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Electronic *vs.* Steric Effects in Octahedral Cobaloximes. Molecular Structure of *Trans*-Chlorobis(dimethylglyoximato)tributylphosphinecobalt(III) and *Trans*-Chlorobis(dimethylglyoximato)trimethylphosphitecobalt(III)

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Crystal data of the title compounds have revealed that crystals of trans-*chlorobis(dimethylglyoximato)-tributylphosphinecobalt(III), (I), are monoclinic, space group* $P2_1/c$ *with* a = *21.494(9),* b = *15.362(5),* c = *18.240(7) Å,* β = *116.94(8)°, Z = 8 and crystals of* trans-*chlorobis(dimethylglyoximato)trimethylphosphitecobalt(III), (II), are orthorhombic, space group* $Pca2_1$ *with* a = *17.210(7),* b = *13.598(5) and* c = *16.600(7) Å, Z = 8. The structures have been solved by three-dimensional Patterson and Fourier methods and refined by the least-squares technique. The final* R *values were 0.041 for (I) and 0.050 for (II), calculated on the basis of 4562 and 1613 independent reflections respectively.*

In both (I) and (II) the two crystallographically independent molecules have a similar structure with some differences in the $Co–PR_3$ *grouping geometry. The Co–P bond lengths, as well as the deformations in the equatorial moiety, for the series* $R_3PCo(dmgH)_2X$*, where X = Cl or C-bonded group, and R = OMe,* Bu^n*, Ph, Chx, are compared. The observed Co–P bond lengths may be rationalized in terms of steric and electronic effects, which appear to be additive to a large extent.*

Introduction

Recently it has been shown [1] that steric effects in octahedral cobaloximes may be responsible for changes in coordination bond lengths which are of the same order of magnitude of those attributable to electronic effects [2–4], although it is often difficult to discern the origin of the observed changes.

In this paper together with the molecular structure of *trans*-chlorobis(dimethylglyoximato)tributylphosphinecobalt(III), I, and of *trans*-chlorobis(dimethylglyoximato)trimethylphosphitecobalt(III), II, we report some evidence that variations of the Co–P axial bond lengths in the series $XCo(dmgH)_2PR_3$, X = Cl, R, may be 'factorized' to a large extent in terms of steric and electronic effects.

Experimental

Crystal Data

$C_{20}H_{41}CoO_4N_4PCl$, (I), M = 527.0, Monoclinic, a = 21.494(9), b = 15.362(5), c = 18.240(7) Å, β = 116.94(8)°, U = 5371.0 Å^3, D_m = 1.30 (by flotation), Z = 8, D_c = 1.30, μ(Mo-Kα) = 8.6 cm^{-1}, r_{max} (crystal) = 0.03 cm. Space group $P2_1/c$. Crystals were obtained by slow evaporation from dichloromethane.

$C_{11}H_{23}CoO_7N_4PCl$, (II), M = 448.7, orthorhombic, a = 17.210(7), b = 13.598(5), c = 16.600(7) Å, U = 3884.8 Å^3, D_m = 1.53, Z = 8, D_c = 1.54, μ(Mo-Kα) = 11.78 cm^{-1}, r_{max} (crystal) = 0.01 cm. Space group $Pca2_1$ from vector distribution of the Patterson map. The original product was recrystallized from a 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-Kα 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-Kα radiation for a maximum 2θ angle of 54° for (I) and 48° for (II). Reflections with $I_0 < 3\sigma(I_0)$ for (I) and $I_0 < 2\sigma(I_0)$ for (II) were rejected, the remainder being corrected for Lorentz and polarization factors. A total of 4562 independent reflections for (I) and 1613 for (II) 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 final anisotropic refinement for all non-hydrogen atoms including the contribution of fixed hydrogen atoms (B = 5Å^2) gave R = 0.041 for (I). The bridge H atoms have been refined isotropically. For (II) the carbon atoms were refined isotropically with the contribution of hydrogen atoms held constant (B = 5Å^2). The final R value was 0.050.

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TABLE I. Atomic Coordinates.

