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Structural Distortions in Alkylcobaloximes Containing Triphenylphosphine as Axial Ligand. The X-Ray Structures of *trans*-bis(dimethylglyoximato)(bromomethyl)-(triphenylphosphine)cobalt(III) and *trans*-bis(dimethylglyoximato)(cyanomethyl)-(triphenylphosphine)cobalt(III)

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The crystal structure of two cobaloximes, [Co-$(CH_2Br)(Hdmg)_2(PPh_3)$] (1) and [Co(CH_2CN)-$(Hdmg)_2(PPh_3)$] (2) (H_2dmg = dimethylglyoxime), are reported and discussed. Compound (1) crystallizes in the space group $P2_1/c$ *with cell parameters* a = *10.221(7),* b = *15.23(1),* c = *19.27(1) Å, β = 108.0-(1)°, Z = 4; (2) crystallizes in the space group* $P2_1/c$ *with cell parameters* a = *8.653(4),* b = *16.55(1),* c = *19.99(1) Å, β = 104.7(1)°, Z = 4. Both structures have been solved by Patterson and Fourier methods and refined by least-squares methods to final* R *values of 0.057(1) and 0.028(2), using 1746(1) and 2950(2) independent reflections. The cobalt atom is displaced 0.065(1) and 0.084(2) Å above the $(Hdmg)_2$ 4-N equatorial donors towards PPh_3, the two Hdmg planes making dihedral angles of 2.7(1) and 11.1° (2) and bending towards the alkyl group. The PPh_3–Co–CH_2Br fragment of (1) is characterized by a P–Co–C angle of 175.1(4)° and Co–P and Co–C bond lengths of 2.399(3) and 1.998(15) Å respectively; the corresponding figures for (2) are 177.7(1)°, 2.391(1) and 2.043(3) Å respectively. The Co–CH_2–Br angle is 125.2(9)° and the C–Br distance is 1.84(1), significantly shorter (~0.1 Å) than values reported for bromoalkyls. The Co–CH_2–CN angle is 116.5(3)° and the C–CN distance is 1.424(5) Å, slightly but significantly shorter (~0.04 Å) than those reported for R_3C-C≡N compounds. The present results are compared with those reported for the analogues [Co(CH_2X)Co$(Hdmg)_2(PPh_3)$], (X = H, t-C_4H_9, CF_3) and discussed in terms of steric and electronic influences. Comparison with the [Co(CH_2X)Co-$(Hdmg)_2$(py)] series is discussed, pointing out the differences provoked by substitution of PPh_3 with py on the geometry of the Co$(CH_2X)(Hdmg)_2$ moiety. In particular the Co–C bond lengths of the PPh_3 derivatives are longer than those of the py analogues by about 0.03 Å, strongly supporting the suggestion that PPh_3 exerts a greater 'steric trans-influence' than pyridine. Furthermore, observed distortions suggest the following order of increasing steric bulk for X: NO_2 ⩽ CN ~ COOMe < CH_3 ~ CF_3 < Br < $SiMe_3$ ⩽ CMe_3. Finally, a general trend of increasing Co–P distances with decreasing ^{13}C chemical shifts of phosphite methyls in {Co$(Hdmg)_2(CH_2X)$[P$(OMe)_3$]} is found.*

Introduction

We have recently shown [1, 2] that in pseudo-octahedral cobaloximes, [Co$(Hdmg)_2(CH_2X)$py] (Hdmg = monoanion of dimethylglyoxime, py = pyridine), the Co–N(py) bond lengths are influenced by the nature of X. The increase of the above distances from 2.028(3) to 2.091(5) Å in the series X = NO_2, CO_2Me, H, CH_3, t-C_4H_9, $SiMe_3$ parallels the increasing σ-donor ability of X. This trend has been interpreted assuming that the X group, increasing the electron density on the carbon atom bound to cobalt, increases its trans-influencing ability along the series. Furthermore, a fairly linear correlation of Co–N(py) distances with the ^{13}C chemical shifts of the t-butyl group in the [Co$(Hdmg)_2(CH_2X)$-(4-t-bupy)] series (4-t-bupy = 4-ter-butylpyridine) was found [2]. A similar structural effect has been observed in [Co$(dmg)_2$ (CH = CH_2)(py)] [3] and {Co$(Hdmg)_2$ [(p-$ClC_6H_4)_2$C=C(Cl)] (py)} [4] where the Co–N(py) bond lengths are 2.073(3) and 2.043-(10) Å respectively. Furthermore, the increasing bulk of X provokes significant structural distortions in the XH_2C·Co·py moiety, such as the lengthening of the Co–C bond and the widening of the Co–CH_2–X

