Preparation and Crystal Structure of *trans*-Carbonylhydridotris(triphenylphosphine)cobalt(I): A Quantitative Assessment of Trigonal Bipyramidal Geometry

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trans-Carbonylhydridotris(triphenylphosphine)cobalt(I) has been prepared in 80% yield *via* carbonylation of [$CoH_3(PPh_3)_3$]. [$Co(CO)H(PPh_3)_3$] is monoclinic, space group $P2_1/c$, with four molecules per unit cell, dimensions a = 17.07(1), b = 11.41(1), c = 25.04(2) Å, β = 107.41(7)°. Its crystal structure has been refined by rigid-body full-matrix isotropic-anisotropic least squares on 1 900 independent counter data to a final R' of 0.038 and R of 0.087. The molecule is a distorted trigonal bipyramid with the hydride and carbonyl ligands in axial positions. Bond lengths in the cobalt co-ordination sphere are: Co–H = 1.41(9), Co–C = 1.70(2), Co–P(av.) = 2.188(8) Å. A new quantitive measure of distortion from trigonal bipyramidal geometry is introduced: the half-open cone angle in [$Co(CO)H(PPh_3)_3$] is 81.6° and the exterior bond-cone axis angle is 1.5°.

It is now beyond dispute that the hydride ligand exerts a stereochemical influence in the majority of transition-metal hydride complexes, and an excellent review of the molecular structures of these complexes has appeared.[1] Nevertheless, in some reported complexes neither the influence nor the existence of the H^- ligand is evident from the results of *X*-ray crystallographic studies. Furthermore, because of the surprising structural variability of five-co-ordinate hydrides, no systematic characterization has been proposed, and it is not yet possible to predict their geometries.

The purpose of the present report is three-fold. First, with the report of the crystal and molecular structure of [$Co(CO)H(PPh_3)_3$] we intend simply to add more information to the growing list of known structures in the hope that systematization of the structural chemistry of five-co-ordinate hydrides may soon be possible. Secondly, we feel that one source of confusion concerning these structures arises from the vague descriptive terms applied to five-co-ordinate geometry in general, and trigonal bipyramidal geometry in particular. We have therefore introduced a quantitative function which assesses distortion from ideal trigonal bipyramidal or monocapped tetrahedral geometry and characterizes the continuous transition from one geometry to the other. Finally, we describe the preparation of [$Co(CO)H(PPh_3)_3$] *via* carbonylation of [$CoH_3(PPh_3)_3$] and report our attempts to react [$Co(CO)H(PPh_3)_3$] with some activated olefins and acetylene.

EXPERIMENTAL

Preparation of [$CoH_3(PPh_3)_3$].—This compound was prepared by a modification of the published procedure.[2] All operations were carried out in an argon system using Schlenk apparatus. Solvents were purged with argon. A solution of $CoCl_2\cdot 6H_2O$ (2.55 g, 10.6 mmol) in hot 95% EtOH (60 ml) was slowly added to a stirred solution of triphenylphosphine (9.0 g, 34 mmol) in hot 95% EtOH (120 ml). The resulting blue solution was boiled for 5 min, toluene (60 ml) was added, and the mixture was allowed to cool to room temperature. It was then added dropwise over a 20 min period to a cold (−10 to −20 °C), vigorously stirred mixture of $NaBH_4$ (3.0 g, 79 mmol) in 95% EtOH (120 ml). Hydrogen evolution was vigorous initially, and a red-brown precipitate formed. Stirring was continued for 2 h at −10 to −20 °C during which time the precipitate changed to brown and then to yellow-brown. Stirring was discontinued, the reaction mixture was set aside for 2 h at −15 °C, and it was then filtered. The residue was then washed with ethanol (2 × 75 ml), water (4 × 75 ml), and ethanol (2 × 75 ml). Filtration and washing of the solid was difficult and slow because of its consistency. The dull, yellow-brown solid which resulted was dried *in vacuo* for 36 h to give 7.47 g (85%) of crude [$CoH_3(PPh_3)_3$].

Preparation of [$Co(CO)H(PPh_3)_3$].—The crude [$CoH_3(PPh_3)_3$] obtained above was extracted with cold (0 °C) toluene (80 ml) to give a dark solution. The dark extract, after being filtered, was cooled to 0 °C and carbon monoxide was bubbled through it for 15 min. No colour change was evident in the dark solution. After the solution had been purged with argon to remove the excess of carbon monoxide, cold pentane (300 ml at 0 °C) was added and the mixture was stirred for 15 min. The dark amber solution was maintained at −20 °C for 48 h, during which time orange-brown crystals separated. Decantation of the dark amber solution, followed by rinsing of the residue with cold pentane (50 ml), gave orange-amber crystals (3.4 g, 37% yield based on $CoCl_2\cdot 6H_2O$) which were dried *in vacuo* for 60 h. This product was recrystallized by dissolving it in the minimum amount of cold toluene (50 ml at 0 °C), adding cold pentane (200 ml), and setting it aside for 48 h at −20 °C. Bright orange crystals of [$Co(CO)H(PPh_3)_3$] were obtained, m.p. 127—132 °C (Found: C, 75.58; H, 5.64. Calc. for $C_{55}H_{46}CoOP_3$: C, 75.5; H, 5.3%). The i.r. spectrum (Nujol mull) includes bands at 1 910s ν(C=O), and 1 955w cm^{-1} ν(Co–H). The time-averaged 100 MHz n.m.r. spectrum in thf shows a quartet (1 : 3 : 3 : 1) at *ca.* τ 23 with $J(^1H-^{31}P)$ 50 Hz, in agreement with previously published results.[3]

Crystal Data.—A well formed crystal of [$Co(CO)H(PPh_3)_3$], elongated along the crystallographic b axis and bounded by faces of the monoclinic forms {100}, {001}, and {110}, measured *ca.* 0.16 × 0.36 × 0.20 mm. This crystal was mounted for diffraction with b approximately collinear with the ϕ axis of the goniometer, and was coated with several layers of thinned Duco cement to protect it from moisture. Preliminary cell constants were obtained from Weissenberg and precession films. Least-squares lattice parameters and intensity data were derived from reflections measured on an Enraf-Nonius PAD-3 card-controlled diffractometer.

