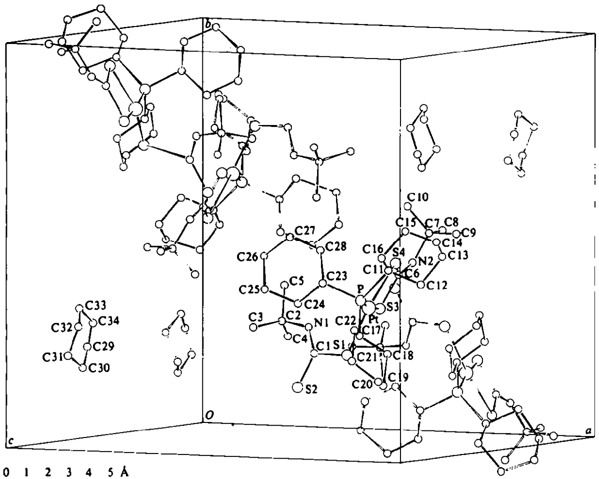

Fig. 2. Clinographic projection of BDCPP showing the molecular packing.

Waals radii is 3·0 Å) and the N—H···S angle of 155°. The molecular packing is shown in Fig. 2.

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trans-Bis(diethylphenylphosphine)dimesitylcobalt(II)

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Abstract

$C_{38}H_{52}CoP_2$, $[Co(C_9H_{11})_2(C_{10}H_{15}P)_2]$, $M_r = 629{\cdot}71$, monoclinic, $P2_1/c$, $a = 10{\cdot}695$ (8), $b = 9{\cdot}310$ (8), $c = 18{\cdot}317$ (16) Å, $\beta = 107{\cdot}21$ (6)°, $U = 1742$ Å^3, $Z = 2$, $D_x = 1{\cdot}200$ Mg m^{-3}, μ(Mo $K\alpha$) = $0{\cdot}573$ mm^{-1}. The Co atom, lying on a centre of symmetry, is planar, four-coordinated by two mesityl ligands and two diethylphenylphosphine groups. All H atoms were located in this redetermination, which was refined for 296 parameters to $R = 0{\cdot}042$ for 2487 independent reflexions.

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Introduction

An earlier crystal structure determination (Owston & Rowe, 1963) of *trans*-bis(diethylphenylphosphine)dimesitylcobalt(II) established planar four-coordination for the low-spin Co atom, the fifth and sixth positions of a potential octahedral geometry apparently being blocked by the α-methyl groups of the mesityl ligands. A highly anisotropic g tensor in which $g_x = 3{\cdot}72$, $g_y = 1{\cdot}96$, $g_z = 1{\cdot}74$, where the molecular frame x,y,z is oriented almost exactly parallel to Co—P, Co—mesityl and the normal to the coordination plane, respectively, has been determined in an ESR study (Bentley, Mabbs, Smail, Gerloch & Lewis, 1970). The interpretation of both g and A tensors, of the solution electronic spectrum and of some incomplete single-crystal paramagnetic susceptibility data, within a restricted, spin-doublet configurational basis, was characterized by a close energetic approach of the z^2 and yz orbitals together with a relatively much larger z^2–xz separation. A recent study of the electronic structure of this complex (Falvello & Gerloch, 1979), which includes a complete determination of the crystal magnetic susceptibility tensor in the temperature range 20–300 K, utilizes the angular overlap model and the complete 120-fold d^7 basis. In confirming the essential nature of the orbital splitting previously proposed, the interpretation of the complete ligand field has emphasized three features of the electronic structure:

(*a*) that the low energy of the xz orbital arises from a significant degree of π back-bonding to the phosphine ligands;

(*b*) that this same phosphine π acidity is particularly responsible for the very large nephelauxetic effect observed;

(*c*) that the close energetic proximity of the z^2 and yz orbitals results from configurational mixing between metal d and s functions. Further, by comparisons with analogues of the present complex, in which mesityl groups are replaced with α-methylnaphthyl and C_6F_5 or C_6Cl_5 groups, it has been proposed that the α-methyl H atoms, lying close to the central metal atom, augment the d–s mixing process.