Atomic coordinates (× 10^4) of non hydrogen atoms for (I) with their e.s.d. s in parentheses.

	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
CO	2314(0)	2421(1)	2542(0)	7347(0)	2282(1)	4680(0)
Cl	2339(1)	2962(1)	1383(1)	7503(1)	1257(1)	5662(1)
P	2284(1)	1904(1)	3692(1)	7223(1)	3329(1)	3755(1)
O(1)	3015(2)	899(3)	2418(3)	8643(2)	3033(4)	5781(3)
O(2)	2890(2)	4018(3)	3370(3)	5995(2)	2639(3)	4506(3)
O(3)	1604(2)	3994(3)	2550(3)	6052(2)	1475(3)	3586(3)
O(4)	1738(2)	815(3)	1745(3)	8711(2)	1844(4)	4895(3)
N(1)	3081(2)	1720(3)	2707(3)	7954(3)	3017(4)	5522(3)
N(2)	3025(2)	3214(3)	3179(3)	6671(2)	2827(3)	4917(3)
N(3)	1537(2)	3145(3)	2303(3)	6752(2)	1496(3)	3863(3)
N(4)	1597(2)	1644(3)	1883(3)	8023(2)	1686(4)	4476(3)
C(1)	4372(4)	1613(6)	3257(5)	8093(5)	4045(6)	6645(4)
C(2)	3694(3)	2081(5)	3103(4)	7664(4)	3472(4)	5895(4)
C(3)	3669(3)	2962(5)	3387(4)	6917(3)	3371(5)	5532(4)
C(4)	4293(4)	3540(6)	3861(5)	6436(4)	3844(6)	5818(4)
C(5)	265(4)	3362(7)	1484(6)	6651(4)	232(5)	2961(4)
C(6)	927(3)	2834(5)	1805(4)	7046(3)	929(4)	3591(4)
C(7)	970(3)	1921(5)	1580(4)	7802(3)	1029(4)	3963(3)
C(8)	323(4)	1378(7)	1049(6)	8277(4)	419(5)	3793(4)
C(9)	3021(4)	1184(6)	4281(4)	8043(4)	3615(5)	3730(4)
C(10)	3338(4)	1110(6)	5209(5)	8262(4)	3065(6)	3197(5)
C(11)	3906(5)	1746(9)	5627(7)	8964(5)	3442(10)	3251(6)
C(12)	4295(6)	1681(10)	6579(6)	9219(6)	3083(13)	2754(7)
C(13)	2266(3)	2776(5)	4374(4)	6599(3)	3051(4)	2706(4)
C(14)	1550(3)	3172(5)	4153(4)	6475(4)	3772(5)	2069(4)
C(15)	1625(4)	3988(5)	4669(4)	5970(4)	3478(6)	1219(4)
C(16)	928(5)	4465(7)	4429(6)	5749(5)	4229(6)	581(5)
C(17)	1523(3)	1236(5)	3443(4)	6958(3)	4408(4)	3966(4)
C(18)	1461(4)	802(5)	4182(4)	6186(4)	4569(5)	3741(4)
C(19)	770(5)	328(7)	3905(6)	6102(4)	5492(5)	4037(5)
C(20)	161(6)	909(10)	3672(10)	5327(5)	5712(7)	3773(7)

Atomic positional parameters (× 10^3) of hydrogen atoms for (I). The hydrogen atoms are numbered according to the atom to which they are bonded.

	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
H(1)	241(4)	86(6)	198(5)	871(4)	240(6)	528(5)
H(2)	213(5)	400(7)	300(6)	599(4)	199(6)	392(5)
H1(C1)	426	102	300	861	401	678
H2(C1)	467	155	386	804	383	713
H3(C1)	462	195	301	794	466	652
H1(C4)	415	410	398	594	365	546
H2(C4)	455	363	352	647	449	576
H3(C4)	461	323	438	657	370	640
H1(C5)	37	394	172	614	28	279
H2(C5)	−7	305	164	682	−36	320
H3(C5)	6	337	87	674	31	247
H1(C8)	46	78	96	877	60	411
H2(C8)	6	167	49	814	43	319
H3(C8)	1	134	131	822	−19	395