$C_{55}H_{46}CoOP_3$, M = 875, Monoclinic, space group $P2_1/c$

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(C_{2h}^5, No. 14), $a = 17.07(1)$, $b = 11.41(1)$, $c = 25.04(2)$ Å, $\beta = 107.41(7)°$, $U = 4\,656$ Å^3, D_m (flotation) $= 1.250(5)$ g cm^{-3}, $Z = 4$, $D_c = 1.248$ g cm^{-3}, $F(000) = 1\,824$, Zr-filtered Mo-$K_{\bar{\alpha}}$ radiation, $\lambda = 0.710\,7$ Å, μ(Mo-$K_{\bar{\alpha}}$) $=$ 5.3 cm^{-1}.

The intensities of 4 516 reflections were measured at 25 ± 3 °C from the $\bar{h}kl$ and $h\bar{k}l$ octants by the θ—2θ scan technique. The 2θ scan rate was 1.0° min^{-1} and the 2θ scan range was $(1.8 + \tan\theta)°$ for $9 \leqslant 2\theta \leqslant 40°$ ($0.1104 \leqslant \sin\theta/2 \leqslant 0.4812$). Only 1 982 reflections were judged to be observed under the criterion $I \geqslant 2\sigma(I)$; the variance of each reduced intensity was estimated as $\sigma^2(I) = C_s + (t_s/t_b)^2(C_1 + C_2)$ where C_s, C_1, and C_2 are the scan and two background counts, t_s is the scan time, and t_b is 20 s, the sum of two 10-s background times.

The preliminary film data indicated that the crystal was an intrinsically weak scatterer at higher angles, and this observation is consistent with the fact that 50% of all the ' unobserved ' data were above $2\theta = 34°$ while only 27% of the observed reflections were above this angle. However, absorption was not considered to be the primary cause of this large proportion of weak high-angle reflections, since μ(Mo-$K_{\bar{\alpha}}$) $= 5.3$ cm^{-1} and $\mu R_{\text{max.}} \simeq 0.2$.

The intensities of three reflections ($0,\bar{6},0$; $\bar{2},\bar{1},\bar{4}$; and $2,0,\bar{8}$) were monitored after every 97 reflections and no systematic change in their intensities was observed during the entire data collection period. Structure amplitudes, $|F_o|$, were extracted from the reduced intensities by application of Lorentz and polarization (Lp) corrections, but absorption was not taken into account. The variance of each structure amplitude was estimated as $\sigma^2(|F_o|) = \sigma^2(I)/4I(\text{Lp})$.

Structural Solution and Refinement.—Both Patterson and direct methods were required to locate initial atomic positions. Since the Patterson synthesis contained numerous peaks of medium-to-large magnitude, no unambiguous image of the four heaviest atoms could be readily discerned. Therefore the statistical phasing procedure of MULTAN [4] was utilized, and an E-map revealed the positions of the cobalt and two phosphorus atoms. Successive Fourier difference syntheses combined with diagonal, and ultimately full-matrix, least-squares refinement revealed the existence of all atoms including the hydride ion and the phenyl hydrogen atoms. Weighted full-matrix least-squares refinement of the model which constrained the phenyl carbon atoms to regular hexagons 1.397 Å on a side yielded an R' of 0.038, and R of 0.087.

The atomic scattering factors used were those of Hanson *et al.*[5] Computer programs used in this work were: ORIENT, DIFSET, DIFDAT (diffractometer calculations),[6] ECALC (normalized structure factors),[7] MULTAN (direct phase determination),[4] RBANG (rigid body angles),[8] ORFLSD (rigid-body least-squares),[9] PLANET (least-

TABLE 1

Fractional cell co-ordinates and isotropic and anisotropic thermal parameters [a] for all atoms in [Co(CO)H(PPh$_3$)$_3$]