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TABLE I. Crystallographic Data for (*1*) and (*2*).

Formula	$C_{27}H_{31}CoN_4O_4PBr$	$C_{28}H_{31}CoN_5O_4P$
M	645.4	591.5
a/Å	10.221(7)	8.653(4)
b/Å	15.23(1)	16.55(1)
c/Å	19.27(1)	19.99(1)
β/°	108.0(1)	104.7(1)
Dm/g·cm^{-3}	1.47	1.40
Dc/g·cm^{-3}	1.50	1.42
Z	4	4
Space group	$P2_1/c$	$P2_1/c$
μ(Mo-Kα)/cm^{-1}	22.1	7.5
Crystal dimensions/cm^3	0.02 × 0.04 × 0.06	0.04 × 0.04 × 0.06
N° of collected reflections	6300	7436
N° of independent reflections ($I > 3\sigma(I)$)	1746	2950
θ max/°	28	28
R	0.057	0.028
R_w	0.072	0.039

angle. These distortions may be mainly attributed to steric interaction with the rigid equatorial ligands. On the other hand, we have also shown that a steric *trans*-influence, due to a bulky group such as PPh_3 lengthening the *trans* bond to cobalt, may decrease the expected electronic *trans*-influencing power of the ligand *trans* to it [5]. Therefore it was of interest to extend these investigations to the series of $[Co(Hdmg)_2(CH_2X)(PPh_3)]$ compounds, for which the derivatives with X = H [6] and t-C_4H_9 [7] have already been structurally characterized. In fact substitution of py by the bulkier PPh_3 ligand should influence [7] the above trends. Thus, we report the crystal and molecular structures of the complexes having X = Br, $[Co(Hdmg)_2(CH_2Br)(PPh_3)]$ (*1*) and X = CN, $[Co(Hdmg)_2(CH_2CN)(PPh_3)]$ (*2*), where Br and CN are both electron-withdrawing groups but with different bulk.

Experimental

Crystal Data

The cell parameters were determined from Weissenberg and precession photographs and refined on a SIEMENS AED single-crystal diffractometer. Crystal data are given in Table I.

One check reflection intensity during the collection of diffraction data, for both complexes, was measured every 100 reflections and did not show any systematic variation throughout the data recording.

The intensities for which $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarization factors but not for absorption.

Solution and Refinement of the Structures

Both structures were solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares methods. The final cycles were carried out by a full-matrix least-squares method including all hydrogen atom contributions (held constant at $B = 5$ Å^2) and anisotropic temperature factors for all non-carbon atoms of (*1*).

Corrections for anomalous dispersion of the Br and Co atoms was applied. For (*2*), the hydrogen atom contributions (held constant at $B = 5$ Å^2) and anisotropic temperature factors for non-hydrogen atoms were included. The final R and Rw values are given in Table I. The final weighting scheme was $W = 1/(A + |F_o| + B|F_o|^2)$ where $A = 27.4$, $B = 0.006$ for (*1*) and $A = 19.2$, $B = 0.008$ for (*2*) were chosen so as to maintain $W(|F_o| - |F_c|)^2$ essentially constant over all ranges of F_o and sin (θ/λ). Atomic scattering factors were those given in ref. 8. All the calculations were done using the computer programs from X-Ray 70 [9]. Final positional parameters of non-hydrogen atoms are given in Table II. Hydrogen atom coordinates, anisotropic thermal parameters, calculated and observed structure factors are available from the Editor.

