leurs homologues dans le méthanesulfonate d'ammonium [1,440 (2) et 1,443 (2) Å] (Wei, 1986). La distance S—C [1,755 (6) Å] est aussi très voisine des distances S—C rencontrées dans le méthanesulfonate d'ammonium [1,750 (3) Å] ou dans le trimésylhydroxylamine $(CH_3SO_2)_2NOSO_2CH_3$ [de 1,737 (3) à 1,746 (2) Å] (Brink & Mattes, 1986).

Dans le cation $[Pt(NH_3)_4]^{2+}$, l'atome de platine est centre de symétrie. Le quadrilatère formé par les quatre atomes d'azote qui lui sont liés est donc plan. Il est, de plus, très proche d'un carré. Les liaisons Pt—N(1) et Pt—N(2) mesurent respectivement 2,046 (4) et 2,047 (7) Å et font entre elles un angle de 90,6 (2)°. Les liaisons Pt—N ont pour longueurs 2,06 (1) Å dans le *cis*-dichloro(diméthyl sulfoxyde)(picoline-2)platine(II) (Melanson & Rochon, 1977) et 2,05 (1) Å dans le bis[trichloro(diméthyl sulfoxyde)platinate(II)] de tétraammineplatine(II) (Khodadad & Rodier, 1987).

La Fig. 1 montre que les cations forment des couches qui s'étendent le long des plans (001). Deux couches d'anions parallèles à la face (001) sont disposées de part et d'autre de chacune des couches de cations.

Les distances N—O permettent d'envisager l'existence de plusieurs liaisons hydrogène. Ainsi, N(1) paraît lié à O(1) [N(1)—O(1) = 2,969 (5) Å] et N(2) à $O(2^{i})$ [$N(2)—O(2^{i})$ = 2,908 (8) Å]. Plusieurs autres distances N—O sont aussi susceptibles de correspondre à des liaisons hydrogène plus faibles ou à de fortes interactions de van der Waals. C'est le cas de $N(1)—O(1^{iii})$ [3,171 (6) Å], de N(2)—O(1) [3,171 (6) Å], de $N(2)—O(1^{iv})$ [3,153 (7) Å] et de $N(2)—O(2^{v})$ [3,108 (9) Å]. Ces dernières n'ont pas été représentées sur la Fig. 1. Le code de symétrie est donné dans le Tableau 2.

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The Structure of $HCo(CO)_3\{P(cyclohexyl)_3\}$

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Abstract. Hydridotricarbonyltricyclohexylphosphinecobalt(I), $[CoH(CO)_3\{(C_6H_{11})_3P\}]$, $M_r = 424\cdot40$, triclinic, $P\bar{1}$, $a = 9\cdot481\ (2)$, $b = 13\cdot975\ (2)$, $c = 9\cdot306\ (3)$ Å, $\alpha = 98\cdot54\ (2)$, $\beta = 112\cdot89\ (2)$, $\gamma = 96\cdot78\ (1)^\circ$, $V = 1102\cdot2\ (4)$ Å^3, $Z = 2$, $D_x = 1\cdot28$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 8\cdot63$ cm^{-1}, $F(000) = 452$, $T = 296$ K, $R = 0\cdot030$, $wR = 0\cdot041$ for 3817 independent reflections. $HCo(CO)_3\{P(cyclohexyl)_3\}$ is approximately trigonal bipyramidal about the cobalt atom. The H and PCy_3 (Cy = cyclohexyl) ligands occupy axial positions with the three equatorial carbonyls leaning toward the hydride ligand.

Introduction. Chemical species of the type $HCo(CO)_3L$ (L = CO or tertiary phosphine) are known to be important catalytic intermediates in hydroformylation reactions. Results of mechanistic studies (Heck & Breslow, 1961; Goetz & Orchin, 1962; Markó, 1962) all suggested that aldehyde reduction occurs *via* addition to $HCo(CO)_3L$, generating an alkoxy intermediate which then undergoes hydrogenolysis to alcoholic products. Very few structural studies have been performed on these $HCo(CO)_3L$ species, probably since most of the commonly encountered $HCo(CO)_3PR_3$ (PR_3 = tertiary phosphine) compounds have low thermal stability [PR_3 (m.p. K): PBu_3 (253), PPh_3 ($d > 293$), $P(OPh)_3$ ($d > 273$), PF_3 (liq.); $P(OCH_2)_3CEt$ ($d > 273$)]. The structure of these species is assumed to be approximately trigonal bipyramidal about the Co atom, with the three carbonyl ligands occupying equatorial positions and the H and PR_3 ligands occupying axial sites. This belief is supported through

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work such as the electron diffraction study of $HCo(CO)_4$ (McNeill & Scholer, 1977) and the X-ray diffraction study of the related compound $HCo(CO)\{PPh_3\}_3$ (Whitfield, Watkins, Tupper & Baddley, 1977). Both of these compounds are trigonal bipyramidal at the Co atom. The three equatorial carbonyls in $HCo(CO)_4$ and the three equatorial phosphines in $HCo(CO)\{PPh_3\}_3$ are bent toward the hydride ligand.