Atom	x	y	z	B
Co	0.2155(1)	0.2976(2)	0.1714(1)	
P(1)	0.2245(2)	0.2906(4)	0.2606(1)	
P(2)	0.3218(2)	0.3302(3)	0.1426(1)	
P(3)	0.1192(2)	0.1916(4)	0.1140(1)	
C	0.1690(9)	0.4304(15)	0.1545(6)	
O	0.1363(7)	0.5237(9)	0.1440(5)	
H	0.2529	0.1860	0.1792	6.0 [b]
C(A1) [c]	0.1245	0.2771	0.2764	2.8(3)
C(A2)	0.0822	0.1717	0.2608	3.9(3)
C(A3)	0.0048	0.1565	0.2680	5.0(4)
C(A4)	−0.0302	0.2468	0.2909	4.9(4)
C(A5)	0.0121	0.3522	0.3065	4.4(4)
C(A6)	0.0895	0.3674	0.2992	4.2(4)
H(A2)	0.1073	0.1071	0.2444	
H(A3)	−0.0254	0.0811	0.2569	
H(A4)	−0.0856	0.2359	0.2961	
H(A5)	−0.0131	0.4168	0.3229	
H(A6)	0.1197	0.4428	0.3104	
C(B1)	0.2801	0.1685	0.3041	2.3(4)
C(B2)	0.2629	0.1388	0.3535	4.1(4)
C(B3)	0.3076	0.0502	0.3878	5.0(4)
C(B4)	0.3695	−0.0087	0.3727	5.5(5)
C(B5)	0.3876	0.0210	0.3233	4.5(4)
C(B6)	0.3420	0.1096	0.2890	2.6(3)
H(B2)	0.2186	0.1810	0.3643	
H(B3)	0.2953	0.0290	0.4232	
H(B4)	0.4015	−0.0721	0.3973	
H(B5)	0.4310	−0.0212	0.3125	
H(B6)	0.3543	0.1309	0.2536	
C(C1)	0.2727	0.4208	0.3031	2.8(3)
C(C2)	0.2437	0.5327	0.2846	3.9(4)
C(C3)	0.2844	0.6317	0.3124	4.5(4)
C(C4)	0.3540	0.6188	0.3586	4.1(4)
C(C5)	0.3830	0.5069	0.3771	5.2(4)
C(C6)	0.3424	0.4079	0.3493	4.9(4)
H(C2)	0.1939	0.5419	0.2515	
H(C3)	0.2637	0.7118	0.2991	
H(C4)	0.3831	0.6896	0.3784	
H(C5)	0.4329	0.4977	0.4102	
H(C6)	0.3631	0.3278	0.3625	
C(L1)	0.3472	0.2168	0.0965	2.0(3)
C(L2)	0.3359	0.0989	0.1073	2.5(3)
C(L3)	0.3497	0.0122	0.0717	4.5(4)
C(L4)	0.3750	0.0435	0.0255	5.9(5)
C(L5)	0.3863	0.1614	0.0148	5.8(4)
C(L6)	0.3724	0.2481	0.0503	4.4(4)
H(L2)	0.3178	0.0765	0.1404	
H(L3)	0.3416	−0.0722	0.0794	
H(L4)	0.3849	−0.0186	0.0001	
H(L5)	0.4044	0.1838	−0.0183	
H(L6)	0.3806	0.3325	0.0426	
C(M1)	0.3195	0.4643	0.1006	1.7(3)
C(M2)	0.3850	0.5431	0.1116	4.1(4)
C(M3)	0.3806	0.6409	0.0773	6.4(5)
C(M4)	0.3106	0.6599	0.0320	5.3(4)
C(M5)	0.2450	0.5812	0.0210	4.3(4)
C(M6)	0.2495	0.4833	0.0553	3.2(4)
H(M2)	0.4351	0.5294	0.1440	
H(M3)	0.4275	0.6973	0.0851	
H(M4)	0.3074	0.7299	0.0074	
H(M5)	0.1949	0.5948	−0.0115	
H(M6)	0.2025	0.4270	0.0475	
C(N1)	0.4218	0.3378	0.1987	2.6(3)
C(N2)	0.4288	0.4214	0.2406	3.8(4)
C(N3)	0.4996	0.4255	0.2865	4.2(4)
C(N4)	0.5633	0.3460	0.2905	4.5(4)
C(N5)	0.5562	0.2623	0.2485	5.0(4)
C(N6)	0.4855	0.2583	0.2026	4.2(4)
H(N2)	0.3832	0.4783	0.2377	
H(N3)	0.5046	0.4853	0.3165	
H(N4)	0.6139	0.3489	0.3233	
H(N5)	0.6018	0.2054	0.2514	
H(N6)	0.4804	0.1984	0.1726	
C(X1)	0.0110	0.2004	0.1173	2.3(3)
C(X2)	−0.0133	0.3038	0.1378	3.9(4)
C(X3)	−0.0954	0.3200	0.1354	5.1(4)

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TABLE 1 (*Continued*)

Atom	x	y	z	B
C(X4)	−0.1531	0.2327	0.1126	4.2(4)
C(X5)	−0.1289	0.1294	0.0922	4.5(4)
C(X6)	−0.0468	0.1132	0.0945	3.3(4)
H(X2)	0.0281	0.3662	0.1541	
H(X3)	−0.1128	0.3939	0.1500	
H(X4)	−0.2119	0.2443	0.1109	
H(X5)	−0.1702	0.0670	0.0759	
H(X6)	−0.0294	0.0392	0.0799	
C(Y1)	0.1002	0.2366	0.0393	2.9(4)
C(Y2)	0.0432	0.3247	0.0163	3.4(3)
C(Y3)	0.0364	0.3684	−0.0371	4.3(4)
C(Y4)	0.0865	0.3240	−0.0673	4.0(4)
C(Y5)	0.1434	0.2360	−0.0444	5.8(5)
C(Y6)	0.1503	0.1923	0.0090	3.6(3)
H(Y2)	0.0074	0.3564	0.0379	
H(Y3)	−0.0044	0.4314	−0.0535	
H(Y4)	0.0816	0.3553	−0.1055	
H(Y5)	0.1793	0.2043	−0.0660	
H(Y6)	0.1911	0.1292	0.0255	
C(Z1)	0.1367	0.0320	0.1138	2.7(3)
C(Z2)	0.1835	−0.0200	0.1637	3.1(4)
C(Z3)	0.2040	−0.1387	0.1646	4.1(4)
C(Z4)	0.1778	−0.2053	0.1157	4.7(4)
C(Z5)	0.1311	−0.1534	0.0658	5.3(4)
C(Z6)	0.1105	−0.0347	0.0649	4.7(4)
H(Z2)	0.2022	0.0277	0.1987	
H(Z3)	0.2374	−0.1760	0.2003	
H(Z4)	0.1925	−0.2902	0.1164	
H(Z5)	0.1123	−0.2011	0.0308	
H(Z6)	0.0771	0.0026	0.0292	

