands are nearly coplanar making dihedral angles of 2.3 and 0.9° in (1) and (2) respectively. Each unit of (1) clathrates 0.125 toluene molecules in large channels around a kind of tetrad rotatory inversion axis. Linear correlations between Co–P bond lengths, Tolman's cone angles, and ^1H n.m.r. chemical shifts are found and discussed in terms of the steric *cis* influence in the $[CoX(Hdmg)_2(PR_3)]$ series.

OUR previous studies on steric and electronic factors in vitamin B_{12} models, namely the octahedral cobaloximes, $[CoX(Hdmg)_2L]$ where L = neutral and X = negative ligands and Hdmg = the monoanion of dimethylglyoxime, have shown that P-donor ligands are able to generate steric distortions in these systems.[1-6] In fact, in addition to electronically originated changes,[1] bending of the equatorial ligands,[2] distortions in the geometry of axial ligands,[5] and lengthening of both Co–L and Co–X bonds,[1,2,4] which may be attributed to steric influences, have been detected and correlated[4] with spectroscopic results.[7-9] Thus we have attempted to interpret some of the ground-state structural effects in terms of 'steric' *trans* and *cis* influences in addition to the already known 'electronic' *trans* influence.[1-6]

We have shown[2] that in the series $[CoX(Hdmg)_2(PR_3)]$ (R = OMe, Me, Bu^n, Ph, cyclo-C_6H_{11}; X = Cl or Me) the Co–P bond length increases with the increasing bulk of the P-donor ligand and correlates linearly with Tolman's cone angles,[10] the phosphite derivatives following the same trend as the phosphines. Thus it was of interest to study the structure of cobaloximes containing P-donor ligands such as $P(OMe)_2Ph$ and $P(OMe)Ph_2$, to see what kind of structural changes arise in going from a phosphine to a phosphite. In this report, the structural analyses of two cobaloximes, *trans*-$[CoCl(Hdmg)_2\{P(OMe)_2Ph\}]$ (1) and *trans*-$[CoCl(Hdmg)_2\{P(OMe)Ph_2\}]$ (2) are presented and discussed.

EXPERIMENTAL

Crystal Data.—$C_{16}H_{25}ClCoN_4O_6P\cdot0.125C_6H_5CH_3$, (1), M = 517.9, Tetragonal, a = 33.78(1), c = 8.421(6) Å, U = 9 609.1 Å^3, D_m = 1.45 (by flotation), Z = 16, D_c = 1.40 g cm^{-3}, $F(000)$ = 260.3, $\mu(\text{Mo-}K_\alpha)$ = 9.6 cm^{-1}, $r_{\text{max.}}$ (crystal) = 0.02 cm, space group I_{41}/a.

$C_{21}H_{27}ClCoN_4O_5P$, (2), M = 540.9, Orthorhombic, a = 18.230(8), b = 15.725(7), c = 17.134(8) Å, U = 4 911.7 Å^3, D_m = 1.45 (by flotation), Z = 8, D_c = 1.46 g cm^{-3}, $F(000)$ = 278, $\mu(\text{Mo-}K_\alpha)$ = 9.4 cm^{-1}, $r_{\text{max.}}$ (crystal) = 0.02 cm, space group *Pbca*.

Crystals of (1) and (2), prepared according to ref. 11, were crystallized from a 1 : 1 mixture of dichloromethane and toluene. Cell parameters were determined from Weissenberg and precession photographs and refined with an on-line automatic single-crystal Siemens diffractometer using Mo-K_α radiation (λ = 0.7107 Å).

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by means of the θ—2θ scan technique and Mo-K_α radiation for a maximum 2θ of 54° for both compounds. Reflections with $I_o > 3\sigma(I_o)$ were rejected, the remainder being corrected for Lorentz-polarization factors. A total of 1 359 independent reflections for (1) and 1 859 for (2) were used in the subsequent calculations. No correction for absorption was applied.

