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Structural Study of Steric Effects in Cobalt Dimethylglyoximates Containing Phosphine Ligands. The Structure of *trans*-Bis(dimethylglyoximato)methyltriphenylphosphinecobalt(III) and of *trans*-Bis(dimethylglyoximato)chlorotricyclohexylphosphinecobalt(III) Toluene Solvate

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The crystal and molecular structure of the title compounds has revealed that crystals of trans-*bis(dimethylglyoximate)methyltriphenylphosphinecobalt(III) (I) are monoclinic space group* $P2_1$ *with* a = *10.406(8),* b = *15.54(1),* c = *8.963(5)* Å, β = *108.75(7)°*, Z = *2 and crystals of* trans-*bis(dimethylglyoximate)chlorotricyclohexylphosphinecobalt(III) (II) are monoclinic, space group* $P2_1/c$ *with* a = *9.501(7),* b = *29.33(1),* c = *12.98(1)* Å, β = *99.0(1)°*, Z = *4. The structures have been solved by three-dimensional Patterson and Fourier methods and refined by the least-squares technique. The final* R *values were 0.032 for (I) and 0.072 for (II), calculated on the basis of 1850 and 1651 independent reflections respectively.*

In (I) the Co–P bond length of 2.418(1) Å *is the largest value so far reported and confirms the strong* trans-*influence of the methyl group (Co–*CH_3*, 2.026(6)* Å*). The coordinated N atoms are coplanar within ±0.015* Å*; the cobalt is displaced of 0.112* Å *above their mean plane towards the phosphine. The two dmgH units are bent away from the phosphine ligand and their mean planes make an angle of 13.6°. The axial bond lengths in (II) are: Co–P 2.369(5)* Å*, Co–Cl 2.294(5)* Å*. The coordinated N atoms are coplanar within 0.007* Å *with Co displaced of 0.10* Å *towards phosphine ligand, whereas the two dmgH mean planes make an angle of 15.7°.*

These results are discussed in terms of steric factors. Correlation with experimental cone angles and n.m.r. results is discussed.

Introduction

Cobaloximes (compounds containing the $Co(dmgH)_2$ unit, where dmgH is the monoanion of dimethylglyoxime) are versatile complexes in that diverse ligands can be accommodated in the two axial positions [1–4]. This property is no doubt due to the intermediate electronic properties of the metal center. For example, at equilibrium, there are approximately equal amounts of the N and S bonded isomers of $LCo(dmgH)_2SCN$, where L = N or P donor ligand [4].

The electronic (*trans* influence and *trans* effect) and steric properties of the axial ligands have been used to explain spectroscopic [1], kinetic [2] and thermodynamic [4] properties of the cobaloxime complexes. Although the structural aspects of the *trans*-influence has received some study [5–9], relatively little structural information is known about the steric effects of axial ligands. An ^1H nmr study of complexes of the type $R_3PCo(dmgH)_2(CH_3OH)^+$, in CH_3OH solution, demonstrated that the dependence of the ^1H shifts on the R_3P ligand could best be understood as arising from a distortion of the $Co(dmgH)_2$ unit from planarity [3]. The expected degree of distortion was related to Tolman's cone angle [10], a measure of the bulkiness of phosphorus donor ligands. The effective cone angle of a phosphorus ligand, in a sterically constrained environment, may be a function of the P to metal bond length.

To gain further insight into these phenomena, and to further establish the proposed mechanism for the ^1H nmr shift dependence, we have determined the crystal structure of *trans*-bis(dimethylglyoximate)methyltriphenylphosphinecobalt(III), (I), and of *trans*-bis(dimethylglyoximate)chlorotricyclohexylphosphinecobalt(III) toluene solvate, (II).

Experimental

The synthesis of the title compounds has been described previously [2, 3]. Both the complexes were crystallized from toluene by slow evaporation.