Results and Discussion

Description and Discussion of the Structures

The atom numbering schemes for the crystallographically independent molecules of structures (*1*) and (*2*) are given in Figs. 1 and 2. Bond lengths and angles are listed in Table III. The four N atoms of the $Co(Hdmg)_2$ unit are coplanar within ±0.016 Å for (*1*) and ±0.004 Å for (*2*). The cobalt atom is displaced from the mean plane towards PPh_3 by 0.065 Å in (*1*) and 0.084 Å in (*2*). The $Co(Hdmg)_2$ unit of (*1*) deviates only slightly from planarity with a bending angle α, between the two Hdmg units, of 2.7°, while it is significantly bent in (*2*) with an α angle of 11.1°.

TABLE II. Fractional Coordinates (×10^4) for Non-Hydrogen Atoms of Compounds *1* and *2*. For *2* the Isotropic Thermal Factors of Carbon Atoms are also Reported.

a) Compound *1*

	x	y	z	B(Å^2)
Co	1900(2)	2246(1)	1877(1)	
Br	3076(2)	1224(1)	3529(1)	
P	1591(3)	2474(2)	605(1)	
O(1)	4745(8)	2705(5)	2228(4)	
O(2)	691(9)	543(5)	1638(5)	
O(3)	−857(9)	1769(6)	1726(5)	
O(4)	3161(9)	3938(5)	2202(4)	
N(1)	3798(8)	2047(6)	2037(4)	
N(2)	1879(10)	1016(6)	1783(5)	
N(3)	32(9)	2443(6)	1805(5)	
N(4)	1974(9)	3478(6)	2028(4)	
C(1)	5644(15)	983(9)	2128(7)	5.5(3)
C(2)	4177(12)	1249(8)	1996(6)	3.8(2)
C(3)	3068(12)	638(8)	1846(6)	3.8(2)
C(4)	3168(14)	−347(10)	1777(7)	5.6(3)
C(5)	−1813(16)	3514(11)	1774(9)	7.0(4)
C(6)	−327(13)	3241(8)	1832(6)	4.1(2)
C(7)	791(12)	3853(8)	1969(6)	4.1(2)
C(8)	698(16)	4840(10)	2044(8)	6.7(4)
C(9)	2237(15)	2156(10)	2953(8)	5.9(3)
C(10)	2404(11)	3500(7)	506(5)	2.8(2)
C(11)	3860(12)	3583(8)	736(6)	3.7(2)
C(12)	4436(13)	4389(9)	718(7)	5.1(3)
C(13)	3682(15)	5146(10)	510(7)	5.7(3)
C(14)	2273(14)	5072(9)	303(7)	5.2(3)
C(15)	1637(12)	4253(8)	293(6)	3.9(2)
C(16)	2307(10)	1609(7)	172(5)	2.6(2)
C(17)	3293(14)	1750(9)	−180(7)	5.0(3)
C(18)	3676(17)	1045(11)	−568(9)	7.0(4)
C(19)	3103(15)	239(10)	−571(8)	6.2(3)
C(20)	2132(14)	98(9)	−245(7)	5.4(3)
C(21)	1729(12)	793(8)	118(6)	3.9(2)
C(22)	−111(11)	2570(7)	−79(5)	2.8(2)
C(23)	−174(12)	2782(8)	−791(6)	3.7(2)
C(24)	−1455(13)	2811(9)	−1356(7)	5.0(3)
C(25)	−2607(14)	2625(9)	−1192(7)	4.6(3)
C(26)	−2584(13)	2424(9)	−502(7)	4.7(3)
C(27)	−1331(12)	2390(7)	71(6)	3.6(2)