Structure Determination and Refinement.—Both structures were solved by conventional Patterson and Fourier methods. The $|F_o - F_c|$ synthesis for (1) revealed the presence of four toluene molecules in a unit cell arranged around the tetrad rotatory inversion axis at $0,\frac{1}{4},\frac{1}{8}$. The final block-diagonal anisotropic refinement for the cobaloxime non-hydrogen atoms, including the contribution from fixed hydrogen atoms (B = 5 Å^2), gave R = 0.030. The toluene carbon atoms were refined isotropically with an occupancy factor of 0.25 for C(19) and C(20) and 0.125 for the others and their hydrogen atoms were not included. The final anisotropic refinement for (2), including the contribution from the hydrogen atoms held constant (B = 5 Å^2), gave a final R = 0.030. The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|)^2$ where A = 84.2 and B = 0.003 for (1) and A = 39.4 and B = 0.004 for (2) were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and $(\sin\theta)/\lambda$.

Final atomic parameters are listed in Tables 1 and 2 together with their estimated standard deviations. Observed and calculated structure factors, anisotropic thermal para-

TABLE 1

Atomic co-ordinates ($\times 10^4$) for compound (1) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co	1 528(0)	1 260(0)	177(1)
Cl	1 855(1)	1 440(0)	2 444(2)
P	1 209(1)	1 086(1)	−2 007(2)
O(1)	2 179(1)	746(2)	−466(7)
O(2)	835(1)	1 091(1)	1 970(6)
O(3)	891(2)	1 778(1)	980(6)
O(4)	2 232(1)	1 423(2)	−1 547(7)
O(5)	1 174(2)	1 458(1)	−3 122(6)
O(6)	1 387(1)	730(1)	−3 008(6)
N(1)	1 817(1)	777(2)	186(7)
N(2)	1 172(1)	950(1)	1 395(6)
N(3)	1 242(2)	1 744(1)	229(7)
N(4)	1 886(2)	1 570(2)	−1 013(7)
C(1)	1 850(3)	82(2)	1 124(12)
C(2)	1 655(2)	483(2)	957(9)
C(3)	1 277(2)	580(2)	1 645(8)
C(4)	1 022(3)	295(2)	2 555(11)
C(5)	1 224(4)	2 446(3)	−597(14)
C(6)	1 412(2)	2 042(2)	−511(9)
C(7)	1 793(3)	1 934(2)	−1 212(9)
C(8)	2 051(4)	2 222(3)	−2 113(13)
C(9)	979(3)	1 428(3)	−4 686(9)
C(10)	1 757(2)	740(3)	−3 882(10)
C(11)	718(2)	892(2)	−1 706(8)
C(12)	408(2)	1 154(3)	−1 460(9)
C(13)	26(2)	989(3)	−1 144(10)
C(14)	−22(3)	581(3)	−1 088(11)
C(15)	282(3)	336(3)	−1 335(11)
C(16)	653(2)	482(2)	−1 652(9)
C(17)	0	2 500	1 250
C(18)	0	2 500	3 321(79)
C(19)	293(13)	2 420(12)	4 344(56)
C(20)	307(15)	2 411(16)	5 873(67)
C(21)	0	2 500	7 097(92)

TABLE 2

Atomic co-ordinates ($\times 10^4$) for compound (2) with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Co	611(0)	1 977(0)	1 399(0)
Cl	727(1)	695(1)	2 021(1)
P	523(1)	3 249(1)	815(1)
O(1)	−836(2)	2 086(2)	2 010(2)
O(2)	1 084(2)	1 191(2)	−20(2)
O(3)	2 054(2)	1 840(2)	794(2)
O(4)	141(2)	2 690(2)	2 851(2)
O(5)	770(2)	3 130(2)	−76(2)
N(1)	−423(2)	1 842(2)	1 401(3)
N(2)	503(2)	1 429(2)	421(2)
N(3)	1 643(2)	2 094(2)	1 397(2)
N(4)	724(2)	2 517(2)	2 380(2)
C(1)	−1 527(4)	1 375(5)	689(5)
C(2)	−709(3)	1 508(3)	777(3)
C(3)	−163(3)	1 273(3)	195(3)
C(4)	−340(4)	875(4)	−587(4)
C(5)	2 754(3)	2 555(4)	2 106(4)
C(6)	1 935(3)	2 435(3)	2 011(3)
C(7)	1 389(3)	2 679(3)	2 595(3)
C(8)	1 571(4)	3 092(4)	3 365(4)
C(9)	869(4)	3 841(4)	−620(3)
C(10)	−415(3)	3 657(3)	786(3)
C(11)	−769(3)	3 956(3)	1 455(3)
C(12)	−1 495(3)	4 231(4)	1 405(4)
C(13)	−1 870(3)	4 187(4)	697(5)
C(14)	−1 526(3)	3 862(4)	44(5)
C(15)	−792(3)	3 596(3)	69(4)
C(16)	1 129(3)	4 071(3)	1 203(3)
C(17)	1 863(3)	4 028(3)	987(3)
C(18)	2 370(3)	4 594(3)	1 305(4)
C(19)	2 151(3)	5 194(3)	1 840(4)
C(20)	1 419(4)	5 256(4)	2 050(4)
C(21)	904(3)	4 694(3)	1 736(3)