(Continued on facing page)

TABLE I. *(Continued)*

H1(C9)	341	136	415	844	358	431
H2(C9)	286	58	405	802	424	354
H1(C10)	296	120	538	831	243	337
H2(C10)	354	50	538	788	309	260
H1(C11)	426	169	541	892	410	314
H2(C11)	369	236	548	935	339	386
H1(C12)	466	214	681	967	331	283
H2(C12)	452	110	673	886	312	217
H3(C12)	395	176	680	929	241	289
H1(C13)	258	326	437	614	290	270
H2(C13)	246	254	495	677	252	253
H1(C14)	131	333	355	628	430	222
H2(C14)	125	273	426	693	394	208
H1(C15)	183	381	526	619	299	103
H2(C15)	196	439	460	554	321	123
H1(C16)	101	499	479	541	401	2
H2(C16)	60	406	450	616	447	56
H3(C16)	73	465	384	551	469	76
H1(C17)	151	77	305	709	485	365
H2(C17)	109	162	316	723	453	457
H1(C18)	187	36	445	589	452	313
H2(C18)	151	124	460	602	412	402
H1(C19)	71	−10	344	639	552	466
H2(C19)	80	−6	438	631	594	380
H1(C20)	−28	52	346	529	631	398
H2(C20)	11	124	315	513	528	403
H3(C20)	20	128	409	505	570	317

The final weighting scheme was $w = 1/(A + |F_0| + B|F_0|^2)$ where $A = 17.0$ and $B = 0.003$ for (I) and $A = 21.0$ and $B = 0.003$ for (II) were chosen so as to maintain $w(|F_0| - |F_c|)^2$ essentially constant over all ranges of $|F_0|$ and $\sin(\theta/\lambda)$.

Final atomic parameters are listed in Tables 1 and II together with their estimated standard deviations. Observed and calculated structure factors and anisotropic temperature factors are available from the Editor.

Atomic scattering factors were calculated according to Ref. 5.

Calculations

All calculations were carried out on a CDC 6200 computer using programs described in Ref. 6.

Results

Structure of I

The numbering scheme for the two crystallographically independent molecules is shown in Fig. 1 and bond lengths and angles are reported in Table III.

The only difference found in the $Co(dmgH)_2$ unit of the two molecules, A and B, concerns the oxime bridges, the other bonding parameters being in the range reported [1–4] for other cobaloximes. In fact in molecule A the bridge hydrogen atoms are closer to O(1) (1.18(7)Å) and O(3) (1.05(8) Å) respectively, suggesting the formulation of the equatorial unit as $Co(dmgH)_2$. On the contrary in molecule B the hydrogen atoms are closer to O(3) (1.04(9) Å) and to O(4) (1.10(10) Å), suggesting a Co(dmg) ($dmgH_2$) structure [8].

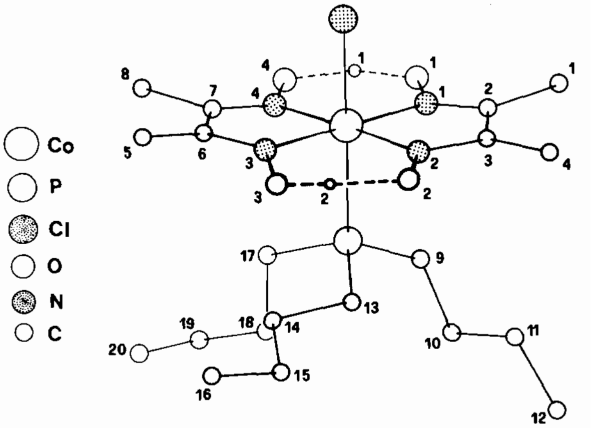

Fig. 1. A view of a molecule of I together with the numbering scheme for both crystallographically independent molecules A and B. The scheme for the equatorial moiety of molecules A and B of II is the same.

The four N donor atoms are coplanar within ±0.02 Å (A) and ±0.004 Å (B), the cobalt atom being displaced above their mean plane towards the Bu_3^nP

TABLE II. Atomic Positional Parameters.