b) Compound *2*

	x	y	z		x	y	z
Co	2856(0)	1654(0)	394(0)	C(3)	3139(4)	2106(2)	−884(2)
P	4088(1)	2887(0)	880(0)	C(4)	2763(6)	2460(3)	−1597(2)
O(1)	5885(3)	950(2)	399(1)	C(5)	−476(5)	1533(3)	1587(2)
O(2)	803(3)	2587(2)	−662(1)	C(6)	947(4)	1481(2)	1288(2)
O(3)	−322(3)	2207(2)	317(1)	C(7)	2393(4)	1026(2)	1593(2)
O(4)	4802(3)	625(1)	1409(1)	C(8)	2660(5)	546(3)	2247(2)
N(1)	4627(3)	1402(2)	48(1)	C(9)	1892(4)	584(2)	−23(2)
N(2)	2193(3)	2178(2)	−470(1)	C(10)	1331(5)	555(2)	−757(2)
N(3)	995(3)	1814(2)	705(1)	C(11)	5838(4)	2841(2)	1619(1)
N(4)	3440(3)	1048(2)	1222(1)	C(12)	7051(4)	3424(2)	1718(2)
N(5)	911(7)	528(3)	−1349(2)	C(13)	8262(4)	3439(2)	2329(2)
C(1)	5829(6)	1425(2)	−944(2)	C(14)	8285(4)	2887(2)	2849(2)
C(2)	4573(4)	1637(2)	−581(2)	C(15)	7118(5)	2293(2)	2747(2)

(continued overleaf)

TABLE II. *(continued)*

	x	*y*	*z*
C(16)	5879(4)	2278(2)	2142(2)
C(17)	2821(4)	3628(2)	1188(2)
C(18)	1342(4)	3858(2)	758(2)
C(19)	421(5)	4445(3)	972(2)
C(20)	945(5)	4792(3)	1623(3)
C(21)	2378(6)	4557(3)	2060(2)
C(22)	3322(5)	3976(2)	1846(2)
C(23)	4818(4)	3425(2)	218(1)
C(24)	6269(4)	3195(2)	96(2)
C(25)	6826(4)	3563(2)	–428(2)
C(26)	5906(5)	4142(2)	–845(2)
C(27)	4456(5)	4364(2)	–738(2)
C(28)	3909(4)	4014(2)	–206(2)

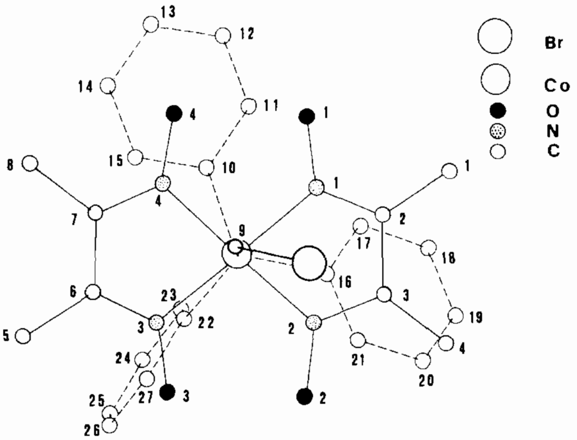

Fig. 1. A view along the Co–P bond of the crystallographically independent molecule of (*1*), together with the numbering scheme for the atoms.

Bond lengths and angles of the Co(Hdmg)$_2$ moiety are quite normal in both compounds. In (*1*) the Ph$_3$P–Co–CH$_2$Br fragment is characterized by a P–Co–C angle of 175.1(4)° and Co–P and Co–C bond lengths of 2.399(3) and 1.998(15) Å respectively. The Co–CH$_2$–Br angle of 125.2(9)° is narrower than that of 129.2(7) found in [Co(Hdmg)$_2$(CH$_2$CMe$_3$)(PPh$_3$)] [7]. The C–Br distance of 1.842(14), although not highly accurate, is significantly shorter than those reported for bromoalkyls, a typical value of 1.953(4) Å being reported for Br(CH$_2$)$_3$Br [10]. On the contrary it appears more comparable

TABLE III. Bond Lengths and Angles in Compounds (*1*) and (*2*).