The earlier structural analysis located all non-hydrogen atoms. The present redetermination of the structure has been undertaken to refine further these parameters and to locate the H atoms.

Experimental

trans-Bis(diethylphenylphosphine)dimesitylcobalt(II) was prepared as a yellow powder from the reaction of mesityl magnesium bromide with dibromobis(diethylphenylphosphine)cobalt(II) (Chatt & Shaw, 1961). Evaporation of a benzene solution gave yellow, plate-like crystals from which a sample 0·45 × 0·36 × 0·22 mm was chosen for the X-ray diffraction measurements.

Diffraction data were gathered by an automatic four-circle diffractometer (Syntex $P2_1$) with Mo $K\alpha$ radiation ($\lambda\bar{\alpha}$= 0·71069 Å). The cell parameters were refined by least squares from the angular positions of 15 strong, centred reflexions.

The intensities of 3651 reflexions were measured, within the range $0 < 2\theta < 55°$. Empirical absorption corrections were made but were, as expected, very small [μ(Mo $K\alpha$) = 0·573 mm^{-1}]. Of the reflexions measured, 3124 were unique; 422 had $F < 3\sigma(F)$ and were considered unobserved.

Refinement of the structure

The refinement began with all non-hydrogen atoms located as previously reported (Owston & Rowe, 1963) and with isotropic thermal parameters. With 2702 reflexions for which $F > 3\sigma(F)$, full-matrix least-squares refinement, followed by refinement with anisotropic thermal parameters on Co and P and finally with all atoms anisotropic, reduced R to 0·065. A difference map at this point revealed 20 of the 26 H atoms.

In the second stage of refinement, 2587 reflexions with $F > 4\sigma(F)$ were used. An overall isotropic temperature factor for the 20 H atoms was refined. A difference map then revealed the remaining six H atoms. During this stage, the lengths of chemically equivalent C—H bonds refined to roughly equal values.

For the final stage of the refinement, chemically equivalent C—H bonds were constrained to the same lengths. In addition, most of the C—H bonds were held fixed at the lengths to which they had refined previously. The only exceptions were C(11)—H(12) and the chemically equivalent C(15)—H(16), which had refined to unacceptably short values and were constrained to 0·92 (±0·02) Å, and C(3)—H(1), C(5)—H(2) and C(13)—H(14), for which no constraints were considered necessary. Each H atom was assigned an independent isotropic temperature factor. This last stage employed 2487 reflexions with $F > 5\sigma(F)$. Weighted full-matrix refinement reduced R to 0·042 and R_w $(=\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|)$ to 0·046, in which $w = 0{\cdot}539/[\sigma^2(F) + 0{\cdot}003F^2]$. In the final cycle no parameter shift exceeded half the e.s.d. The largest peak on a final difference map had a magnitude of 0·435 e Å^{-3} and was located near the Co atom.

The positional and thermal parameters of the non-hydrogen atoms shifted insignificantly during the second and third stages of the refinement.

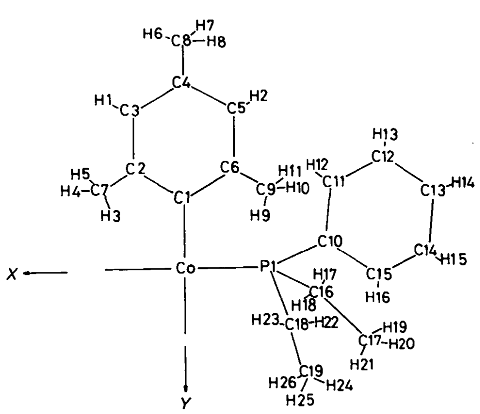

Fig. 1. *trans*-Co(mesityl)$_2$(PPhEt$_2$)$_2$: atom numbering in the asymmetric unit. The Co atom lies on a centre of symmetry and the coordinate frame defines principal axes of the g tensor.