meters, and hydrogen-atom co-ordinates are listed in Supplementary Publication No. SUP 23293 (22 pp.).* Atomic scattering factors were calculated according to ref. 12. All calculations were carried out on a CDC CYBER 170/720 computer using programs described in ref. 13.

RESULTS

Descriptions of the Structures.—The numbering scheme for (1) and (2) is shown in Figures 1 and 2. Relevant bond lengths and angles are reported in Table 3.

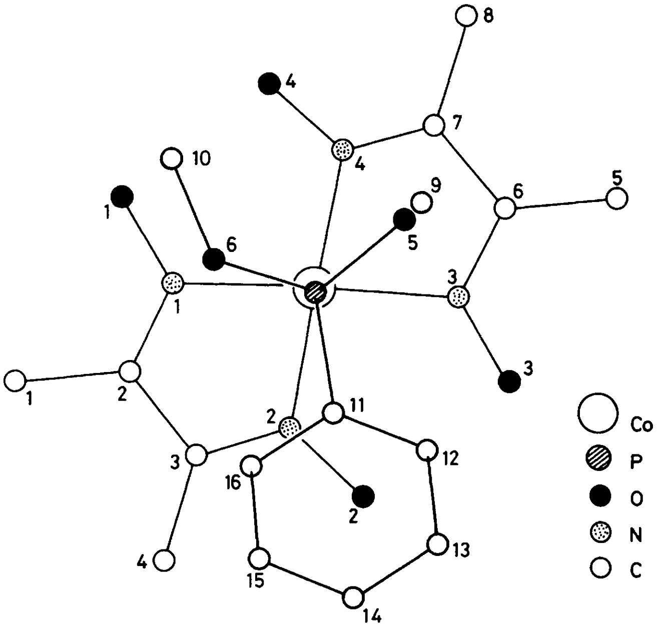

FIGURE 1 Atom-numbering scheme for compound (1), showing the orientation of the P ligand with respect to the equatorial unit. The Cl atom is obscured

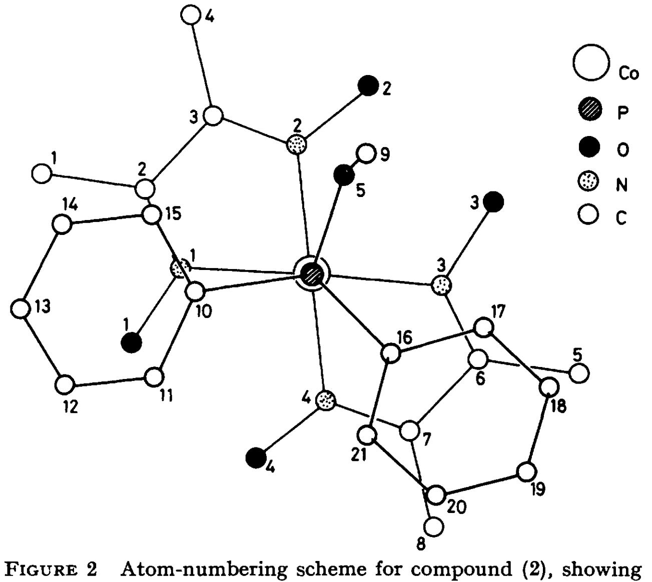

FIGURE 2 Atom-numbering scheme for compound (2), showing the orientation of the P ligand with respect to the equatorial unit. The Cl atom is obscured