Atomic positional parameters (× 10^4) and isotropic temperature factors for (II) with their e.s.d. s in parentheses

	Molecule A				Molecule B			
	x	*y*	*z*	$B(Å^2)$	*x*	*y*	*z*	$B(Å^2)$
CO	3848(1)	106(1)	4974(1)		1323(1)	5094(1)	2431(1)	
Cl	3077(2)	1440(3)	5174(3)		627(3)	6464(3)	2082(3)	
P	4618(2)	−1131(3)	4780(3)		2060(2)	3803(3)	2699(3)	
O(1)	2467(7)	−967(8)	4493(8)		−41(6)	4154(8)	2973(6)	
O(2)	4506(6)	347(9)	6523(7)		1934(7)	5082(8)	798(7)	
O(3)	5162(6)	1188(9)	5443(7)		2658(7)	6129(8)	1831(7)	
O(4)	3173(7)	−69(10)	3425(7)		692(6)	5141(9)	3997(7)	
O(5)	5309(6)	−1101(10)	5419(8)		2437(12)	3729(11)	3514(11)	
O(6)	5122(7)	−1152(9)	3989(7)		2754(9)	3659(12)	2116(13)	
O(7)	4176(6)	−2149(7)	4900(8)		1658(8)	2841(9)	2491(10)	
N(1)	2938(7)	−718(9)	5100(9)		436(6)	4308(8)	2328(7)	
N(2)	3902(8)	−120(11)	6129(8)		1393(7)	4787(9)	1342(7)	
N(3)	4686(7)	927(8)	4831(7)		2246(6)	5910(9)	2466(7)	
N(4)	3718(7)	318(10)	3848(8)		1284(7)	5431(10)	3528(8)	
C(1)	2066(11)	−1510(14)	6088(11)	4.7(4)	−411(10)	3314(14)	1467(11)	4.2(4)
C(2)	2809(9)	−970(11)	5831(9)	3.2(3)	255(9)	3924(11)	1629(9)	3.0(3)
C(3)	3354(10)	−625(12)	6415(10)	3.7(3)	843(9)	4211(11)	1009(10)	3.1(3)
C(4)	3341(11)	−853(13)	7289(11)	4.5(4)	774(10)	3891(13)	157(11)	4.1(3)
C(5)	5500(13)	1983(16)	3918(14)	6.2(5)	3042(11)	6907(14)	3304(12)	4.7(4)
C(6)	4816(9)	1243(12)	4110(10)	3.3(3)	2369(10)	6293(12)	3135(10)	3.5(3)
C(7)	4242(10)	869(13)	3516(11)	3.9(3)	1822(9)	6014(11)	3776(9)	2.9(3)
C(8)	4229(12)	1174(15)	2637(13)	5.6(4)	1880(11)	6323(13)	4626(11)	4.5(4)
C(9)	6110(14)	−1037(18)	5349(15)	7.2(6)	2039(16)	3516(20)	4272(18)	8.9(7)
C(10)	4830(12)	−1485(15)	3204(12)	5.1(4)	3539(19)	4131(22)	2373(19)	10.0(8)
C(11)	4638(10)	−3095(13)	4985(11)	4.6(4)	1922(13)	1876(17)	2473(14)	6.9(5)

Atomic coordinates (× 10^3) of hydrogen atoms for (II)

	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
H1(C1)	172	−175	565	−72	325	200
H2(C1)	176	−122	653	−23	265	131
H3(C1)	226	−222	636	−76	360	106
H1(C4)	379	−51	756	123	419	−18
H2(C4)	330	−152	739	29	416	−11
H3(C4)	284	−48	750	80	319	11
H1(C5)	580	219	446	332	711	282
H2(C5)	534	265	369	337	664	372
H3(C5)	592	172	357	282	760	355
H1(C8)	383	77	232	146	607	497
H2(C8)	476	103	237	181	710	462
H3(C8)	412	187	259	239	620	486
H1(C9)	640	−88	580	238	350	475
H2(C9)	614	−14	507	179	280	425
H3(C9)	634	−129	487	157	396	439
H1(C10)	526	−147	278	402	410	201
H2(C10)	439	−108	302	377	399	296
H3(C10)	465	−220	325	351	496	244
H1(C11)	426	−366	506	143	140	233
H2(C11)	497	−304	547	202	163	307
H3(C11)	496	−320	450	232	171	214
H(1)	280	−40	370	35	460	370
H(2)	495	60	610	230	560	120