Table 1. *Fractional coordinates* ($\times 10^4$; $\times 10^3$ *for* H)

	x	y	z
Co(1)	0	0	0
P(1)	1573 (1)	1639 (1)	116 (1)
C(1)	–967 (3)	1373 (3)	472 (2)
C(2)	–757 (3)	1338 (3)	1273 (2)
C(3)	–1489 (4)	2170 (4)	1626 (2)
C(4)	–2467 (3)	3093 (4)	1214 (2)
C(5)	–2676 (3)	3155 (4)	433 (2)
C(6)	–1958 (3)	2323 (4)	60 (2)
C(7)	258 (4)	341 (5)	1768 (2)
C(8)	–3260 (5)	3972 (6)	1616 (3)
C(9)	–2324 (4)	2414 (5)	–806 (2)
C(10)	2427 (3)	2163 (4)	1109 (2)
C(11)	1988 (4)	3294 (5)	1458 (2)
C(12)	2631 (6)	3677 (6)	2205 (3)
C(13)	3708 (6)	2924 (7)	2617 (3)
C(14)	4149 (5)	1799 (6)	2293 (3)
C(15)	3520 (4)	1405 (5)	1547 (2)
C(16)	2932 (4)	1169 (4)	–262 (2)
C(17)	4016 (5)	2276 (6)	–170 (3)
C(18)	1062 (4)	3420 (4)	–316 (2)
C(19)	734 (5)	3471 (5)	–1182 (2)
H(1)	–128 (4)	211 (5)	214 (3)
H(2)	–329 (4)	378 (4)	14 (2)
H(3)	65 (4)	–21 (4)	146 (2)
H(4)	–11 (5)	–33 (4)	203 (3)
H(5)	98 (3)	75 (5)	215 (2)
H(6)	–407 (4)	418 (7)	124 (3)
H(7)	–281 (6)	453 (6)	205 (3)
H(8)	–379 (8)	333 (8)	180 (5)
H(9)	–195 (6)	164 (5)	–101 (4)
H(10)	–222 (6)	336 (3)	–98 (3)
H(11)	–324 (2)	238 (6)	–107 (3)
H(12)	132 (3)	386 (4)	118 (2)
H(13)	228 (4)	441 (3)	241 (3)
H(14)	400 (5)	320 (6)	313 (3)
H(15)	490 (3)	131 (5)	257 (3)
H(16)	379 (3)	66 (3)	133 (2)
H(17)	252 (3)	100 (4)	–79 (1)
H(18)	325 (4)	32 (3)	3 (2)
H(19)	469 (4)	198 (6)	–37 (3)
H(20)	441 (5)	261 (6)	33 (2)
H(21)	370 (4)	311 (4)	–46 (3)
H(22)	174 (3)	409 (3)	–11 (2)
H(23)	33 (3)	369 (4)	–16 (2)
H(24)	58 (5)	438 (3)	–141 (3)
H(25)	7 (4)	287 (4)	–149 (2)
H(26)	145 (3)	321 (5)	–135 (3)

Table 1 gives the positional parameters* of all atoms, Tables 2 and 3 the bond lengths and angles. The atom numbering is shown in Fig. 1.

Discussion

The Co, P and C atom backbone of the molecules, Fig. 2, is not significantly different from that reported by

Table 2. *Bond lengths* (Å)