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TABLE I. Atomic Positional Parameters.

a) Atomic Positional Parameters ($\times 10^4$) of Non-hydrogen Atoms for (I) with Their e.s.d's. in Parentheses.

	X	*Y*	*Z*
Co	1808(1)	4988(1)	3148(1)
P	4068(1)	4528(1)	4675(1)
O(1)	1118(4)	5436(3)	5907(4)
O(2)	1442(5)	3348(3)	1557(5)
O(3)	2279(5)	4531(3)	261(4)
O(4)	1858(4)	6637(3)	4521(4)
N(1)	1175(4)	4798(3)	4874(5)
N(2)	1276(5)	3803(3)	2770(6)
N(3)	2245(4)	5166(3)	1285(5)
N(4)	2085(4)	6174(3)	3357(5)
C(1)	130(7)	3797(6)	6326(8)
C(2)	709(5)	4029(4)	5027(7)
C(3)	771(6)	3451(4)	3781(7)
C(4)	267(7)	2537(5)	3597(10)
C(5)	2836(7)	6205(6)	−475(7)
C(6)	2480(5)	5958(4)	972(6)
C(7)	2379(6)	6562(4)	2179(6)
C(8)	2474(7)	7516(4)	2048(8)
C(9)	−133(6)	5273(4)	1863(8)
C(10)	5144(5)	4182(3)	3505(6)
C(11)	5354(5)	4799(4)	2447(6)
C(12)	6249(6)	4621(5)	1597(7)
C(13)	6912(6)	3830(5)	1775(7)
C(14)	6713(6)	3229(4)	2814(7)
C(15)	5823(5)	3400(4)	3670(6)
C(16)	5274(5)	5241(3)	6090(6)
C(17)	6658(6)	5040(5)	6575(7)
C(18)	7584(7)	5570(5)	7681(8)
C(19)	7143(6)	6268(4)	8332(7)
C(20)	5778(6)	6458(4)	7869(6)
C(21)	4831(6)	5945(4)	6740(6)
C(22)	3980(5)	3619(3)	5952(6)
C(23)	4084(6)	3758(4)	7535(6)
C(24)	3876(6)	3085(5)	8468(7)
C(25)	3597(7)	2267(4)	7828(7)
C(26)	3481(6)	2107(4)	6271(7)
C(27)	3651(6)	2787(4)	5309(6)

b) Atomic Positional Parameters ($\times 10^3$) of Hydrogen Atoms for (I). The hydrogen atoms are numbered according to the atom to which they are bonded.

	X	*Y*	*Z*
H1(C1)	22	431	706
H2(C1)	66	331	698
H3(C1)	−84	364	589
H1(C4)	−11	239	448
H2(C4)	103	213	366
H3(C4)	−47	246	257
H1(C5)	302	684	−47
H2(C5)	209	605	−146
H3(C5)	369	589	−48
H1(C8)	238	780	302
H2(C8)	172	773	111
H3(C8)	337	768	194
H(C11)	484	535	229
H(C12)	641	506	86
H(C13)	753	369	116
H(C14)	720	267	296
H(C15)	569	297	441
H(C17)	698	453	612
H(C18)	856	544	800
H(C19)	780	664	910
H(C20)	546	695	835
H(C21)	385	608	640
H(C23)	434	434	800
H(C24)	391	320	958
H(C25)	349	178	850
H(C26)	327	152	582
H(C27)	355	268	419
H(1)	160	600	520
H(2)	190	390	80

Crystal Data

$C_{27}H_{32}CoO_4N_4P$, (I), M = 566.5, Monoclinic, a = 10.406(8), b = 15.54(1), c = 8.963(5) Å, β = 108.75(7)°, U = 1372.5 Å^3, D_m = 1.36, Z = 2, D_c = 1.37, μ(Mo-Kα) = 9 cm^{-1}, r_{max}(crystal) = 0.03 cm. Space group $P2_1$ from structure refinement. $C_{26}H_{47}ClCoO_4N_4P \cdot C_6H_5CH_3$, (II), M = 697.2, Monoclinic, a = 9.501(7), b = 29.33(1), c = 12.98(1) Å, β = 99.0(1)°, U = 3572.0 Å^3, D_m = 1.35, Z = 4, D_c = 1.30, μ(Mo-Kα) = 8 cm^{-1}, r_{max}(crystal) = 0.02 cm. Space group $P2_1/c$.