a) bond lengths/Å	*1*	*2*	b) bond angles/°	*1*	*2*
Co–P	2.399(3)	2.391(1)	P–Co–C(9)	175.1(4)	177.70(11)
Co–C(9)	1.998(15)	2.043(3)	N(1)–Co–P	89.7(3)	90.99(8)
Co–N(1)	1.892(9)	1.881(3)	N(I)–Co–C(9)	88.9(5)	86.8(1)
Co–N(2)	1.882(9)	1.888(3)	N(I)–Co–N(2)	80.6(4)	81.5(1)
Co–N(3)	1.895(9)	1.886(3)	N(1)–Co–N(3)	175.0(4)	174.7(1)
Co–N(4)	1.896(9)	1.891(3)	N(1)–Co–N(4)	98.2(4)	98.2(1)
N(1)–O(1)	1.36(1)	1.360(3)	N(2)–Co–P	92.9(3)	88.84(8)
N(1)–C(2)	1.29(2)	1.305(4)	N(2)–Co–C(9)	91.4(5)	91.6(1)
N(2)–O(2)	1.36(1)	1.347(3)	N(2)–Co–N(3)	99.7(4)	98.6(1)
N(2)–C(3)	1.32(2)	1.309(5)	N(2)–Co–N(4)	176.8(3)	175.2(1)
N(3)–O(3)	1.35(1)	1.368(3)	N(3)–Co–P	95.3(3)	94.34(8)
N(3)–C(6)	1.28(2)	1.301(4)	N(3)–Co–C(9)	86.1(5)	87.9(1)
N(4)–O(4)	1.35(1)	1.340(3)	N(3)–Co–N(4)	81.2(4)	81.2(1)
N(4)–C(7)	1.31(2)	1.309(5)	N(4)–Co–P	90.0(3)	95.99(8)
C(1)–C(2)	1.50(2)	1.494(6)	N(4)–Co–C(9)	85.6(5)	83.6(1)
C(2)–C(3)	1.43(2)	1.458(5)	Co–C(9)–Br	125.2(9)	
C(3)–C(4)	1.51(2)	1.499(5)	Co–C(9)–C(10)		116.5(3)
C(5)–C(6)	1.54(2)	1.501(6)	C(9)–C(10)–N(5)		178.5(5)
C(6)–C(7)	1.44(2)	1.455(4)	Co–P–C(10)	108.3(3)	
C(7)–C(8)	1.52(2)	1.497(5)	Co–P–C(16)	114.7(3)	
C(9)–Br	1.84(1)		Co–P–C(22)	122.8(4)	
C(9)–C(10)		1.424(5)	Co–P–C(11)		119.0(1)
C(10)–N(5)		1.147(5)	Co–P–C(17)		117.4(1)
P–C(10)	1.81(1)		Co–P–C(23)		108.8(1)
P–C(16)	1.83(1)		C(10)–P–C(16)	108.2(5)	
P–C(22)	1.83(1)		C(10)–P–C(22)	102.7(5)	
P–C(11)		1.829(3)	C(16)–P–C(22)	98.9(5)	
P–C(17)		1.851(4)	C(11)–P–C(17)		101.4(1)
P–C(23)		1.835(3)	C(11)–P–C(23)		103.7(1)
C–C (phenyl, mean)	1.39(2)	1.392(16)	C(17)–P–C(23)		105.0(2)

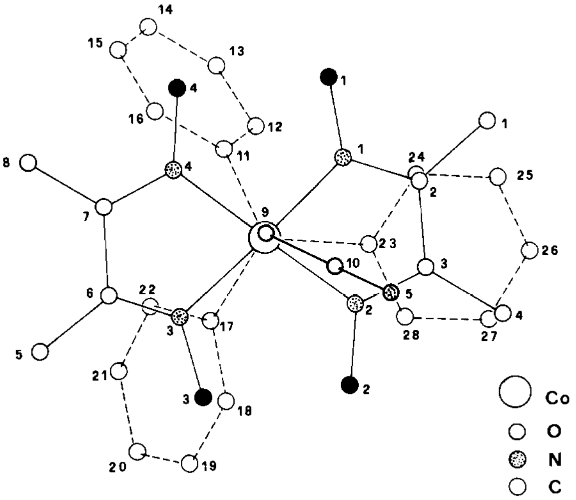

Fig. 2. A view along the Co–P bond of the crystallographically independent molecule of (*2*), together with the numbering scheme for the PPh_3 and CH_2CN ligands. The numbering scheme for the atoms of the $(Hdmg)_2$ unit is the same as in Fig. 1.