P(1)–Co(1)	2·234 (1)	H(1)–C(3)	0·90 (4)
C(1)–Co(1)	1·994 (3)	H(2)–C(5)	0·92 (4)
C(10)–P(1)	1·843 (3)	H(3)–C(7)	0·94 (2)
C(16)–P(1)	1·838 (4)	H(4)–C(7)	0·95 (2)
C(18)–P(1)	1·849 (4)	H(5)–C(7)	0·96 (2)
C(2)–C(1)	1·418 (4)	H(6)–C(8)	0·96 (2)
C(6)–C(1)	1·415 (5)	H(7)–C(8)	0·96 (2)
C(3)–C(2)	1·391 (5)	H(8)–C(8)	0·95 (2)
C(7)–C(2)	1·510 (5)	H(9)–C(9)	0·95 (2)
C(4)–C(3)	1·391 (5)	H(10)–C(9)	0·95 (2)
C(5)–C(4)	1·383 (5)	H(11)–C(9)	0·96 (2)
C(8)–C(4)	1·518 (5)	H(12)–C(11)	0·91 (2)
C(6)–C(5)	1·401 (5)	H(13)–C(12)	0·91 (2)
C(9)–C(6)	1·520 (5)	H(14)–C(13)	0·93 (6)
C(11)–C(10)	1·384 (5)	H(15)–C(14)	0·93 (2)
C(15)–C(10)	1·398 (5)	H(16)–C(15)	0·89 (2)
C(12)–C(11)	1·384 (6)	H(17)–C(16)	0·95 (2)
C(13)–C(12)	1·368 (8)	H(18)–C(16)	0·96 (2)
C(14)–C(13)	1·356 (8)	H(19)–C(17)	0·94 (2)
C(15)–C(14)	1·381 (6)	H(20)–C(17)	0·94 (2)
C(17)–C(16)	1·523 (5)	H(21)–C(17)	0·94 (2)
C(19)–C(18)	1·520 (6)	H(22)–C(18)	0·95 (2)
		H(23)–C(18)	0·95 (2)
		H(24)–C(19)	0·94 (2)
		H(25)–C(19)	0·95 (2)
		H(26)–C(19)	0·94 (2)

Table 3. *Bond angles* (°)

C(1)–Co(1)–P(1)	89·6 (1)	C(15)–C(14)–C(13)	120·5 (5)
C(10)–P(1)–Co(1)	114·5 (1)	C(14)–C(15)–C(10)	120·9 (4)
C(16)–P(1)–Co(1)	117·3 (1)	C(17)–C(16)–P(1)	117·2 (3)
C(16)–P(1)–C(10)	102·6 (2)	C(19)–C(18)–P(1)	115·0 (3)
C(18)–P(1)–Co(1)	116·9 (1)		
C(18)–P(1)–C(10)	100·5 (2)	C(6)–C(1)–C(2)	115·5 (3)
C(18)–P(1)–C(16)	102·6 (2)	C(3)–C(2)–C(1)	122·0 (3)
C(2)–C(1)–Co(1)	119·3 (2)	C(7)–C(2)–C(1)	120·0 (3)
C(6)–C(1)–Co(1)	124·9 (2)	C(7)–C(2)–C(3)	117·8 (3)
		C(4)–C(3)–C(2)	121·8 (4)
		C(5)–C(4)–C(3)	117·0 (3)
C(11)–C(10)–P(1)	121·4 (3)	C(8)–C(4)–C(3)	120·5 (4)
C(15)–C(10)–P(1)	121·3 (3)	C(8)–C(4)–C(5)	122·5 (4)
C(15)–C(10)–C(11)	117·3 (4)	C(6)–C(5)–C(4)	122·4 (3)
C(12)–C(11)–C(10)	121·0 (5)	C(5)–C(6)–C(1)	121·2 (3)
C(13)–C(12)–C(11)	120·3 (5)	C(9)–C(6)–C(1)	120·8 (3)
C(14)–C(13)–C(12)	120·0 (4)	C(9)–C(6)–C(5)	117·9 (3)