Cell parameters were determined from Weissenberg 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 $2\theta_{max}$ 50° for both compounds. Reflexions having $I_o < 3\sigma(I_o)$ were rejected and the remainder were corrected for Lorentz polarization factors. A total of 1850 independent reflexions for (I) and of 1651 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 method. The final anisotropic refinement for all non-hydrogen atoms including however the contribution of fixed hydrogen atoms (set at B = 5 Å^2) gave R 0.032 for (I). In the case of (II) carbon atoms were refined isotropically, and the contribution of hydrogen atoms (set at B = 5 Å^2), held constant, was also included. The toluene molecules, which show some amount of disorder on the

TABLE II. Positional Parameters and Temperature Factors.

a) Atomic Co-ordinates (× 10^4) and Isotropic Temperature Factors for (II) together with Their e.s.d's. in Parentheses

	X	*Y*	*Z*	B(A^2)
Co	1079(2)	1633(1)	728(2)	
Cl	3191(4)	1746(1)	118(4)	
P	–1114(4)	1531(1)	1351(4)	
O(1)	1902(12)	710(4)	1147(10)	
O(2)	–253(11)	2031(4)	–1207(10)	
O(3)	642(11)	2585(3)	236(9)	
O(4)	2731(11)	1249(4)	–2580(9)	
N(1)	1208(13)	1004(4)	365(10)	
N(2)	186(12)	1648(5)	–644(11)	
N(3)	1139(12)	2276(4)	1027(9)	
N(4)	2166(12)	1637(4)	2089(10)	
C(1)	930(21)	405(7)	–896(16)	5.3(5)
C(2)	762(17)	873(6)	–516(14)	3.8(4)
C(3)	129(17)	1253(6)	–1213(13)	3.8(4)
C(4)	–430(21)	1195(7)	–2356(16)	5.5(5)
C(5)	2159(18)	2899(6)	2148(15)	4.3(4)
C(6)	1851(16)	2403(5)	1859(13)	2.7(3)
C(7)	2412(17)	2031(6)	2557(14)	3.8(4)
C(8)	3268(20)	2079(6)	3602(16)	4.9(4)
C(9)	–2003(15)	2086(5)	1593(12)	2.7(3)
C(10)	–3135(17)	2084(6)	2259(14)	3.9(4)
C(11)	–3519(17)	2576(6)	2518(14)	3.7(4)
C(12)	–4013(20)	2840(6)	1519(16)	5.0(4)
C(13)	–2913(19)	2826(6)	787(15)	4.6(4)
C(14)	–2592(15)	2328(5)	517(13)	2.8(3)
C(15)	–996(16)	1246(5)	2623(13)	3.1(3)
C(16)	–192(18)	1494(6)	3599(14)	4.1(4)
C(17)	–483(19)	1282(6)	4639(15)	5.0(4)
C(18)	–78(22)	778(7)	4692(17)	5.8(5)
C(19)	–843(18)	515(6)	3689(14)	4.0(4)
C(20)	–514(18)	737(6)	2684(14)	4.3(4)
C(21)	–2389(15)	1145(5)	500(12)	2.8(3)
C(22)	–3619(17)	942(6)	1064(14)	3.7(4)
C(23)	–4389(19)	561(6)	342(14)	4.5(4)
C(24)	–4958(19)	720(6)	–741(15)	4.5(4)
C(25)	–3756(20)	943(6)	–1290(16)	4.9(4)
C(26)	–3077(16)	1334(5)	–565(13)	3.2(3)
C(27)	6690(35)	5123(9)	1677(23)	
C(28)	5801(33)	4732(9)	1303(18)	
C(29)	6120(33)	4393(10)	688(23)	
C(30)	5104(39)	4046(13)	405(30)	
C(31)	3782(35)	4035(11)	659(25)	
C(32)	3474(32)	4387(12)	1383(24)	
C(33)	4429(29)	4759(10)	1672(24)	

b) Atomic Positional Parameters (× 10^3) for Hydrogen Atoms for (II)