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

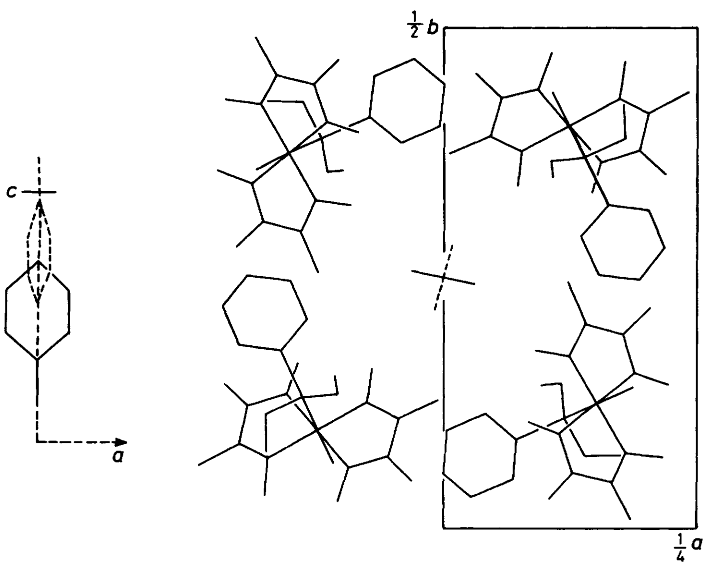

FIGURE 3 The crystal packing of compound (1) projected along the *c* axis showing the channel where the toluene molecules are clathrated. On the left the two possible orientations of the toluene molecules viewed along the *b* axis are shown

In compound (1) the four N atoms of the $(Hdmg)_2$ unit are coplanar within ±0.007 Å and the cobalt atom is displaced 0.02 Å above their mean plane towards the axial P atom. Correspondingly, the two Hdmg units are nearly coplanar, their mean plane making an angle of 2.3°. The Co–Cl and Co–P bond lengths are 2.288(2) and 2.213(2) Å, with a P–Co–Cl angle of 179.63(8)°. The $Ph(MeO)_2P$ group is characterized by P–O bond lengths of 1.574(5) and 1.588(5) Å and a P–C bond length of 1.800(7) Å. Its orientation with respect to the equatorial ligand is shown in Figure 1.

TABLE 3

Bond lengths (Å) and angles (°) for compounds (1) and (2)

	(1)	(2)
Co–Cl	2.288(2)	2.290(1)
Co–P	2.213(2)	2.242(1)
Co–N(1)	1.901(5)	1.898(4)
Co–N(2)	1.898(5)	1.895(4)
Co–N(3)	1.898(5)	1.890(4)
Co–N(4)	1.887(6)	1.894(4)
N(1)–O(1)	1.344(7)	1.343(6)
N(1)–C(2)	1.306(9)	1.300(7)
N(2)–O(2)	1.325(7)	1.353(6)
N(2)–C(3)	1.316(8)	1.298(7)
N(3)–O(3)	1.351(8)	1.338(5)
N(3)–C(6)	1.316(9)	1.295(7)
N(4)–O(4)	1.346(8)	1.362(6)
N(4)–C(7)	1.278(10)	1.292(7)
C(1)–C(2)	1.511(11)	1.513(9)
C(2)–C(3)	1.442(10)	1.456(8)
C(3)–C(4)	1.502(11)	1.514(8)
C(5)–C(6)	1.508(12)	1.513(8)
C(6)–C(7)	1.462(12)	1.463(7)
C(7)–C(8)	1.512(14)	1.509(8)
P–O(5)	1.574(5)	1.602(3)
P–O(6)	1.588(5)	—
P–C(10)	—	1.827(5)
P–C(11)	1.800(7)	—
P–C(16)	—	1.825(5)
O(5)–C(9)	1.476(9)	1.467(7)
O(6)–C(10)	1.449(9)	—
C–C(phenyl) mean	1.386(13)	1.394(8)
N(1)–Co–N(2)	81.3(2)	81.2(2)
N(1)–Co–N(3)	178.4(3)	179.1(2)
N(1)–Co–N(4)	98.7(2)	99.0(2)
N(1)–Co–Cl	88.7(2)	89.5(1)
N(1)–Co–P	91.4(2)	91.7(1)
N(2)–Co–N(3)	98.0(2)	98.4(2)
N(2)–Co–N(4)	179.3(2)	179.5(2)
N(2)–Co–Cl	90.1(2)	91.2(1)
N(2)–Co–P	89.6(2)	90.2(1)
N(3)–Co–N(4)	82.0(3)	81.4(2)
N(3)–Co–Cl	89.9(2)	89.7(1)
N(3)–Co–P	90.0(2)	89.1(1)
N(4)–Co–Cl	89.2(2)	88.4(1)
N(4)–Co–P	91.1(2)	90.2(1)
Cl–Co–P	179.6(1)	178.3(1)
Co–P–O(5)	108.7(2)	107.5(1)
Co–P–O(6)	117.2(2)	—
Co–P–C(11)	115.4(2)	—
Co–P–C(10)	—	113.1(2)
Co–P–C(16)	—	115.2(2)
O(5)–P–O(6)	108.5(3)	—
O(5)–P–C(11)	107.8(3)	—
O(6)–P–C(11)	98.6(3)	—
O(5)–P–C(10)	—	106.1(2)
O(5)–P–C(16)	—	105.1(2)
C(10)–P–C(16)	—	109.1(2)