TABLE III. Bond Lengths (A) and Angles (°) in (I) with their e.s.d. s in Parentheses

Bond lengths	Molecule A	Molecule B
Co–Cl	2.295(2)	2.293(2)
Co–P	2.271(2)	2.258(2)
Co–N(1)	1.876(5)	1.876(5)
Co–N(2)	1.887(4)	1.889(5)
Co–N(3)	1.886(5)	1.894(4)
Co–N(4)	1.888(4)	1.892(6)
N(1)–O(1)	1.349(7)	1.335(7)
N(1)–C(2)	1.305(7)	1.313(11)
N(2)–O(2)	1.350(7)	1.330(5)
N(2)–C(3)	1.317(8)	1.303(8)
N(3)–O(3)	1.366(7)	1.353(6)
N(3)–C(6)	1.301(7)	1.299(9)
N(4)–O(4)	1.359(7)	1.344(5)
N(4)–C(7)	1.276(7)	1.310(8)
C(1)–C(2)	1.53(1)	1.534(9)
C(2)–C(3)	1.46(1)	1.441(10)
C(3)–C(4)	1.51(1)	1.535(12)
C(5)–C(6)	1.51(1)	1.518(9)
C(6)–C(7)	1.48(1)	1.458(8)
C(7)–C(8)	1.53(1)	1.518(11)
P–C(mean)	1.825(8)	1.836(9)
C–C(butyl mean)	1.52(1)	1.52(1)
O(1)–H(1)	1.18(7)	1.39(10)
O(4)–H(1)	1.31(9)	1.10(10)
O(2)–H(2)	1.46(10)	1.46(9)
O(3)–H(2)	1.05(8)	1.04(9)
Bond Angles		
Co–N(1)–O(1)	123.0(3)	123.3(5)
Co–N(1)–C(2)	116.0(5)	115.3(5)
Co–N(2)–O(2)	122.7(3)	122.1(4)
Co–N(2)–C(3)	116.1(4)	115.3(4)
Co–N(3)–O(3)	122.5(3)	123.3(4)
Co–N(3)–C(6)	116.8(5)	117.1(3)
Co–N(4)–O(4)	121.6(3)	123.1(5)
Co–N(4)–C(7)	117.5(5)	116.8(4)
P–Co–Cl	179.2(1)	177.6(1)
N(1)–Co–N(2)	82.2(2)	82.4(3)
N(1)–Co–N(3)	176.0(2)	177.4(2)
N(1)–Co–N(4)	98.3(2)	98.1(3)
N(2)–Co–N(3)	98.5(2)	98.5(2)
N(2)–Co–N(4)	178.7(2)	177.0(3)
N(3)–Co–N(4)	81.0(2)	80.9(2)
N(1)–C(2)–C(1)	122.7(7)	122.2(7)
N(1)–C(2)–C(3)	113.6(6)	113.3(6)
N(2)–C(3)–C(2)	111.9(5)	113.4(7)
N(2)–C(3)–C(4)	122.5(7)	121.5(5)
N(3)–C(6)–C(5)	123.3(7)	124.1(6)
N(3)–C(6)–C(7)	111.9(5)	112.6(5)
N(4)–C(7)–C(6)	112.5(5)	112.4(6)
N(4)–C(7)–C(8)	124.8(7)	124.2(5)
O(1)–N(1)–C(2)	121.0(5)	121.2(5)
O(2)–N(2)–C(3)	121.0(5)	122.5(6)
O(3)–N(3)–C(6)	120.2(5)	119.5(5)
O(4)–N(4)–C(7)	120.9(5)	119.7(6)
C(1)–C(2)–C(3)	123.7(6)	124.5(8)
C(2)–C(3)–C(4)	125.6(6)	125.1(6)
C(5)–C(6)–C(7)	124.8(6)	123.4(7)
C(6)–C(7)–C(8)	122.7(6)	123.4(5)
Co–P–C(mean)	112.1(3)	114.1(3)
C–P–C(mean)	106.6(4)	104.5(3)
P–C–C(mean)	118.3(6)	117.1(5)
C–C–C(butyl mean)	112.9(8)	112.1(8)