TABLE II. *(Continued)*

	X	*Y*	*Z*
H1(C1)	135	19	–31
H2(C1)	155	39	–145
H3(C1)	–4	27	–120
H1(C4)	–77	151	–268
H2(C4)	–123	98	–249
H3(C4)	36	109	–276
H1(C5)	169	311	159
H2(C5)	322	296	225
H3(C5)	181	299	282
H1(C8)	352	177	393
H2(C8)	274	225	410
H3(C8)	419	224	357
H(C9)	–121	229	199
H1(C10)	–399	193	186
H2(C10)	–282	191	292
H1(C11)	–433	257	295
H2(C11)	–268	273	294
H1(C12)	–493	272	110
H2(C12)	–418	318	164
H1(C13)	–325	300	12
H2(C13)	–201	297	114
H1(C14)	–350	217	19
H2(C14)	–188	231	4
H(C15)	–201	122	275
H1(C16)	86	150	357
H2(C16)	–53	184	356
H1(C17)	4	145	527
H2(C17)	–155	130	470
H1(C18)	100	75	473
H2(C18)	–32	63	534
H1(C19)	–51	18	370
H2(C19)	–190	52	368
H1(C20)	54	73	267
H2(C20)	–101	57	205
H(C21)	–180	87	34
H1(C22)	–323	82	178
H2(C22)	–432	119	116
H1(C23)	–370	31	31
H2(C23)	–521	44	69
H1(C24)	–541	46	–117
H2(C24)	–575	95	–71
H1(C25)	–303	71	–140
H2(C25)	–418	107	–200
H1(C26)	–227	149	–91
H2(C26)	–377	158	–47
H(1)	260	100	180
H(2)	15	240	–30

Fourier map, were treated anisotropically. The final *R* value was 0.072.

The final weighting scheme was $w = 1/(A + |F_o| + B|F_o|^2)$ where $A = 7.0$, $B = 0.01$ for (I) and $A = 12$, $B = 0.034$ for (II) 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 Table I 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. 11.

Calculations

All calculations were carried out on a CDC 6200 computer using programs described in Ref. 12.

TABLE III. Bond Lengths (Å) and Angles (°) of Interest with Their e.s.d's. in Parentheses for Compounds (I) and (II).