with C–Br values reported for tetrabromoethylene (1.882(3) Å) [11] and for *cis*-dibromoethylene (1.872(2) Å). This shortening, also detected for the C–CN bond in (*2*) (see below), may be due to the increased amount of s character in the C–Br bond due to the large deviation of the $Co–CH_2–Br$ angle from the tetrahedral values. In (*2*) the $Ph_3P–Co–CH_2CN$ fragment is characterized by Co–P and Co–C distances of 2.391(1) and 2.043(3) Å and by a P–Co–C angle of 177.7(1)°. The $Co–CH_2–CN$ angle is 116.5(3)° whereas the C–C and C–N distances are 1.424(5) and 1.147(5) Å respectively. The C–C bond length is slightly shorter than those reported for $CR_3–C{\equiv}N$ compounds [13] (mean 1.464(5) Å), while the CN bond length falls within the range observed for $C{\equiv}N$ triple bonds [14] (mean 1.158(3) Å). The $CH_2–CN$ bond lies almost over the Co–N(2) equatorial bond as it has been found in all py derivatives [2] and in $[Co(R)(Hdmg)_2R(PPh_3)]$ ($R = CH_2CMe_3$, CH_2CF_3). On the contrary the $CH_2–Br$ bond in (*2*) lies between two equatorial Co–N bonds (Fig. 1). Such a different orientation corresponds to slightly different values of the C(9)–Co–N (equatorial) bond angles (Table III). The orientation of PPh_3 with respect to the equatorial ligand is nearly the same as shown in Figs. 1 and 2.

Structural Comparisons

The most relevant geometrical parameters of the $XCH_2–Co–PPh_3$ grouping in the series $X = CF_3$, CN, Br, H, $t\text{-}C_4H_9$ are given in Table IV. The overall trends of the Co–P and Co–C bond lengths are similar to those found for the pyridine analogues [2], although in the latter the difference between the Co–N(py) distances in the derivatives with X = H and $X = t\text{-}C_4H_9$ is less enhanced. The Co–C bond length, when $X = t\text{-}C_4H_9$, is significantly longer than the others, which are all very similar. Unfortunately, the Co–C distance, when X = Br, is not accurate enough to allow comparison. These bond lengths however are longer than those reported for the corresponding py analogues [2], by about 0.03 Å. This observation gives support to the suggestion [5, 7] that PPh_3 exerts a greater steric *trans*-influence than pyridine.

Correspondingly the P–Co–C angles bend away from 180° much more than the py analogues. Finally, the widening of the $Co–CH_2–X$ angle, increases with the increasing bulk of X but it does not appear to be influenced by the bulk of the L ligand [7]. On the contrary, the trend of the bending angle between the two Hdmg moieties, α, and of the displacement of cobalt from the equatorial coordination plane (always towards PPh_3), d, appears different from that found in pyridine derivatives, where small values of α (from 0.2 to 5.2°) and of d (from 0 to 0.04 Å) have been reported [2]. Data of Table IV show that when the alkyl group is bulky, d, and expecially α, are significantly smaller than those of derivatives having X = H, CN. This may be interpreted by assuming that the bulky alkyl group opposes the bending of the Hdmg halves due to the PPh_3 ligand [16, 6]. Data refering to the derivative with $X = CF_3$ suggest that the CH_2CF_3 group has a steric hindrance smaller than expected, since the $Co–CH_2–CF_3$ angle is similar to that reported for $[Co(Hdmg)_2(CH_2CH_3)(Py)]$ [17] (122.4(8)°). This is mainly due to the large deforma-

TABLE IV. Relevant Structural Data for $[Co(CH_2X)(Hdmg)_2(PPh_3)]$ Compounds.