Atom	β_{11}	β_{22}	β_{33}
Co	0.003 08(11)	0.005 22(21)	0.001 29(5)
P1	0.003 25(23)	0.006 80(43)	0.001 55(9)
P2	0.003 79(23)	0.004 74(46)	0.001 54(9)
P3	0.003 12(22)	0.007 04(48)	0.001 45(9)
C	0.003 9(10)	0.011 4(23)	0.001 3(4)
O	0.007 1(8)	0.009 9(15)	0.003 8(3)

Atom	β_{12}	β_{13}	β_{23}
Co	0.000 46(16)	0.000 63(5)	0.000 32(10)
P1	0.000 37(31)	0.000 75(11)	0.000 10(19)
P2	−0.000 04(27)	0.000 99(11)	−0.000 07(16)
P3	0.000 39(31)	0.000 53(11)	0.000 35(19)
C	0.000 9(12)	0.000 5(5)	0.000 9(8)
O	0.003 1(9)	0.002 0(4)	0.002 1(6)

[a] The anisotropic thermal factor is of the form $\exp\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2(\beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]\}$. [b] All hydrogen atoms were assigned a B value of 6.0. [c] The phenyl ring carbon and hydrogen atomic positions are listed here for convenience and are derived from the group parameters listed in the Supplementary Publication. C(A1) symbolizes carbon 1 (attached to phosphorus) of ring A, *etc.*

squared planes),[10] ORTEP (plotting and drawing),[11] and XRAY67 (Patterson and Fourier synthesis, diagonal least-squares, bond lengths, and bond angles).[12] Observed and calculated structure factors, and rigid-group parameters of the phenyl rings, are listed in Supplementary Publication No. SUP 21862 (6 pp., 1 microfiche).* Table 1 lists positional and thermal parameters of all atoms and Table 2 lists some relevant intramolecular lengths and angles and intermolecular contacts.

DISCUSSION

Preparation and Reactions of $[Co(CO)H(PPh_3)_3]$.—Misono *et al.*[13] reported the isolation of three complexes, $[Co(CO)_3(PPh_3)]_2$, $[Co(CO)H(PPh_3)_3]$, and $[Co(CO)_2H(PPh_3)_2]$, from the reaction wherein carbon monoxide was bubbled through a benzene solution of $[CoH(N_2)(PPh_3)_3]$ at room temperature. The authors stated that these carbonyl complexes of cobalt were also prepared by using $[CoH_3(PPh_3)_3]$ instead of the dinitrogen complex, but no details were given. The preparation of $[Co(CO)H(PPh_3)]$ from the dinitrogen complex was also reported by Yamamoto *et al.*[14] In addition, treatment of carbonyl (π-cyclo-octenyl)-π-cyclo-octa-1,5-dienecobalt with triphenylphosphine gives $[Co(CO)H(PPh_3)_3]$.[3]

TABLE 2

Important intramolecular bond lengths and contact distances (Å) and bond angles (°). The estimated standard deviations (in parentheses) neglect covariances

Co–H	1.41(9)	P(1)–C(C1)	1.870(9)
Co–P(1)	2.194(5)	P(2)–C(L1)	1.870(9)
Co–P(2)	2.176(5)	P(2)–C(M1)	1.851(9)
Co–P(3)	2.195(4)	P(2)–C(N1)	1.860(8)
Co–C	1.704(17)	P(3)–C(X1)	1.876(9)
C–O	1.194(20)	P(3)–C(Y1)	1.872(9)
P(1)–C(A1)	1.871(9)	P(3)–C(Z1)	1.846(9)
P(1)–C(B1)	1.847(9)		
H–Co–C	174(8)	Co–P(2)–C(N1)	115.2(3)
H–Co–P(1)	86(8)	Co–P(3)–C(X1)	119.7(4)
H–Co–P(2)	79(6)	Co–P(3)–C(Y1)	112.0(4)
H–Co–P(3)	79(5)	Co–P(3)–C(Z1)	117.1(3)
Co–C–O	178(1)	P(1)–Co–P(2)	122.1(1)
Co–P(1)–C(A1)	115.3(3)	P(2)–Co–P(3)	114.4(1)
Co–P(1)–C(B1)	119.7(4)	P(1)–Co–P(3)	117.2(1)
Co–P(1)–C(C1)	115.8(3)	C–Co–P(1)	99.8(4)
Co–P(2)–C(L1)	117.2(3)	C–Co–P(2)	98.0(3)
Co–P(2)–C(M1)	116.8(4)	C–Co–P(3)	82.8(3)
H · · · P(1)	2.53(18)	O · · · H(C2)	2.582(13)
H · · · P(2)	2.36(14)	C(L1) · · · H(N6)	2.501(10)
H · · · P(3)	2.38(12)	C(M1) · · · H(L6)	2.523(13)
H · · · H(B6)	2.22(14)	H(A2) · · · H(Z2)	2.422(13)
H · · · H(L2)	2.09(15)	H(A6) · · · H(C2)	2.485(13)
H · · · H(Z2)	2.12(12)	H(X6) · · · H(Z6)	2.544(13)
C · · · H(X2)	2.511(18)	H(Y6) · · · H(Z6)	2.448(13)