a) Bond Lengths	(I)	(II)
Co–Cl	–	2.294(5)
Co–C(9)	2.026(6)	–
Co–P	2.418(1)	2.369(5)
Co–N(1)	1.889(5)	1.913(12)
Co–N(2)	1.921(5)	1.849(13)
Co–N(3)	1.887(5)	1.924(12)
Co–N(4)	1.866(5)	1.901(12)
N(1)–O(1)	1.371(6)	1.41(2)
N(1)–C(2)	1.313(8)	1.22(2)
N(2)–O(2)	1.354(7)	1.37(2)
N(2)–C(3)	1.305(9)	1.37(2)
N(3)–O(3)	1.356(6)	1.40(2)
N(3)–C(6)	1.303(8)	1.24(2)
N(4)–O(4)	1.349(6)	1.37(2)
N(4)–C(7)	1.334(8)	1.31(2)
C(1)–C(2)	1.516(11)	1.48(3)
C(2)–C(3)	1.451(9)	1.50(2)
C(3)–C(4)	1.505(10)	1.51(3)
C(5)–C(6)	1.508(9)	1.52(2)
C(6)–C(7)	1.461(8)	1.46(2)
C(7)–C(8)	1.493(9)	1.47(3)
b) Bond Angles		
Co–N(1)–O(1)	122.8(4)	116.9(9)
Co–N(1)–C(2)	117.7(4)	121(1)
Co–N(2)–O(2)	122.6(4)	126(1)
Co–N(2)–C(3)	115.9(4)	118(1)
Co–N(3)–O(3)	124.0(4)	119.5(8)
Co–N(3)–C(6)	116.4(4)	118(1)
Co–N(4)–O(4)	123.0(4)	122.8(9)
Co–N(4)–C(7)	115.8(4)	118(1)
P–Co–Cl	–	178.9(2)
P–Co–C(9)	175.4(2)	–
N(1)–Co–N(2)	80.7(2)	79.8(6)
N(1)–Co–N(4)	98.9(2)	100.9(5)
N(2)–Co–N(3)	97.0(2)	99.5(6)
N(3)–Co–N(4)	82.6(2)	79.2(5)
N(1)–C(2)–C(1)	123.2(6)	125(2)
N(1)–C(2)–C(3)	111.9(6)	112(2)
N(2)–C(3)–C(2)	113.7(5)	109(1)
N(2)–C(3)–C(4)	121.6(6)	127(2)
N(3)–C(6)–C(5)	122.7(6)	124(1)
N(3)–C(6)–C(7)	112.6(5)	114(1)
N(4)–C(7)–C(6)	112.6(5)	110(1)
N(4)–C(7)–C(8)	123.3(6)	123(2)
O(1)–N(1)–C(2)	119.3(5)	122(1)
O(2)–N(2)–C(3)	121.5(5)	115(1)
O(3)–N(3)–C(6)	119.6(5)	121(1)
O(4)–N(4)–C(7)	120.8(5)	119(1)
C(1)–C(2)–C(3)	124.8(6)	123(2)
C(2)–C(3)–C(4)	124.7(7)	124(2)
C(5)–C(6)–C(7)	124.7(6)	122(1)
C(6)–C(7)–C(8)	123.9(6)	126(2)

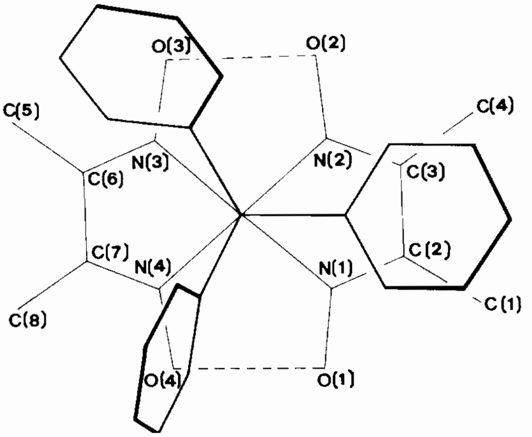

Figure 1. Numbering scheme for Co(dmgH)$_2$ moiety for both (I) and (II) compounds. A typical orientation of PPh$_3$ with respect to equatorial ligands is also shown.

Results

Molecular Structure of (I) and (II)

The crystals of compounds (I) and (II) contain discrete molecules of Ph$_3$PCo(dmgH)$_2$CH$_3$ and Chx$_3$PCo(dmgH)$_2$Cl, respectively. The numbering scheme of the Co(dmgH)$_2$X (X = Cl, CH$_3$) moiety of both compounds is given in Figure 1. The numbering schemes for PPh$_3$ and PChx$_3$ are shown in Figure 2. Both lengths and angles of interest are given in Table III. The overall geometry of both complexes is as expected, but the fine details appear of interest. In (I) the Co–P distance of 2.418(1) Å is the largest value so far reported and confirms the strong *trans*-influencing ability of the CH$_3$ group [8]. In fact the corresponding values given by two independent determinations [6, 13] of the structure of Ph$_3$PCo(dmgH)$_2$Cl are 2.327(4) Å and 2.310(7) Å.