ligand by 0.042 and 0.044 Å respectively. The two dmgH moieties make a dihedral angle of 10.6° (A) and 12.3° (B), whereas they make angles of 5.3 and 5.6° in molecule A and 6.2 and 6.4° in molecule B with the coordination plane. We observe that the slight difference in the Co–P distances, 2.271(2) and 2.258(2) Å in A and B molecules respectively, reflects also slight differences in the distortions on the equatorial moiety. The shorter Co–P bond length corresponds to a more coplanar arrangement of the N donor atoms and to a more pronounced bending of the two dmgH units. On the other hand the axial Co–Cl bond lengths are nearly equal in both A and B molecule, being 2.295(2) and 2.293(2) Å respectively. Their mean value is equal to that reported for $\mathrm{Chx_3PCo(dmgH)_2Cl}$ [1] (2.294(5) Å) and slightly larger than that found in $\mathrm{Ph_3PCo(dmgH)_2Cl}$ [2] (2.277(2) Å).

Finally, all the butyl groups adopt an approximate *trans* conformation in molecule B as found in $\mathrm{Bu_3^nPCo(dmgH)_2C_5H_4N}$ [9]. In molecule A, however, one butyl group, C(17)–C(20), has an approximate *gauche* conformation, with a torsion angle around the C(18)–C(19) bond of 73.0°. Since in $\mathrm{Bu_3^nP\,Co(dmgH)_2}$xanthinato [3] two of the butyl groups have a *gauche* conformation, these differences are undoubtedly due to the crystal packing.

Structure of II

The numbering scheme for the equatorial moiety of the two crystallographically independent molecules A and B is the same as in Fig. 1. Bond lengths and angles are reported in Table IV. No difference between the bond lengths and angles of the two $\mathrm{Co(dmgH)_2}$ units may be detected within the experimental errors. The four donor atoms are coplanar within ±0.001 Å in A and ±0.006 Å in B, the cobalt atom being displaced above their mean plane toward the $\mathrm{P(OMe)_3}$ group by 0.03 and 0.01 Å respectively. Furthermore the two dmgH moieties make a dihedral angle of 6.7(A) and 1.5°(3); correspondingly the Co–P distance is 2.165(4) Å in A and 2.211(4) Å in B. Such a difference in the Co–P bond lengths, as already observed in compound I, follows the difference in the distortions of the equatorial moiety. Thus the shorter Co–P distance corresponds to a greater

TABLE IV. Bond Lengths (Å) and Angles (°) in (II) with Their e.s.d. s in Parentheses.