The crystals of $[Co(CO)H(PPh_3)_3]$ used in this diffraction study were prepared according to the details given in the Experimental section. This procedure is quite tedious because of difficulty in the filtering and washing of $[CoH_3(PPh_3)_3]$, which has a mud-like consistency and is extremely air-sensitive. Subsequently, we improved the procedure considerably simply by carbonylating the crude, unwashed suspension of $[CoH_3(PPh_3)_3]$ instead of isolating it prior to carbonylation. The yield was then increased from 37 to 80%, and the time required for the synthesis was decreased from several days to several hours. Previous workers[15,16] have reported the melting point (decomp.) to be 172—173 and 176—178 °C. The $[Co(CO)H(PPh_3)_3]$ samples which we have prepared at least half

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

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[16] D. D. Titus, A. A. Orio, R. E. Marsh, and H. B. Gray, *Chem. Comm.*, 1971, 332.

a dozen times decompose in the range 128—132 °C, and we have no explanation for these contrasting results.

In view of our previous studies of the reactions of $[Ir(CO)H(PPh_3)_3]$ with activated olefins and acetylenes,[17-21] we had hoped to investigate comparable reactions of $[Co(CO)H(PPh_3)_3]$. However, it was found that the reactivity of $[Co(CO)H(PPh_3)_3]$ with these unsaturated molecules is much less than that of the iridium analogue. No reaction occurred between $[Co(CO)H(PPh_3)_3]$ and a ten-fold excess of fumaronitrile in toluene at —5 °C during 1 h. At room temperature during 3 h, i.r. monitoring showed gradual disappearance of the ν(CO) band in $[Co(CO)H(PPh_3)_3]$, and no new bands indicative of the formation of an olefin complex appeared as the solution darkened. Dimethyl fumarate did not react with $[Co(CO)H(PPh_3)_3]$ at 15 °C during 1 h. However, tetracyanoethylene (tcne) and $[Co(CO)H(PPh_3)_3]$, in equimolar amounts in toluene at 0 °C, did react immediately to give a dark solution whose i.r. spectrum showed bands at 1 945, 1 995, and 2 120—2 150 cm^{-1}, probably due to the formation of a keteniminato-complex. After the solution had been set aside for 24 h at —20 °C all the i.r. bands in the 1 900—2 200 cm^{-1} region had disappeared; no complex was isolated. During the course of our investigation, a