The co-ordinated N atoms are coplanar within ±0.015 Å, the cobalt atom is displaced of 0.112 Å from their mean plane towards the phosphine. Correspondingly, the two dmgH units are bent away from the phosphine ligand and their planes make an angle of 13.6° as shown in Figure 2a. Such distortions are significantly larger than those previously found in cobaloximes where the corresponding figures do not exceed those of Ph$_3$PCo(dmgH)$_2$Cl (0.05 Å and 6.0°). The values found here approach those reported for Ph$_3$PRh(dmgH)$_2$Cl [13], where the interplanar angle is 17.1° and the Rh out-of-plane distance is 0.126 Å. Data relative to such distortions in cobaloxime complexes containing phosphine ligand (Table IV) will be discussed later. The Co–CH$_3$ bond length of 2.026(6) Å appears slightly longer than those reported for other methylcobaloximes, which are in the range from 1.990(5) to 2.009(7) Å. However the bond length is slightly shorter than those reported for alkylcobaloximes with cobalt

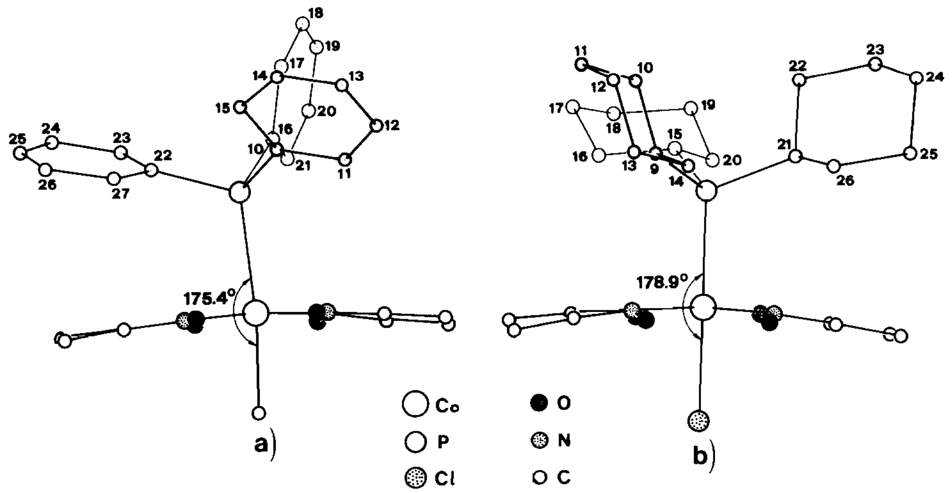

Figure 2. Side view of the molecules of (I) (a) and of (II) (b),showing the bending of equatorial ligands. The numbering scheme for carbon atoms of phosphine in both compounds is also shown.

TABLE IV. Values of α(°) Interplanar Angles and Metal Out-of-plane (Å) in Octahedral Metal Dimethylglyoximates Containing Phosphine Ligands.

	α	Out-of-plane
Ph_3P–Co(dmgH)$_2$Cl[a]	6	0.05
Ph_3P–Co(dmgH)$_2NO_2$[b]	8	0.04
Ph_3P–Co(dmgH)$_2CH_3$[c]	14	0.11
Chx_3P–Co(dmgH)$_2$Cl[c]	16	0.10
Bu_3P–Co(dmgH)$_2$–N-xa[d,h]	4	0.02
Bu_3P–Co(dmgH)$_2$–C-py[e,h]	5	0.03
Ph_3P–Rh(dmgH)$_2$Cl[f]	17	0.13
[Ph_3P–Rh(dmgH)$_2$]$_2$[g]	4	0.01

[a] Ref. 6. [b] Ref. 9. [c] Present work. [d] Ref. 7. [e] Ref. 15. [f] Ref. 14. [g] Ref. 17. [h] N-xa = xanthinato anion, C-py = pyridine bonded through 4-C atom to Co.

bonded carbon atom bearing side chains (2.040(6) Å in ($MeCO_2$·H_2C)Co(dmg)$_2$py [15] and 2.067(8) Å in (MeOOC·CH(Me))·Co(dmgH)$_2$·NH_2·CH(Ph)Me [16]).