In compound (2) the four N atoms of the $(Hdmg)_2$ unit are coplanar within ±0.003 Å and the cobalt atom is displaced 0.01 Å above their mean plane towards the P axial donor. The two Hdmg units are coplanar, their mean planes making an angle of 0.9°. The P–Co–Cl fragment is characterized by Co–Cl and Co–P bond lengths of 2.290(1) and 2.242(1) Å and by a P–Co–Cl bond angle of 178.26(6)°. The $Ph_2(MeO)P$ group is characterized by P–C bond lengths of 1.825(5) and 1.827(5) Å and a P–O bond length of 1.602(3) Å. Its orientation with respect to the equatorial ligand is shown in Figure 2.

The bond lengths and angles in the $Co(Hdmg)_2$ moiety are quite normal[1-5] in both (1) and (2).

Crystal packing of (1). The crystal of (1) is built up by $[CoCl(Hdmg)_2\{P(OMe)_2Ph\}]$ molecules arranged in such a way as to form large channels arranged around the tetrad rotatory inversion axes at 0,¼,⅛, *etc.* The toluene molecules, having two different orientations, are clathrated in these channels and aligned along their axes (Figure 3). The occupancy factor of the toluene molecules suggests that there is an average of one molecule per channel in each alternate unit cell. The crystal packing is shown in Figure 3.

DISCUSSION

The Co–P bond lengths in $[CoCl(Hdmg)_2(PR_3)]$ and $[CoMe(Hdmg)_2(PR_3)]$ complexes are plotted against Tolman's cone angles in Figure 4. As already suggested,[2] a good linear relationship appears in both cases, showing that the Co–P lengthening is dominated by the bulk of the P-donor ligand. If PPh_3 derivatives are excluded, the correlation coefficients are 0.9923 and 0.9998 respectively. The above trends confirm the previous suggestion,[14] based on the n.m.r. chemical shift trends, that the Tolman's cone angle of 145° for PPh_3 is too low for these series of compounds. A value of 156°, derived from the lines of Figure 4, should take better account of the steric interaction of PPh_3 with the equatorial $(Hdmg)_2$ ligands. The chemical shifts of CH_3OH reported for the series $[Co(Hdmg)_2(MeOH)(PR_3)]^+$ [14] are plotted against Co–P bond lengths in Figure 5. In this case, the phosphine derivatives fit a linear trend (correlation coefficient of 0.9961) while a different linear trend, with a correlation coefficient of 0.9996, may be suggested for the series $[CoCl(Hdmg)_2L]$ [L = $P(OMe)_3$, $P(OMe)_2Ph$, $P(OMe)Ph_2$, and PPh_3]. This line intercepts that corresponding to $[CoCl(Hdmg)_2(PR_3)]$ complexes. As expected the PPh_3 derivatives fit well the linear relationship of Figure 5.

