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Structure of Dichlorobis(trimethylphosphine oxide)cobalt(II)

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Abstract. $[\mathrm{CoCl_2(C_3H_9OP)_2}]$, $M_r = 314{\cdot}0$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}686\,(3)$, $b = 11{\cdot}271\,(3)$, $c = 11{\cdot}975\,(4)$ Å, $V = 1442\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}446\,(1)$ g cm^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}70926$ Å, $\mu = 17{\cdot}4$ cm^{-1}, $F(000) = 644$, $T = 293$ K, $R = 0{\cdot}0482$ for 1351 observed reflections. The title compound is a mononuclear cobalt complex with approximate tetrahedral coordination of the two Cl and two O atoms around the central Co atom. Important bond lengths: Co—Cl 2·256 (2), Co—O 1·960 (3), P—O 1·508 (3), P—C 1·771 (4) Å.

Introduction. Adducts of $\mathrm{Co^{II}}$ halides with phosphine oxides have been the subject of detailed spectroscopic studies (Cotton, Barnes & Bannister, 1960; Brodie, Hunter, Rodley & Wilkins, 1968; Hunter, Langford, Rodley & Wilkins, 1968; Kato & Akimoto, 1974) and two complexes with aryl-substituted phosphine oxides have been structurally characterized [$\mathrm{(Ph_3PO)_2CoCl_2}$: Mangion, Smith & Shore (1976); $\mathrm{(Bz_3PO)_2CoCl_2}$: Santos & Mascarenhas (1979)]. We report here the first crystal structure of a simple alkyl derivative, $\mathrm{(Me_3PO)_2CoCl_2}$.

Experimental. The title compound was prepared by mixing ethanol solutions of $\mathrm{CoCl_2}$ and trimethylphosphine oxide as described by Pickard & Kenyon (1906). Dark blue, cube-shaped single crystals were obtained by recrystallization from acetone. Crystal 0·25 × 0·25 × 0·25 mm. Hilger & Watts diffractometer, $\theta/2\theta$ scan mode with $5 < 2\theta < 60°$, *hkl* range: $0 \le h \le 15$, $0 \le k \le 15$, $0 \le l \le 16$. Cell parameters obtained by least-squares refinement from setting angles of 20 automatically centred high-angle reflections ($20 \le 2\theta \le 55°$). 2061 independent, non-systematically absent (in $P2_12_12_1$) reflections measured, 710 considered as unobserved ($|F| \le 4\sigma|F|$). No absorption or secondary-extinction corrections. Structure solved by Patterson and Fourier methods (*SHELX77*; Sheldrick, 1977). No intensity drop of three standard reflections measured after each block of 97 reflections. H atoms calculated and refined with constrained C—H bond lengths of 0·96 Å, H—C—H angles of 104·7° (refined value), and a common temperature factor.

Least-squares refinement based on *F*. Scattering factors for all atoms except Co included in the *SHELX77* program (Sheldrick, 1977); for Co from

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International Tables for X-ray Crystallography (1974). 173 parameters. Final conventional R factor 0·0482 for 1351 structure factors; $wR = 0{\cdot}0438$; $w = 1{\cdot}0937/\sigma^2(|F|) + 0{\cdot}0005F^2$. Final difference map showed no peak higher than 0·4 or less than –0·5 e Å^{-3}; all Δ/σ values < 0·01. Plots performed with *ORTEP*II (Johnson, 1976).

Discussion. Final atomic coordinates are given in Table 1; bond lengths and angles are listed in Table 2.* Fig. 1 shows the molecular structure and atom-numbering scheme. The central Co$^{\rm II}$ ion is tetrahedrally coordinated by two Cl ligands and two O atoms. While the Cl–Co–O angles differ less than 1·5° from the tetrahedral angle, the deviations for the Cl–Co–Cl angle [114·3 (1)°] and the O–Co–O angle [104·5 (2)°] are more severe. This coordination geometry is very similar to that found in $(Bz_3PO)_2CoCl_2$ (Santos & Mascarenhas, 1979) and $(Ph_3PO)_2CoCl_2$ (Mangion, Smith & Shore, 1976). There are, however, substantial differences in the Co–O–P angles. With 131·5 (3) and 131·6 (3)° the Co–O–P angles in $(Me_3PO)_2CoCl_2$ are even smaller than those found for $(Me_3PO)_2Co(NO_3)_2$ (Cotton & Soderberg, 1963). Significantly higher values have been reported for both $(Bz_3PO)_2CoCl_2$ [157·4 (8), 153·0 (8)°] (Santos & Mascarenhas, 1979) and $(Ph_3PO)_2CoCl_2$ [1·152·4 (5), 152·8 (5)°] (Mangion, Smith & Shore, 1976). The Co–Cl [2·256 (2) Å] and Co–O [average 1·960 (3) Å] bonds are somewhat shorter than the corresponding