Here we present the crystal and molecular structure of $HCo(CO)_3\{PCy_3\}$ (Cy = cyclohexyl), a species of the type $HCo(CO)_3L$ that is a stable solid at ambient temperature. $HCo(CO)_3\{PCy_3\}$ is trigonal bipyramidal about the Co atom with the H and PCy_3 ligands occupying axial positions. The three equatorial carbonyls are bent toward the hydride ligand.

Experimental. Crystals of $HCo(CO)_3\{PCy_3\}$ were grown from hexane. A flat clear yellow plate (0·5 × 0·5 × 0·1 mm) was mounted on the tip of a glass fiber with epoxy cement. The unit-cell parameters were derived from the least-squares best fit of 25 reflections ($41{\cdot}66 \leq 2\theta \leq 44{\cdot}86°$). Data were collected ($2\theta$–$\omega$ scans) using a Rigaku AFC5S automated four-circle diffractometer [Rigaku *CRYSTAN/TEXTL* (3:2:1) Automatic Data Collection Series (Molecular Structure Corporation, 1988)] through the *hkl* range 0 to 12, −18 to 17, −12 to 10 respectively, with 5352 reflections measured, 5044 independent reflections processed, $R_{\text{int}} = 0{\cdot}8\%$, 1227 reflections unobserved [$I < 3\sigma(I)$], $2\theta_{\max} = 55°$, and $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}65$ Å^{-1}. Three standards were measured every 150 reflections, showing a 6·3% linear decay in intensity. The structure was solved using the direct-methods program in *SHELXS*86 (Sheldrick, 1986), which located the Co and P atoms. Further difference Fourier syntheses using the *TEXSAN* (v. 2·0) structure analysis package (Molecular Structure Corporation, 1988) located the remaining non-hydrogen atoms and the hydride ligand. Idealized H-atom positions on the cyclohexyl rings were calculated and refined with isotropic temperature factors in the final stages of structure refinement. Full-matrix least-squares refinement (based on F) minimized $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o)]^{-1}$ with all non-hydrogen atoms refined anisotropically. The data were corrected for absorption (ψ scans, transmission range 0·7889–1·0000), decay, and Lp effects. Refinement converged with $R = 0{\cdot}030$, $wR = 0{\cdot}041$, $(\Delta/\sigma)_{\max} = 0{\cdot}02$, $(\Delta\rho)_{\max} = 0{\cdot}36$ e Å^{-3}, No. observ./No. var. = 10·3, and $S = 1{\cdot}20$. Scattering factors: non-hydrogen atoms (Cromer & Waber, 1974), hydrogen (Stewart, Davidson & Simpson, 1965).[*]