X	Co–P(Å)	Co–C(Å)	$Co–CH_2–X$(°)	P–Co–C(°)	d(Å)	α(°)
$t\text{-}C_4H_9$ [a]	2.460(1)	2.117(9)	129.2(7)	166.6(3)	0.04	2.2
H [b]	2.418(1)	2.026(6)		175.4(2)	0.11	14.0
Br [c]	2.399(3)	1.998(15)	125.2(9)	175.1(4)	0.07	2.7
CN [c]	2.391(1)	2.043(3)	116.5(3)	177.7(1)	0.08	11.1
CF_3 [d]	2.383(1)	2.036(3)	121.1(3)	170.9(1)	0.04	1.7

[a] Ref. 7. [b] Ref. 6. [c] Present work. [d] Ref. 15.

TABLE V. Comparison between Co–P Bond Lengths (Å) in [Co(R)(Hdmg)$_2$(PPh$_3$) and ^{13}C Chemical Shifts in {Co(R)(Hdmg)$_2$[P(OMe)$_3$]}.

R	Co–P	^{13}C^a
CH$_2$CMe$_3$^{b}	2.460(1)	52.36
CH$_3$^{c}	2.418(1)	52.24
CH$_2$Br^d	2.399(3)	52.87
CH$_2$CN^d	2.391(1)	53.40
CH$_2$CF$_3$^{e}	2.383(1)	53.19
NO$_2$	2.393(3)^f 2.365(4)^g	54.57
Br^h	2.331(4)	55.07
Cl^i	2.327(2)	55.19

^{a}Chemical shift (ppm) of P(O^{13}CH$_3$)$_3$ ligand, ref. 18. ^{b}Ref. 7. ^{c}Ref. 6. ^{d}Present work. ^{e}Ref. 15. ^{f}N. Bresciani-Pahor, M. Calligaris and L. Randaccio, *Inorg. Chim. Acta, 27,* 47 (1978). ^{g}A. I. Shkurpelo, Yu. A. Simonov, O. A. Bologa and T. I. Malinovski, *Crystallografia (Russ.), 248,* 1120 (1979). ^{h}N. Bresciani-Pahor, M. Calligaris, G. Nardin and L. Randaccio, *Gazz. Chim. Ital., 111,* 147 (1981). ^{i}S. Brückner and L. Randaccio, *J. Chem. Soc. Dalton Trans.,* 1017 (1974).

tions observed in the bond lengths and angles of this grouping which allow a shorter Co–C bond and a narrower Co–CH$_2$–CF$_3$ angle than expected [15].

We have already speculated [7] that, owing to the steric interaction of the CH$_2$X group with the equatorial ligand, observed geometrical distortions may take place in the following order of the increasing energy requirement: i) deformation of C–Co–N (equatorial) and of py (or PPh$_3$)–Co–C bond angles ii) opening of Co–CH$_2$–X bond angle iii) lenthening of the Co–C bond length.

On this basis, geometrical distortions found in [Co(Hdmg)$_2$(CH$_2$X)L] with L = py, PPh$_3$ suggest the following order on increasing steric bulk for X: NO$_2$ $\leqslant$ CN ~ COOMe < CH$_3$ ~ CF$_3$ < Br < SiMe$_3$ $\leqslant$ CMe$_3$. Substitution of py by PPh$_3$ does not alter the general trend, but provokes a small but significant increase of the Co–C bond length and a slight decrease of the L–Co–C bond angle. Finally, the effects of the actual bulk of X may be significantly reduced if the X-group itself may be sensibly distorted as in the case of CF$_3$ which has 'soft' C–F electron bonding pairs. In Table V the Co–P bond lengths in [Co(Hdmg)$_2$R(PPh$_3$)] and the ^{13}C chemical shifts of phosphite methyls in {Co(Hdmg)$_2$(R)[P(OMe)$_3$]} [18] are reported. Although a general trend of increasing Co–P distances with decreasing chemical shifts is observed, there is a scattering from a linear relationship larger than that found in the corresponding py complexes [2]. This may be due to the different nature of the Co–P bond in phosphine and phosphites and/or to the different bulk between PPh$_3$ and P(OMe)$_3$ ligands. Such differences are certainly less enhanced when py and t-bupy are compared.

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