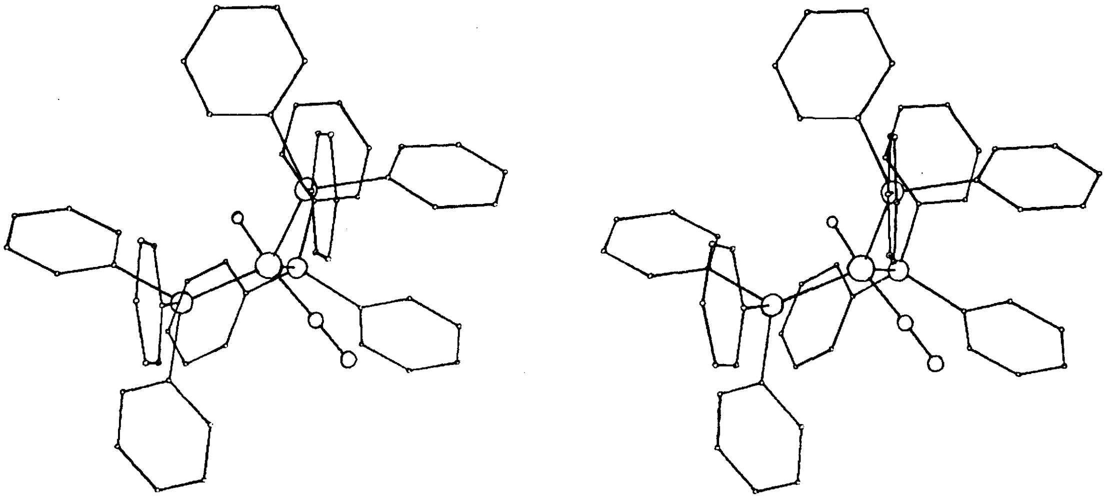

FIGURE 1 Stereoscopic representation of $[Co(CO)H(PPh_3)_3]$

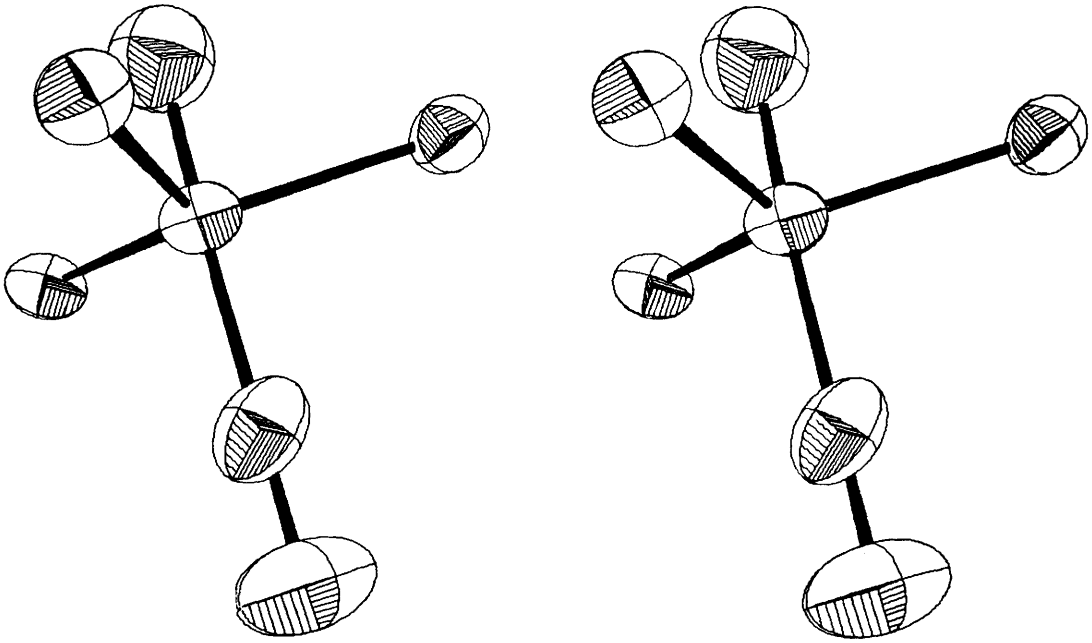

FIGURE 2 Stereoview of the co-ordination sphere of $[Co(CO)H(PPh_3)_3]$; thermal ellipsoids represent 50% probability surface

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[17] W. H. Baddley and M. Shirley Fraser, *J. Amer. Chem. Soc.*, 1969, **91**, 3361.

[18] J. S. Ricci, M. Shirley Fraser, J. A. Ibers, and W. H. Baddley, *J. Amer. Chem. Soc.*, 1970, **92**, 3489.

[19] M. Shirley Fraser, G. F. Everitt, and W. H. Baddley, *J. Organometallic Chem.*, 1972, **35**, 403.

[20] M. Shirley Fraser and W. H. Baddley, *J. Organometallic Chem.*, 1972, **36**, 377.

[21] W. H. Baddley and G. B. Tupper, *J. Organometallic Chem.*, 1974, **67**, C16.

report appeared describing the isolation of $[Co(CO)H(PPh_3)_2(tcne)]$ from the reaction of $[Co(CO)H(PPh_3)_3]$ and tcne in toluene at room temperature during 1 d.[22] The activated acetylenes dimethyl acetylenedicarboxylate and hexafluorobut-2-yne, both of which react readily with $[Ir(CO)H(PPh_3)_3]$, did not react at 0—15 °C with $[Co(CO)H(PPh_3)_3]$, so a planned investigation of reactions of activated olefins and acetylenes with the cobalt complex was abandoned.

Structure of $[Co(CO)H(PPh_3)_3]$.—Figure 1 is a stereoscopic view of $[Co(CO)H(PPh_3)_3]$. The co-ordination polyhedron about the cobalt atom (Figure 2) is derived from a trigonal bipyramid with triphenylphosphine ligands occupying the three equatorial sites and the carbonyl and hydride ligands occupying axial positions. The polyhedron is distorted such that the Co lies 0.31 Å from the plane defined by the phosphorus atoms * in the direction of the carbonyl; that is, the phosphine ligands are bent toward the hydride position. As a result, there are P–H contact distances which range from 2.36 to 2.53 Å (Table 2), considerably less than the van der Waals contact distance of 3.1 Å calculated from Pauling's values.[23] In addition, there are three close (<2.3 Å) intramolecular contacts between the hydride and *ortho*-hydrogen atoms on three phenyl rings. The hydride is thus effectively shielded from the extramolecular environment by the triphenylphosphine ligands.

TABLE 3

Five-co-ordinate transition metal hydrides

Compound	M–H/Å	D/Å [a]	Φ/°	β_1/°	β_2/°	Ref.
$[Co(CO)H(PPh_3)_3]$	1.41 (9)	0.31	81.6	1.5	4.7	
$[CoH(N_2)(PPh_3)_3]$ (I) [b]	1.64 (11)	0.32	81.5	1.2	13.6	15
$[CoH(N_2)(PPh_3)_3]$ (II)	1.67 (12)	0.28	82.4	1.8	13.2	
$[CoH\{PPh(OEt)_2\}_4]$	1.54	0.49	76.6	5.9	*c*	16
$[CoH(PF_3)_4]$ (2)	*d*	0.78	67.8	5.9	*d*	24
$[CoH(PF_3)_4]$ (3)	*d*	0.59	73.2	5.1	*d*	
$[RuH(NO)(PPh_3)_3]$	*e*	0.55	76.4	8.3	*e*	*f*
$[RuClH(PPh_3)_3]$	1.70 (15)	*g*	*g*	*g*	*g*	*h*
$[Rh(CO)H(PPh_3)_3]$	1.60 (12)	0.36	81.1	5.5	6.5	*i*
$[RhClH(PPh_3)_2(SiCl_3)]$	1.48	*g*	*g*	*g*	*g*	*j*
$[RhH(PPh_3)_4]$	*e*	0.70	72.1	0.0 [k]	*e*	*l*
$[Rh(AsPh_3)H(PPh_3)_3]$	*e*	*c*	*c*	*c*	*e*	*m*
$[IrH(NO)(PPh_3)_3]^+$	*e*	0.51	77.5	4.0	*e*	*n*
$[Ir(CO)H(fumn)(PPh_3)_2]$	*e*	0.00 [k]	90.0 [k]	0.0 [k]	*e*	*o*
$[Ir(CO)_2H(PPh_3)_2]$	1.7 (2)	0.23	83.5	5.1	*c*	25