In compound (II) the Co–P distance of 2.369(5) Å is significantly longer than that in the analogous Ph_3P derivative [2] (2.327(4) Å), whereas the Co–Cl distances are nearly equal in both complexes. For (II) this bond length is 2.294(5) Å, and for Ph_3PCo(dmgH)$_2$Cl is 2.277(4) and 2.274(7) Å in the two independent determinations. Furthermore the cobalt atom in (II) is displaced of 0.100 Å towards Chx_3P from the mean plane of nitrogen atoms which are coplanar within ±0.007 Å.

The two dmgH units are bent away from the phosphine, their planes making a dihedral angle of 15.7°.

These results, such as the lengthening of the Co–P bond length and the bending of the equatorial ligands, may be interpreted as mainly due to steric factors, as we will discuss in the next Section.

The typical orientation of the phosphine ligand with respect to the equatorial ligand is shown in Figure 1 in the case of CH_3Co(dmgH)$_2PPh_3$. It is such that one dmgH unit is just below one phenyl group, being roughly parallel, whereas the other unit is nearly in the middle of the other two phenyl groups which are much more tilted towards the equatorial ligand. On that side (Figure 2) a small twist of C(6) and C(7) atoms with respect to N(3), N(4) atoms is detected in contrast with the nearly strict coplanarity of the other dmgH moiety. Such an orientation and a similar small distortion may be observed in the other PPh_3 derivatives as well as in ClCo(dmgH)$_2$-$PChx_3$ complex. However comparison of Figures 2a) and 2b) shows that in the latter compound the Cl–Co–$PChx_3$ angle of 178.9(2)° is significantly less bent than that found in PPh_3 derivatives, 175.4(2) in (I), 175.6(3) in NO_2Co(dmgH)$_2PPh_3$ [9] and 176.5(1) in ClCo(dmgH)$_2PPh_3$ [6].

Discussion

On the basis of observed deformation of the Co(dmgH)$_2$ system for several L_1Co(dmgH)$_2L_2$ complexes, it has been suggested that the equatorial ligand has a noticeable rigidity [8]. Such deformations may be expressed by means of the interplanar angle α between the two dmgH moieties and by the out-of-plane displacement of cobalt from coordination plane. The values, given in Table IV, for phosphine derivatives are comparatively larger than those previously reported for the octahedral cobaloximes [8]. Furthermore a larger metal out-of-plane displacement corresponds to larger interplanar angles. These data however suggest that, although the bulki-

TABLE V. Co–P Bond Lengths (Å), α Angles (°) and Out-of-plane (Å) for Some Phosphine Derivatives. Methyl Resonances of Coordinated Methanol (σ_{MMR}) for the Series [$R_3PCo(dmgH)_2CH_3OH]^+$ and Calculated Cone Angle (IMCA).

	Co–P	α	Out-of-plane	σ_{MMR}[d]	IMCA[e]
$Chx_3PCo(dmgH)_2Cl$[a]	2.369(5)	16	0.10	7.460	3.90, 135
$Ph_3PCo(dmgH)_2Cl$[b]	2.327(4)	6	0.05	7.395	3.36, 125
	2.310(7)	–	–		
$Bu_3PCo(dmgH)_2N$-Xa[c]	2.285(2)	4	0.02	7.230 (Cl)	3.32, 124