Bond Lengths	Molecule A	Molecule B
Co–Cl	2.272(4)	2.289(5)
Co–P	2.165(4)	2.211(4)
Co–N(1)	1.94(1)	1.87(1)
Co–N(2)	1.94(1)	1.86(1)
Co–N(3)	1.84(1)	1.94(1)
Co–N(4)	1.90(1)	1.88(1)
N(1)–O(1)	1.34(2)	1.37(2)
N(1)–C(2)	1.28(2)	1.31(2)
N(2)–O(2)	1.38(2)	1.36(2)
N(2)–C(3)	1.26(2)	1.35(2)
N(3)–O(3)	1.35(2)	1.31(2)
N(3)–C(6)	1.29(2)	1.25(2)
N(4)–O(4)	1.28(2)	1.34(2)
N(4)–C(7)	1.30(2)	1.29(2)
C(1)–C(2)	1.54(2)	1.44(2)
C(2)–C(3)	1.43(2)	1.50(2)
C(3)–C(4)	1.48(3)	1.49(3)
C(5)–C(6)	1.58(3)	1.46(3)
C(6)–C(7)	1.49(2)	1.47(2)
C(7)–C(8)	1.52(3)	1.48(2)
P–O(5)	1.59(1)	1.50(2)
P–O(6)	1.57(1)	1.55(2)
P–O(7)	1.59(1)	1.52(1)
O(5)–C(9)	1.39(3)	1.46(4)
O(6)–C(10)	1.47(2)	1.56(4)
O(7)–C(11)	1.52(2)	1.39(3)
Bond Angles		
Co–N(1)–O(1)	123.7(11)	120.4(8)
Co–N(1)–C(2)	113.4(11)	120.2(10)
Co–N(2)–O(2)	115.5(10)	128.7(9)
Co–N(2)–C(3)	115.0(12)	118.9(10)
Co–N(3)–O(3)	122.5(9)	123.5(9)
Co–N(3)–C(6)	117.2(10)	113.9(10)
Co–N(4)–O(4)	124.1(10)	121.2(10)
Co–N(4)–C(7)	115.0(11)	115.8(11)
P–Co–Cl	178.0(2)	175.7(2)
N(1)–Co–N(2)	80.8(6)	80.6(5)
N(1)–Co–N(3)	177.5(5)	176.5(5)
N(1)–Co–N(4)	95.7(6)	101.5(5)
N(2)–Co–N(3)	100.7(6)	96.0(5)
N(2)–Co–N(4)	176.0(6)	178.0(5)
N(3)–Co–N(4)	82.7(5)	82.0(5)
N(1)–C(2)–C(1)	123(1)	126(1)
N(1)–C(2)–C(3)	116(1)	110(1)
N(2)–C(3)–C(2)	115(1)	110(1)
N(2)–C(3)–C(4)	120(2)	128(1)
N(3)–C(6)–C(5)	122(2)	123(2)
N(3)–C(6)–C(7)	113(1)	115(1)
N(4)–C(7)–C(6)	112(2)	113(1)
N(4)–C(7)–C(8)	124(2)	122(1)
O(1)–N(1)–C(2)	123(1)	119(1)
O(2)–N(2)–C(3)	129(1)	112(1)
O(3)–N(3)–C(6)	120(1)	122(1)
O(4)–N(4)–C(7)	121(1)	123(1)
C(1)–C(2)–C(3)	121(1)	124(1)
C(2)–C(3)–C(4)	126(2)	122(1)
C(5)–C(6)–C(7)	125(2)	121(2)
C(6)–C(7)–C(8)	124(2)	125(1)
Co–P–O(mean)	113.2(5)	115.2(7)
O–P–O(mean)	105.4(7)	102.9(10)
P–O–C(mean)	126(1)	125(2)

coplanarity of the N atoms and to a more pronounced bending of the two dmgH planes. Although the two crystallographically independent Co–P distances are different, they are both significantly shorter than that of 2.256(4) Å found in (MeO)$_3$PCo(dmgH)$_2$CH$_3$. On the other hand the Co–Cl bond lengths of 2.272(4) and 2.289(5) Å in A and B respectively are very similar and their mean does not differ from the values found in I and in other R$_3$P(dmgH)$_2$Cl compounds [9].

Discussion

The available Co–P distances for a series of *trans*-R$_3$PCo(DH)$_2$X compounds, (R = OMe, Bu^n, Ph, Chx; X = Cl, C-bonded group), are collected in Table V together with the cobalt displacement, *d*, above the coordination plane and the α angles between the two dmgH halves. The values are arranged following the increasing bulkiness of the phosphines along the column and the increasing *trans*-influencing ability of X along the row.