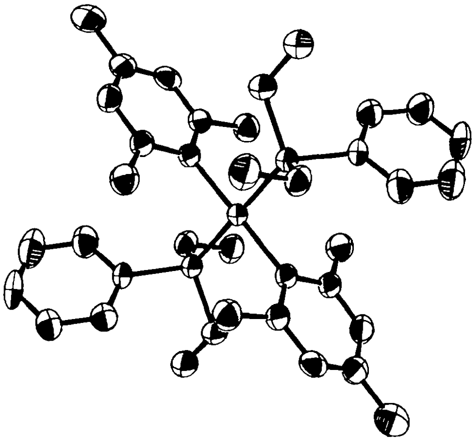

Fig. 2. *trans*-Co(mesityl)$_2$(PPhEt$_2$)$_2$: molecular geometry showing steric blocking of two octahedral coordination sites by mesityl α-methyl groups.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34674 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

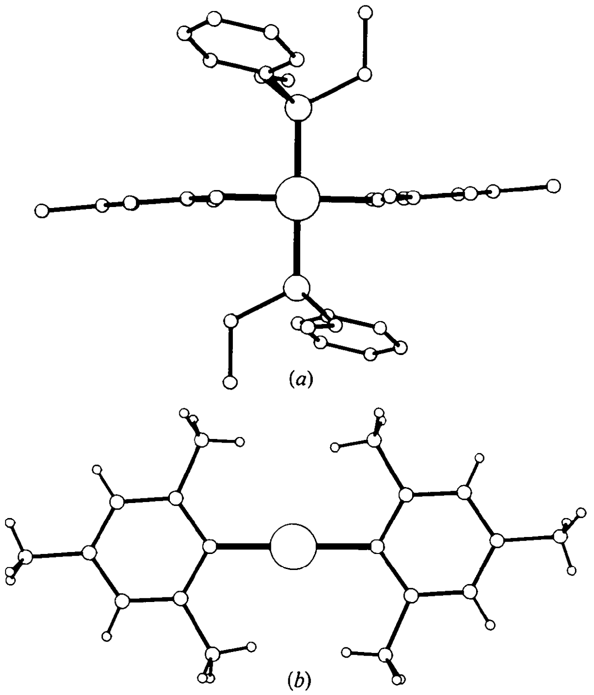

Fig. 3. *trans*-Co(mesityl)$_2$(PPhEt$_2$)$_2$: coordination of mesityl ligands showing slight 'misdirected valency' of donor C atom and asymmetry of Co···H contacts.

Owston & Rowe (1963). The ethyl and phenyl substituents of the phosphines are swept back from the Co atom in that all C—P—C bond angles are less than the idealized tetrahedral value. A rationale of this form of phosphine stereochemistry has been given by Mason & Meek (1977) in terms of an increased *s* character of the P atom orbital directed towards the central metal.

The planar mesityl groups lie almost exactly perpendicular to the coordination plane: the angle is 90·6 (9)°. As required by the inversion centre, the two mesityl groups are coparallel; they are not, however, coplanar (Fig. 3*a*). Their planes lie 0·324 (10) Å apart with the Co atom mid-way between. As reported earlier, the orientation of the mesityl groups is such that the fifth and sixth octahedral coordination sites are blocked by the α-methyl groups. There is no evidence for facile rotation of these methyl groups and there are two close Co···H contacts of 2·56 [Co···H(3)] and 2·79 Å [Co···H(9)]. The asymmetry of these close contacts (Fig. 3*b*) is consistent with a further small coordination distortion in which the Co atom lies 0·188 (10) Å from the local mesityl diads.

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The Structure of Potassium Tris(monochloroacetato)stannate(II)

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Abstract

K[Sn(C$_2$H$_2$ClO$_2$)$_3$], K$^+$. C$_6$H$_6$Cl$_3$O$_6$Sn$^-$, is monoclinic, space group $B2_1/c$ (non-standard form of $P2_1/c$) with a = 15·96 (2), b = 11·80 (2), c = 14·19 (2) Å, β = 99·40 (10)°, Z = 8. Final R = 0·049 for 2433 reflexions. The structure consists of discrete [Sn(ClCH$_2$CO$_2$)$_3$]$^-$ ions and independent cations. The Sn atoms are in distorted trigonal pyramidal sites with Sn—O 2·14, 2·18 and 2·18 Å. A distorted octahedral

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