[a] D = metal-to-equatorial plane distance, Φ = half-open cone angle, β_1 = exterior bond-cone axis angle, β_2 = interior bond-cone axis angle. [b] Two crystallographically independent molecules. [c] Reported information insufficient for computation. [d] Hydride unobserved, but three models proposed. The two favoured models are shown in this Table. [e] Hydride unobserved. [f] C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 1094. [g] Geometry neither trigonal bipyramidal nor monocapped tetrahedral. [h] A. C. Skapski and P. G. H. Troughton, *Chem. Comm.*, 1968, 1230. [i] S. J. LaPlaca and J. A. Ibers, *J. Amer. Chem. Soc.*, 1963, **85**, 3501; *Acta Cryst.*, 1965, **18**, 516. [j] K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 440. [k] Required by symmetry. [l] R. W. Baker and P. Pauling, *Chem. Comm.*, 1969, 1495. [m] R. W. Baker, B. Ilmaier, P. J. Pauling, and R. S. Nyholm, *Chem. Comm.*, 1970, 1077. [n] D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1479. [o] K. W. Muir and J. A. Ibers, *J. Organometallic Chem.*, 1969, **18**, 175.

The three Co–P bond lengths in $[Co(CO)H(PPh_3)_3]$ are statistically equivalent, and the mean value of 2.188(8) Å compares favourably with the mean value of 2.192(6) Å found in the isoelectronic species $[CoH(N_2)(PPh_3)_3]$.[15] Shorter Co–P bonds have been observed in $[CoH\{PPh(OEt)_2\}_4]$ [16] [mean 2.113(3) Å] and $[CoH(PF_3)_4]$ [24] [mean 2.052(5) Å], but this is expected since the π-acceptor capability of the phosphine ligands is increasing in these two compounds.

The Co–C and P–C bond lengths found in $[Co(CO)H(PPh_3)_3]$ are within the range of values reported for cobalt carbonyls and triphenylphosphine ligands respectively. Due to lack of precision in the hydride position (estimated as 0.1 Å in each of the three co-ordinates), the Co–H bond length of 1.41(9) Å does not differ significantly from *any* of the transition metal-hydride distances listed in Table 3. We therefore judge the Co–C, Co–H, and P–C bonds to be normal in this compound.

Five-co-ordinate Geometry.—During an attempt to correlate and compare the structure of $[Co(CO)H(PPh_3)_3]$ with those of other hydrides, it became obvious that the descriptive vocabulary for five-co-ordinate geometry is sadly lacking. The terms 'distorted trigonal bipyramid' and 'distorted tetrahedron' are used more as a matter of semantic preference than of quantitative measure. At the other extreme, detailed comparisons of interbond angles generally fail to elucidate the true nature and extent of distortions. The one simple measure most quoted, the perpendicular distance of the central atom from the 'equatorial plane,' is also unsatisfactory as discussed below. We propose a straightforward quantitative formulation of five-co-ordinate geometry (excluding square pyramidal) which is in effect a normal co-ordinate treatment of the distortion as a whole.

Symmetric depression of the three equatorial bonds of a trigonal bipyramidal molecule toward one of the axial positions (the *interior* position) results in a continuous transformation of the co-ordination polyhedron

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* The equation of this plane is $-6.67x + 10.23y - 2.10z = 0.93$, where x,y,z are fractional crystal co-ordinates.

[22] Y. Kubo, A. Yamamoto, and S. Ikeda, *J. Organometallic Chem.*, 1973, **60**, 165.

[23] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd edn., 1960, p. 260.

[24] B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 2403.

from trigonal bipyramidal to monocapped tetrahedral. The three depressed bonds define the lateral surface of a cone of revolution, and the half-open angle Φ (Figure 3) defines the amount of distortion. Thus, $\Phi = 90°$ represents a perfect trigonal bipyramid while $\Phi = 70.5288°$ represents a perfect tetrahedron. We suggest that $\Phi \approx 80°$ is a natural demarcation point between 'distorted trigonal bipyramidal' and 'distorted monocapped tetrahedral.' Adopting this criterion, only five of the compounds listed in Table 3 should be described by the former term, while five others are of the latter variety.

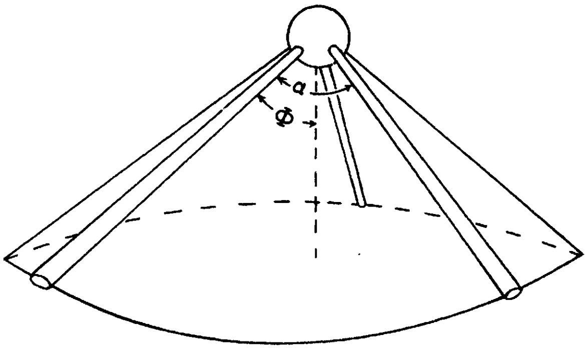

FIGURE 3 Three vectors define a cone of half-open angle Φ. The intervector angle is α

If the depression of the equatorial bonds is not symmetric, then one or both of the axial bonds will not be collinear with the cone axis, and the angle between a bond and the cone axis represents the amount of asymmetry in the distortion. In the five-co-ordinate hydrides listed in Table 3, the angles between the metal–hydride bonds (invariably the bonds in the interior of the cones) and the cone axes vary considerably, but little credence can be placed on these values due to the low accuracy of the hydride position. A more faithful measure of the asymmetry of the distortions in these complexes is the exterior bond-cone axis angle. Thus, both $[Co(CO)H(PPh_3)_3]$ and $[CoH(N_2)(PPh_3)]$ suffer equivalent distortions with equivalent (and low) asymmetry, while $[RuH(NO)(PPh_3)_3]$, for example, shows a larger distortion which is also highly asymmetric.