As far as the Co–P bond length, which varies from 2.165(4) to 2.418(1) Å, is concerned, its lengthening in each series having the same *trans* ligand X, clearly follows the increasing bulkiness of the phosphines rather than their basicity. This trend appears to be confirmed by the correlation between Co–P bond lengths and phosphine experimental cone angles (ECA) obtained from n.m.r. data [10], as shown in Fig. 2. On the contrary no correlation is observed with the electronic parameter ν of the phosphines, as defined by Tolman [11]. In the chloro derivative series, the out-of-plane cobalt, *d*, appears to follow the same trend varying from 0.01–0.03 Å in the P(OMe)$_3$ derivative to 0.10 Å in the PChx$_3$ one. On the contrary the values of the angle of bending, α, show no clear correlation with the bulkiness of the phosphine and, in addition, it varies in the same compound for the two crystallographically independent molecules. This may indicate that the crystal packing influences the bending of the dmgH units. The *d* and α values in organocobaloximes are not compared since they do not represent a sufficient set of data. The Co–Cl bond lengths do not show large variations,

TABLE V. Co–P Bond Lengths (Å), d(Å) and α(°) Values for the Series $R_3PCo(dmgH)_2X$.

		Cl	–C	
$P(OMe)_3$	Co–P	2.165(4), 2.211(4)[a]	2.256(4)[d]	
	d	0.03 , 0.01	0.10	X = Me
	α	7 , 1	10	
PBu^n_3	Co–P	2.271(2), 2.258(2)a	2.342(1)[e]	
	d	0.04 , 0.04	0.03	X = $-C_5H_4N$
	α	11 , 12	5	
PPh_3	Co–P	2.327(2)[b]	2.418(1)[c]	
	d	0.05	0.11	X = Me
	α	6	14	
$PChx_3$	Co–P	2.369(5)[c]		
	d	0.10	–	
	α	16		

[a]Present work. [b]Ref. 2. [c]Ref. 1. [d]Ref. 10. [e]Ref. 9.

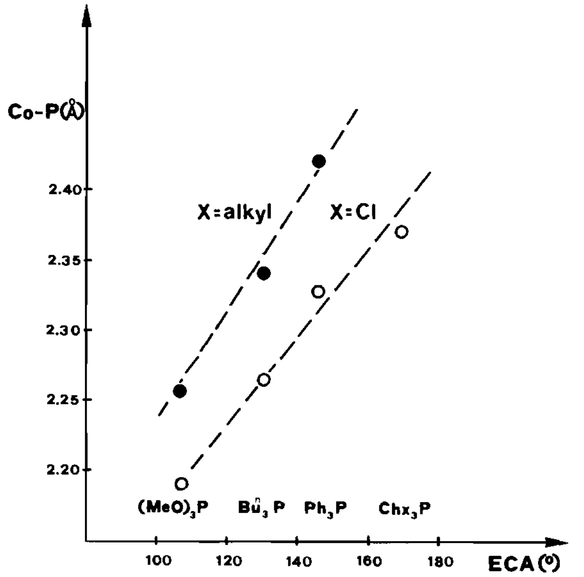

Fig. 2. Correlation between Co–P bond lengths and experimental cone angles (ECA).

the lowest value being 2.277(2) Å in $PPh_3Co(dmgH)_2Cl$, the highest 2.294(2) Å in both Chx_3P and Bu^n_3P derivatives.

Beside the 'steric' lengthening of the Co–P bond, occurring along the columns of Table II, a further lengthening is detected when the *trans* Cl is replaced by a strong donor ligand such as a σ-carbon-bonded group. This *trans*-influence was expected and is attributable mainly to electronic effects [1]. Figures, reported in Table V, indicate that the 'steric' lengthening nearly adds to the 'electronic' one. Thus the lengthening of 0.15 Å of the Co–P bond in $PPh_3Co(dmgH)_2CH_3$ with respect to the mean value of 2.265(2) Å in $PBu^n_3Co(dmgH)_2Cl$ may be ascribed in part (0.06 Å) to the increased bulkiness of the phosphine and in part (0.09 Å) to the *trans*-influence of the methyl group.

A comparison of the *d* and α values in $P(OMe)_3Co(dmgH)_2X$, with X = Cl and CH_3, supports the previous observation [1] that in the methyl-cobaloximes the distortions of the $Co(dmgH)_2$ unit are significantly larger than those found in the corresponding chloro derivative. This has been attributed to the more 'compact' bulk of Cl as compared with that of CH_3, which opposes more efficiently to the bending of the equatorial ligand provoked by the phosphine on the opposite side.

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