[a] Present work. [b] Ref. 6. [c] Ref. 7. [d] Ref. 3. [e] The first figure is the solid cone angle and the second is the circular cone angle (°). Circular cone angles for $Ph_3PCo(dmgH)_2X$ (X = CH_3 and NO_2) are 125 and 127° respectively.

ness of the phosphine ligand is primarily responsible for the overall distortion, also the bulkiness of the trans-ligand has some importance. In fact α and out-of-plane distortions in $CH_3Co(dmgH)_2PPh_3$ are twice those found in $ClCo(dmgH)_2PPh_3$ and similar to those of $ClCo(dmgH)_2PChx_3$, despite of the increased Co–P distance. The *trans* Cl atom, which has a more "compact" bulk than CH_3, opposes more efficiently to the bending of the equatorial ligand provoked by the phosphine. This effect seems particularly clear in $ClRh(dmgH)_2PPh_3$ [14] and $PPh_3(dmgH)_2Rh$–Rh $(dmgH)_2PPh_3$ [17], where the Rh out-of-plane and α angle are 0.01 Å and 3.6° in the latter and 0.13 Å and 17.1° in the former. The bending which lessens repulsive interaction between PPh_3 and equatorial ligand, encounters less opposition from Cl in the mononuclear complex than from the two dmgH groups of the other metal in the dinuclear complex. Consequently the Rh–P is 2.327(1) Å in the monomer and 2.430(5) Å in the dimer.

Another consequence of the different steric size of the phosphine ligand is clearly illustrated by the trend of Co–P distances found in $PChx_3$, PPh_3 and PBu_3 derivatives, which are reported in Table V. The PBu_3 derivative, however, has the N-bonded xanthinato anion in the *trans* position instead of Cl. However it is reasonable to assume that the *trans*-influence of these two ligands are comparable.

Furthermore the lengthening of Co–P distances in going from PBu_3 to $PChx_3$ parallels the increase of the Co out-of-plane (from 0.02 to 0.10 Å) and the interplanar α angle (from 4° to 16°). These data, especially the trend of Co–P bond lengths, correlate well with the methyl resonance of co-ordinated methanol (σ_{MMR}) reported for a series of $[R_3PCo(dmgH)_2OHCH_3]^+$ compounds [3] (Table V). The experimental cone angle (IMCA) calculated according to the method of Immirzi and Musco [18] is also given in Table V.

It was previously shown that the most important parameter of the phosphorus donor ligand in influencing δ_{MMR} was steric size. In the same way, it appears that ligand steric size is the most important factor in determining the degree of bending of the $(dmgH)_2$ ligand. This conclusion is also supported by the corresponding trend of experimental cone angles of the co-ordinated phosphine ligands. Since it is now clear that cone angles depend on the other ligands in the coordination sphere [18], the accumulation of data on systems in which only the P donor ligand is changed seems to be particularly important.

TABLE VI. Structural Data and Oxime Methyl Resonances (σ_{OMR}) for the Series $Ph_3PCo(dmgH)_2X$.

X	Co–P (Å)	α (°)	Out-of-plane (Å)	σ_{OMR}[d]
Cl[a]	2.327(4)	6°	0.05	7.99
NO_2[b]	2.392(3)	8°	0.04	8.02
CH_3[c]	2.418(1)	14°	0.11	8.18

[a] Ref. 6. [b] Ref. 9. [c] Present work. [d] H. A. O. Hill and K. G. Morallee, *J. Chem. Soc. A*, 554 (1969).

In Table VI, comparisons can be found between structural parameters for $Ph_3PCo(dmgH)_2X$ complexes and spectroscopic parameters. There is a general consistency in these data, but relatively little can be made of these trends at this time. In particular, the variation in ^1H nmr shifts in systems such as $LCo(dmgH)_2X$, where X is varied, have been interpreted in terms of the *trans* influence of X. The data in Table VI show that the bending of the $(dmgH)_2$ ligand system is also changing when L = Ph_3P. Clearly, further work is needed and such studies are in progress in these laboratories.

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