Table 1. *Atomic parameters with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$(Å^2)
Co	0·42980 (10)	–0·00436 (9)	0·06082 (8)	0·0488 (9)
Cl(1)	0·4210 (2)	–0·0832 (2)	–0·1122 (2)	0·066 (2)
Cl(2)	0·6257 (2)	0·0260 (2)	0·1250 (2)	0·063 (2)
P(1)	0·3428 (2)	0·2496 (2)	0·1429 (2)	0·050 (2)
P(2)	0·2274 (2)	–0·1828 (2)	0·1571 (2)	0·047 (2)
O(1)	0·3368 (6)	0·1453 (4)	0·0642 (5)	0·063 (6)
O(2)	0·3426 (5)	–0·1065 (4)	0·1683 (4)	0·056 (6)
C(1)	0·4479 (11)	0·3595 (9)	0·0946 (8)	0·084 (12)
C(2)	0·1930 (9)	0·3162 (10)	0·1556 (9)	0·080 (12)
C(3)	0·3892 (9)	0·2066 (7)	0·2790 (7)	0·061 (9)
C(4)	0·2592 (9)	–0·3138 (8)	0·0792 (8)	0·068 (10)
C(5)	0·1726 (9)	–0·2275 (9)	0·2888 (7)	0·065 (10)
C(6)	0·1041 (9)	–0·1044 (9)	0·0902 (9)	0·080 (12)
H(1)	0·534 (3)	0·337 (6)	0·083 (6)	0·098 (8)
H(2)	0·421 (6)	0·390 (6)	0·024 (3)	0·098 (8)
H(3)	0·452 (7)	0·428 (4)	0·142 (5)	0·098 (8)
H(4)	0·163 (7)	0·351 (6)	0·088 (3)	0·098 (8)
H(5)	0·121 (5)	0·278 (6)	0·187 (5)	0·098 (8)
H(6)	0·209 (7)	0·382 (4)	0·204 (4)	0·098 (8)
H(7)	0·333 (5)	0·152 (4)	0·314 (6)	0·098 (8)
H(8)	0·469 (3)	0·168 (5)	0·281 (6)	0·098 (8)
H(9)	0·396 (6)	0·271 (4)	0·331 (5)	0·098 (8)
H(10)	0·287 (6)	–0·292 (6)	0·006 (3)	0·098 (8)
H(11)	0·318 (5)	–0·372 (5)	0·104 (6)	0·098 (8)
H(12)	0·183 (4)	–0·358 (6)	0·066 (6)	0·098 (8)
H(13)	0·233 (5)	–0·269 (5)	0·333 (6)	0·098 (8)
H(14)	0·150 (6)	–0·160 (4)	0·333 (5)	0·098 (8)
H(15)	0·100 (4)	–0·278 (5)	0·289 (7)	0·098 (8)
H(16)	0·085 (6)	–0·030 (3)	0·126 (5)	0·098 (8)
H(17)	0·129 (7)	–0·083 (6)	0·016 (3)	0·098 (8)
H(18)	0·025 (3)	–0·143 (5)	0·081 (6)	0·098 (8)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co–Cl(1)	2·256 (2)	Co–Cl(2)	2·256 (2)
Co–O(1)	1·958 (5)	Co–O(2)	1·962 (5)
P(1)–O(1)	1·508 (5)	P(2)–O(2)	1·508 (5)
P(1)–C(1)	1·770 (9)	P(2)–C(4)	1·780 (8)
P(1)–C(2)	1·775 (9)	P(2)–C(5)	1·756 (8)
P(1)–C(3)	1·770 (8)	P(2)–C(6)	1·776 (8)
Cl(1)–Co–Cl(2)	114·3 (1)	O(1)–Co–O(2)	104·5 (2)
Cl(1)–Co–O(1)	109·7 (2)	Cl(1)–Co–O(2)	110·6 (2)
Cl(2)–Co–O(1)	109·4 (2)	Cl(2)–Co–O(2)	107·8 (2)
Co–O(1)–P(1)	131·5 (3)	Co–O(2)–P(2)	131·6 (3)
O(1)–P(1)–C(1)	111·6 (4)	O(2)–P(2)–C(4)	111·4 (4)
O(1)–P(1)–C(2)	110·2 (4)	O(2)–P(2)–C(5)	110·8 (4)
O(1)–P(1)–C(3)	112·0 (4)	O(2)–P(2)–C(6)	111·2 (4)
C(1)–P(1)–C(2)	107·7 (6)	C(4)–P(2)–C(5)	107·2 (5)
C(1)–P(1)–C(3)	108·4 (5)	C(4)–P(2)–C(6)	108·5 (5)
C(2)–P(1)–C(3)	106·8 (5)	C(5)–P(2)–C(6)	107·5 (5)

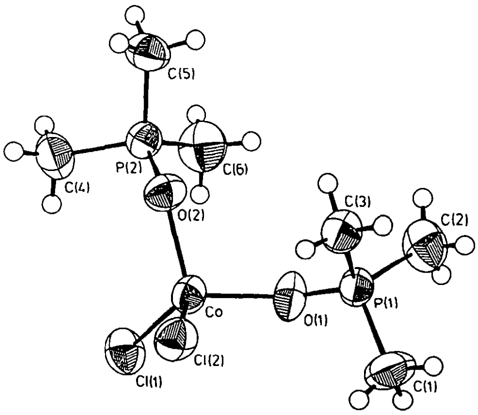

Fig. 1. *ORTEP*II plot (Johnson, 1976) of the molecular structure.