Table 1. *Positional parameters and* B_{eq} (Å^2) *for* $HCo(CO)_3\{PCy_3\}$

$B_{\text{eq}} = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

	x	y	z	B_{eq}
Co1	0·82904 (3)	0·29437 (2)	0·24440 (3)	3·41 (1)
P1	0·64846 (5)	0·24280 (3)	0·32892 (5)	2·52 (1)
O1	0·7317 (2)	0·1429 (2)	−0·0423 (2)	7·34 (8)
O2	0·7678 (3)	0·4925 (1)	0·2301 (3)	7·3 (1)
O3	1·1248 (2)	0·2955 (2)	0·5066 (3)	7·24 (8)
C1	0·7644 (3)	0·2009 (2)	0·0712 (3)	4·51 (8)
C2	0·7878 (3)	0·4139 (2)	0·2354 (3)	4·70 (9)
C3	1·0054 (3)	0·2926 (2)	0·4086 (3)	4·55 (8)
C11	0·6595 (2)	0·1242 (1)	0·3955 (2)	2·82 (5)
C12	0·8145 (3)	0·1270 (2)	0·5344 (3)	4·36 (7)
C13	0·8129 (3)	0·0314 (2)	0·5955 (3)	4·86 (8)
C14	0·7762 (3)	−0·0575 (2)	0·4642 (3)	4·69 (9)
C15	0·6256 (3)	−0·0597 (2)	0·3226 (3)	4·27 (7)
C16	0·6273 (3)	0·0353 (1)	0·2614 (3)	3·81 (7)
C21	0·4488 (2)	0·2181 (1)	0·1647 (2)	3·00 (6)
C22	0·4099 (3)	0·3067 (2)	0·0890 (3)	4·30 (8)
C23	0·2538 (3)	0·2810 (2)	−0·0563 (3)	4·95 (9)
C24	0·1226 (3)	0·2361 (2)	−0·0191 (3)	5·6 (1)
C25	0·1607 (3)	0·1477 (3)	0·0527 (5)	6·5 (1)
C26	0·3145 (3)	0·1750 (2)	0·2025 (3)	4·83 (9)
C31	0·6423 (2)	0·3330 (1)	0·4955 (2)	3·05 (6)
C32	0·5651 (3)	0·2895 (2)	0·5948 (3)	4·54 (8)
C33	0·5483 (4)	0·3712 (2)	0·7137 (4)	5·8 (1)
C34	0·7044 (4)	0·4350 (2)	0·8214 (3)	5·5 (1)
C35	0·7855 (4)	0·4773 (2)	0·7278 (3)	5·4 (1)
C36	0·8018 (3)	0·3969 (2)	0·6074 (3)	4·39 (7)
H1	0·940 (4)	0·323 (2)	0·182 (4)	7·9 (8)

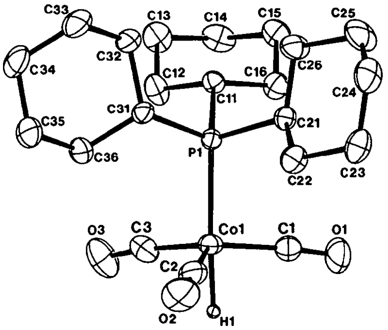

Fig. 1. *ORTEP* (Johnson, 1976) diagram of $HCo(CO)_3\{PCy_3\}$ showing 30% thermal probability ellipsoids and atom labeling (hydrogen atoms on cyclohexyl rings omitted). Selected bond distances and angles are given in Table 2.

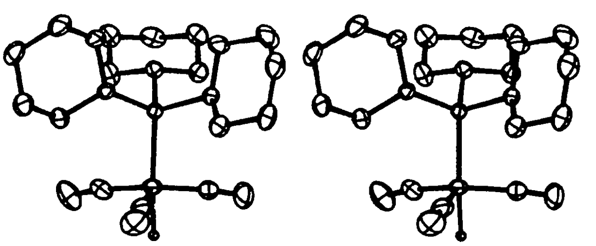

Fig. 2. Stereoview of $HCo(CO)_3\{PCy_3\}$ (hydrogen atoms on cyclohexyl rings omitted).

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51385 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* $HCo(CO)_3\{PCy_3\}$

Co1–H1	1·43 (3)	C14–C15	1·514 (3)
Co1–C1	1·759 (3)	C15–C16	1·521 (3)
Co1–C2	1·767 (3)	C21–C22	1·527 (3)
Co1–C3	1·779 (3)	C21–C26	1·529 (3)
Co1–P1	2·2347 (7)	C22–C23	1·523 (3)
P1–C11	1·855 (2)	C23–C24	1·510 (4)
P1–C21	1·864 (2)	C24–C25	1·506 (5)
P1–C31	1·872 (2)	C25–C26	1·531 (4)
O1–C1	1·141 (3)	C31–C32	1·532 (3)
O2–C2	1·141 (3)	C31–C36	1·532 (3)
O3–C3	1·136 (3)	C32–C33	1·536 (3)
C11–C12	1·524 (3)	C33–C34	1·503 (4)
C11–C16	1·532 (3)	C34–C35	1·505 (4)
C12–C13	1·528 (3)	C35–C36	1·532 (3)
C13–C14	1·508 (4)		