The metal-to-equatorial plane distance, *D*, is a deceptive measure of the distortion, since it is a function not only of the angle of depression of the equatorial bonds (of which Φ is a direct function) but also of the distance from the central atom to the three points which define the equatorial plane. Some of these points may be quite arbitrary, as in the case of $[Ir(CO)_2H(PPh_3)_2]$.[25] The authors' choice of the midpoint of one C–O bond was fortuitous since the Ir–(mid-CO) distance is nearly equal to the two Ir–P distances. Only under this condition will *D* correlate well with Φ, a condition which also holds for most of the compounds in Table 3 for obvious reasons. However, in the general case, meaningful comparisons between compounds with *different* equatorial ligands is not possible when *D* is the only measure of distortion.

If the three equatorial bonds are numbered arbitrarily then α_1, α_2, and α_3 are the interbond angles between bonds 2 and 3, 3 and 1, and 1 and 2 respectively. The angle Φ is a function of these three angles:

$$\tan^2\Phi = 2(1 - \cos\alpha_1)(1 - \cos\alpha_2)(1 - \cos\alpha_3)V^{-2}$$

where

$$V^2 = 1 - \cos^2\alpha_1 - \cos^2\alpha_2 - \cos^2\alpha_3 + 2\cos\alpha_1\cos\alpha_2\cos\alpha_3$$

If all angles are equal ($\alpha = \alpha_1 = \alpha_2 = \alpha_3$) the expression is much simplified:

$$\tan^2\Phi = 2(1 - \cos\alpha)^3/(1 - 3\cos^2\alpha + 2\cos^3\alpha)$$

An excellent approximation may be obtained, if the three angles are not too different, by using the average $[\alpha \approx (\alpha_1 + \alpha_2 + \alpha_3)/3]$. The function $\Phi(\alpha)$ is shown in Figure 4.

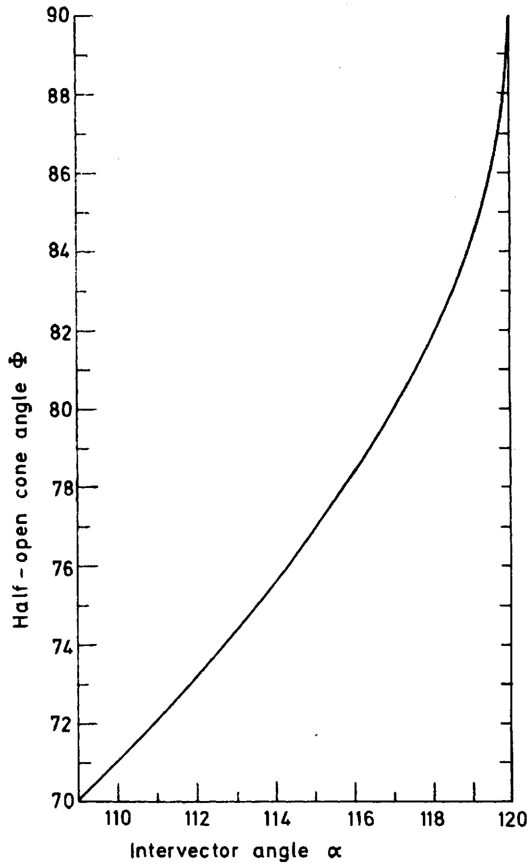

FIGURE 4 Plot of Φ(α) *versus* α

An axial bond makes angles γ_1 and γ_2 with equatorial bonds 1 and 2. The angle between the axial bond and the cone axis is then β:

$$\cos\beta = \cos\Phi[(\cos\gamma_1 + \cos\gamma_2)/(1 + \cos\alpha_3)] \pm u/\sin\alpha_3[1 - 2\cos^2\Phi/(1 + \cos\alpha_3)]^{\frac{1}{2}}$$

where

$$u = (1 - \cos^2\gamma_1 - \cos^2\gamma_2 - \cos^2\alpha_3 + 2\cos\gamma_1\cos\gamma_2\cos\alpha_3)^{\frac{1}{2}}$$

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[25] M. Ciechanowicz, A. C. Skapski, and P. G. H. Troughton, Collected Abstracts, VIIIth International Congress of Crystallography, Stony Brook, N.Y., 1969, p. s172; *Acta Cryst.*, 1969, **12**, s172.

Care must be taken in using this function since there is a sign ambiguity in the square root. Reference to the physical model allows ready selection of the correct quadrant for β.

The usefulness of the conic description may be demonstrated by its application to the structure of [CoH(PF_3)$_4$] investigated by Frenz and Ibers.[24] Due to disorder imposed by the crystal symmetry, the hydride ion was not observed. However, three possible structural models were proposed, two of which (models 2 and 3, Table 5) were favoured by the authors on the basis of idealized P · · · H and F · · · H distances. The half-open cone angle in model 2 is much smaller than the angle in model 3, smaller even than in a regular tetrahedron, for which there is no known precedent. On the basis of the cone angles and the non-bonded distances therefore, model 3 is preferable to model 2.

We feel that the conic description for trigonal bipyramidal complexes is an extremely useful quantitative tool, and urge authors to use this description in their discussions. The function lends itself readily to structural correlation since it provides a common reference for structure which may differ widely in detail. Application of this description to broad classes of complexes may even hasten the systematization of five-co-ordinate geometry.

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