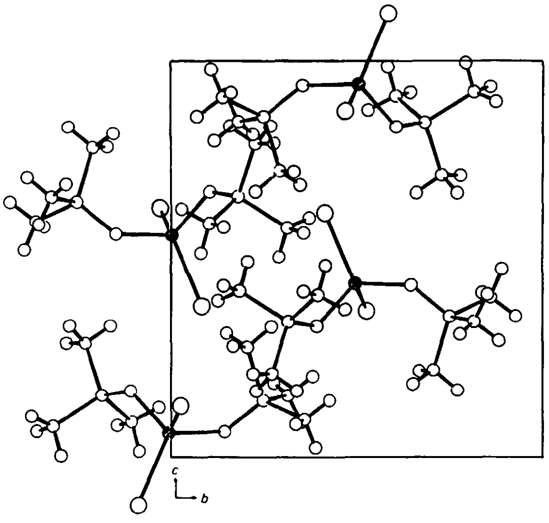

Fig. 2. Contents of the unit cell (projection on *bc*).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43218 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bonds in $(Bz_3PO)_2CoCl_2$ (Santos & Mascarenhas, 1979) but longer than those in $(Ph_3PO)_2CoCl_2$ (Mangion, Smith & Shore, 1976). As in other metal halide adducts of trimethylphosphine oxide a slight lengthening of the P–O bond [1·508 (3) Å in $(Me_3PO)_2CoCl_2$] compared to uncoordinated Me_3PO [1·476 (2) Å] (Wilkins, Hagen, Hedberg, Shen & Hedberg, 1975) is observed. The average P—C bond length in $(Me_3PO)_2CoCl_2$ is 1·771 (4) Å. Fig. 2 shows the contents of the unit cell.

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Structure of 3-(η^2,η^2-1,5-Cyclooctadiene)-3-pallada-1,2-dicarba-*closo*-dodecaborane(11)

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Abstract. $[3\text{-}(\eta^2,\eta^2\text{-}C_8H_{12})\text{-}3,1,2\text{-}PdC_2B_9H_{11}]$, $M_r = 346·9$, orthorhombic, *Pbca*, $a = 13·2485$ (18), $b = 11·549$ (3), $c = 19·589$ (3) Å, $V = 2997·3$ (12) Å^3, $Z = 8$, $D_x = 1·538$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 1·20$ mm^{-1}, $F(000) = 1392$, room temperature, $R = 0·035$ for 3217 unique observed reflections. Crystallographic study of the title compound yields slipping distortion parameters which imply that the previously suggested correlation with B(8) chemical shift may not be fully applicable.

Introduction. The title compound, (1), is one of a number of products isolated from the reaction between $[(cod)Pd(\eta\text{-}C_5H_5)]BF_4$ (cod = 1,5-cyclooctadiene) and $Tl[TlC_2B_9H_{11}]$ at room temperature in CH_2Cl_2 (Smith & Welch, 1986*a*). Separation by thin layer chromatography (CH_2Cl_2, *n*-hexane 2:1 eluant) afforded the product as a purple band ($R_f = 0·7$) in low yield (< 5%). Although the compound has previously been synthesized by a different route (Colquhoun, Greenhough & Wallbridge, 1985) no diffraction study was reported. However, the structure of this species is important in respect of the conformation and slipping distortion of the $\{Pd(ene)_2\}$ fragment relative to the $C_2B_9H_{11}$ cage, and therefore we have undertaken the crystallographic determination described herein.

Experimental. Purple irregular plate (0·5 × 0·3 × 0·05 mm), from solvent diffusion using CH_2Cl_2 and *n*-hexane; CAD-4 diffractometer, 25 reflections centred ($13·5 < \theta < 14·5°$), graphite-monochromated Mo $K\alpha$; for data collection $\theta_{max} = 30°$, ω–2θ scans in 96 steps, ω-scan width $0·8° + 0·35° \tan\theta$, rapid prescan after which reflections with $I > 0·67\sigma(I)$ remeasured such that final net intensity had $I > 5\sigma(I)$ subject to a maximum measuring time of 75 seconds; two octants of data (*hkl* and $-h-kl$, 7942 reflections) measured over 111 X-ray hours with no detectable decay or movement; systematic absences ($0kl$: $k = 2n + 1$, $h0l$: $l = 2n + 1$, $hk0$: $h = 2n + 1$) uniquely define space group. 4360 unique data, $R_{int} = 0·0263$; for structure solution and refinement 3217 reflections with $F > 2\sigma(F)$ retained (h 0→18, k 0→16, l 0→27), Patterson synthesis (Pd) and difference-Fourier methods; post-solution empirical absorption correction (*DIFABS*, Walker & Stuart, 1983), full-matrix least-squares refinement on *F*,

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