H1–Co1–P1	177 (1)	C21–P1–Co1	111·03 (6)
H1–Co1–C1	79 (1)	C31–P1–Co1	114·44 (6)
H1–Co1–C2	85 (1)	O1–C1–Co1	175·2 (2)
H1–Co1–C3	80 (1)	O2–C2–Co1	176·9 (2)
C1–Co1–C2	121·6 (1)	O3–C3–Co1	173·8 (2)
C1–Co1–C3	118·6 (1)	C12–C11–C16	109·5 (2)
C1–Co1–P1	97·31 (8)	C12–C11–P1	112·6 (1)
C2–Co1–C3	113·4 (1)	C16–C11–P1	113·7 (1)
C2–Co1–P1	96·34 (8)	C11–C12–C13	110·8 (2)
C3–Co1–P1	102·09 (8)	C14–C13–C12	111·5 (2)
C11–P1–C21	102·79 (9)	C13–C14–C15	111·3 (2)
C11–P1–C31	105·81 (9)	C14–C15–C16	111·9 (2)
C11–P1–Co1	116·01 (6)	C15–C16–C11	110·4 (2)
C21–P1–C31	105·6 (1)	C22–C21–C16	109·8 (2)
C22–C21–P1	113·1 (1)	C32–C31–P1	115·7 (1)
C26–C21–P1	116·6 (1)	C36–C31–P1	113·5 (1)
C23–C22–C21	111·9 (2)	C31–C32–C33	111·1 (2)
C24–C23–C22	112·3 (2)	C34–C33–C32	110·8 (2)
C25–C24–C23	110·7 (2)	C33–C34–C35	111·7 (2)
C24–C25–C26	111·0 (3)	C34–C35–C36	111·9 (2)
C21–C26–C25	111·0 (2)	C35–C36–C31	110·8 (2)
C32–C31–C36	109·4 (2)		

Discussion. The crystal structure of the title compound consists of ordered molecules of $HCo(CO)_3\{PCy_3\}$ with no unusually short intermolecular contacts. The ligand geometry around the Co atom is approximately trigonal bipyramidal with the three carbonyls occupying equatorial positions and the hydride and PCy_3 ligands occupying axial sites. An *ORTEP* (Johnson, 1976) diagram of the molecule showing 30% thermal probability ellipsoids is given in Fig. 1, and a stereoview of the molecule is shown in Fig. 2. Positional parameters are given in Table 1 and intramolecular distances and angles in Table 2. The Co—P bond length is 2·2347 (7) Å, which is slightly longer than the Co—P distances of 2·188(ave.) Å in $HCo(CO)\{PPh_3\}_3$ (Whitfield *et al.*, 1977), 2·113(ave.) Å in $HCo\{PPh(OEt)_2\}_4$ (Titus, Orio, Marsh & Gray, 1971), and 2·052(ave.) Å in $HCo(PF_3)_4$ (Frenz & Ibers, 1970). The Co—H bond length [1·43 (3) Å] is statistically indistinguishable from those found in other molecules: $HCo(CO)\{PPh_3\}_3$ [1·41 (9) Å], $HCo(CO)_4$ [1·56 (3) Å] (McNeill & Scholer, 1977), $HCo\{PPh(OEt)_2\}_4$ [1·54 Å], and $HCo(N_2)\{PPh_3\}_3$ [1·64 (11) and 1·67 (12) Å from two crystallographically independent molecules] (Davis, Payne & Ibers, 1969*a*,*b*). The equatorial carbonyls in $HCo(CO)_3\{PCy_3\}$ are bent toward the hydride ligand with an average H—Co—C bond angle of 81°. This bending of the equatorial ligands toward the hydride is also observed in $HCo(CO)\{PPh_3\}_3$, $HCo\{PPh(OEt)_2\}_4$, and $HCo(N_2)\{PPh_3\}_3$ [81·6, 76·6, 81·5 and 82·4° (from two crystallographically independent molecules) respectively]. The observed distortion from an ideal trigonal bipyramid can be expected due to steric effects from the small size of the hydride as compared to the ligand *trans* to it.

IR of $HCo(CO)_3\{PCy_3\}$ ($\tilde{\nu}_{CO}$ of crystals in hexane): 2045 (*m*), 1995 (*w*), 1965 (*s*), 1951 (*sh*), 1932 (*w*) cm^{-1}; ^1H NMR in $CDCl_3$ (room temperature): hydride shift at $\delta = -10{\cdot}98$, $J_{P-H} = 40{\cdot}5$ Hz. Previously reported for this compound (Wood & Garrou, 1984): IR ($\tilde{\nu}_{CO}$, solvent not specified) at 2038 (*m*), 1953 (*s*) cm^{-1}; ^1H NMR (223 K) hydride shift at $\delta = -10{\cdot}1$, $J_{P-H} = 51$ Hz; ^{31}P NMR shift at 70·5 p.p.m.

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