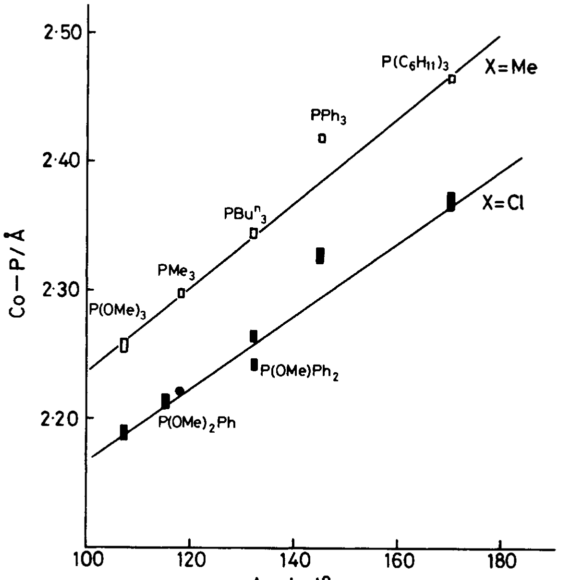

FIGURE 4 Plot of Co–P bond lengths in $[CoX(Hdmg)_2(PR_3)]$ (X = Cl or Me) against Tolman's cone angle. The Co–P distance for $[CoCl(Hdmg)_2(PMe_3)]$ is suggested to be 2.22 Å in ref. 4. X is $C_5H_4N^-$ instead of Me in the PBu^n_3 derivative. The length of the vertical bars is twice the estimated standard deviation (e.s.d.) of the corresponding bond length. The full circle represents the expected value for the PMe_3 derivative. The Co–P bond lengths are from ref. 2 and the present work

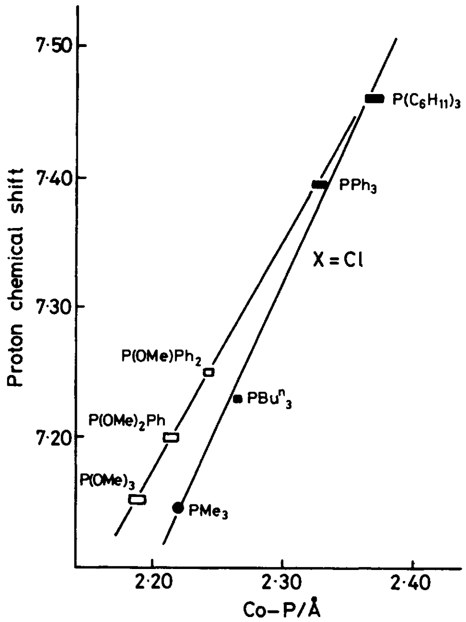

FIGURE 5 Plot of ^1H chemical shifts in the series $[Co(Hdmg)_2(MeOH)(PR_3)]^+$ against the Co–P bond lengths of Figure 4 for X = Cl. The length of the horizontal bars is twice the e.s.d. of the corresponding bond length. The full circle represents the expected value of the PMe_3 derivative. The ^1H chemical shifts are from ref. 14

The above trends may tentatively be interpreted as a consequence of changes of electron density at cobalt. In fact it may be assumed that the lengthening of the Co–P bond causes an increase of the *p* character in the P-donor orbital, which in turn donates less electron charge to cobalt. Consequently, the methanol ^1H chemical shift in the phosphine series $[Co(Hdmg)_2(MeOH)(PR_3)]^+$ increases from PMe_3 to $P(cyclo\text{-}C_6H_{11})_3$. Whether the increase of chemical shifts originates from through-bond or through-space interactions is a matter for discussion.[9]

In conclusion, the trends of Figure 4 indicate that Co–P bond lengths in both phosphine and phosphite complexes are a good measure of their bulk (cone angle) for the interaction with the rigid equatorial ligand, *i.e.* the steric *cis* influence.[4] On the contrary, the trends of Figure 5 suggest that ^1H chemical shifts may be a good measure of the bulk only for the phosphine series, since it appears that there is a gradual change in the ^1H chemical shifts from phosphites to phosphines. This lends support to the previous suggestion [15] that both electronic and steric factors in phosphites are important.

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