Allogons. 1. Low Temperature X-ray Crystal Structures of the Trigonal Bipyramidal and Square-Pyramidal Forms of $HCo(CO)_2(PPh_3)_2$

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Dicarbonylbis(triphenylphosphine)cobalt hydride $[HCo(CO)_2(PPh_3)_2]$ (**1**) has been prepared from the reaction of $HCo(CO)_4$ with PPh_3. Recrystallization of the isolated product from acetonitrile led to yellow crystals suitable for X-ray diffraction. The structures of both a trigonal bipyramidal (TBP) form and a square-pyramidal (SP) form of **1** were determined by X-ray diffraction from two crystals grown in the *same* crystallization. **1(TBP)** crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.608(2)$ Å, $b = 12.543(2)$ Å, $c = 13.029(2)$ Å, $\alpha = 65.67(2)°$, $\beta = 82.31(2)°$, $\gamma = 82.37(2)°$, $V = 1559.6(5)$ Å^3, and $Z = 2$ at $T = 123(5)$ K, with final residuals of $R(F) = 0.039$, $R_w(F) = 0.046$, and $S(F) = 1.25$ for 5645 observed reflections and 391 parameters. **1(SP)** crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.956(2)$ Å, $b = 12.558(3)$ Å, $c = 16.862(5)$ Å, $\alpha = 98.99(2)°$, $\beta = 93.64(2)°$, $\gamma = 111.50(2)°$, $V = 1590.1(7)$ Å^3, and $Z = 2$ at $T = 123(5)$ K, with final residuals of $R(F) = 0.039$, $R_w(F) = 0.042$, and $S(F) = 1.60$ for 5958 observed reflections and 353 parameters. These are the first crystal structures of a mononuclear hydridodicarbonylbis(phosphine)cobalt complex to be reported. Moreover, this is the first report that we are aware of in which two allogons of a neutral five coordinate metal complex have been structurally characterized. The TBP form has the hydride ligand in an axial position, *trans* to a carbonyl ligand. This geometry is similar to those reported in all previous structures of $HCo(L)_n(PR_3)_{4-n}$ complexes ($n = 0-4$, $n \neq 2$). The more unusual SP form has a carbonyl ligand [C(1)–O(1)] in the axial position. This structure exhibits disorder of the phenyl rings of one phosphine ligand, although generally the molecular geometry is quite precisely defined. The Co–H distances of 1.37(3) and 1.45(4) Å, for the TBP and SP forms, respectively, are comparable to those determined in other cobalt hydride structures.

Introduction

The existence of metal complexes which can adopt more than one coordination geometry without a change in ligand coordination mode have been known for some time. Such species exhibit a form of geometric isomerism which differs from the most common form in which isomers with identical coordination geometries are related by an interchange of ligands. Kilbourn and Powell have suggested the term *allogons*[1] to describe the tetrahedral and square-planar forms of dibromobis(benzyldiphenylphosphine)nickel(II) and this term will be used hereafter to indicate geometric isomers of a metal complex which have different coordination geometries. The existence of allogons, albeit with one form perhaps being quite short-lived, is implicit in mechanisms such as Berry Pseudorotation for 5-coordinate complexes, and the trigonal twist and Ray-Dutt twist for 6-coordinate complexes. However, it is less common for two allogons to be isolable.

In this paper the crystal structures of trigonal bipyramidal and square-pyramidal allogons of $[HCo(CO)_2(PPh_3)_2]$ (**1**) are described. The structures have been determined by low temperature X-ray diffraction and demonstrate that each structure contains only $[HCo(CO)_2(PPh_3)_2]$ molecules, i.e., no solvent molecules are incorportated into the lattice.

Experimental Section

$HCo(CO)_2(PPh_3)_2$ (**1**) was obtained as a byproduct from the reaction in toluene/hexane solution of PPh_3 with $HCo(CO)_4$, prepared *in situ* according to the procedure of Sternberg et al.[2] The crude product, containing both $HCo(CO)_3(PPh_3)$ and $HCo(CO)_2(PPh_3)_2$ was further reacted with the diamine DABCO (1,4-diazabicyclo[2.2.2]octane) to prepare the salt $(DABCO)H^+Co(CO)_3(PPh_3)^-$. The absence of the salt $(DABCO)H^+Co(CO)_2(PPh_3)_2$- among the products suggests that **1** is not acidic enough to protonate the diamine. A more detailed description of the salt $(DABCO)H^+Co(CO)_3(PPh_3)^-$ is presented elsewhere.[3] **1** was isolated from the final product mixture by recrystallization from acetonitrile solution to yield air/moisture-stable yellow crystals suitable for X-ray diffraction. ^1H NMR spectral data for **1** were in accord with those reported by Misono and co-workers.[4] As neither the structure of **1** nor that of any $HCo(CO)_2L_2$ complex had been reported, a single crystal X-ray diffraction study was undertaken. Subsequent examination by X-ray diffraction revealed that two types of yellow crystals were present. This was not apparent from the external morphology, but rather initially from the fact that the two types of crystals differed by a 2% in their unit cell volumes. The two structures were subsequently determined to be trigonal bipyramidal **1(TBP)** and square-pyramidal **1(SP)** allogons of $HCo(CO)_2(PPh_3)_2$.

The two crystal structures were solved by direct methods, and after data were corrected for absorption by semi-empirical methods[5] the structures were refined to convergence by full-matrix least-squares using the SHEXTL suite of programs.[5] For **1(TBP)** all non-hydrogen atoms were refined anisotropically; phenyl hydrogen atoms were refined using a riding model, and with fixed isotropic displacement parameters. For **1(SP)** disorder was evident in the phenyl rings of one of the two PPh_3 groups. One of the rings (C(41)–C(46)) was described using a single orientation, the disorder being evident from the slightly elongated

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Table 1. Data Collection, Structure Solution, and Refinement Parameters for **1**(**TBP**) and **1**(**SP**)

	1(**TBP**)	**1**(**SP**)
cryst system	triclinic	triclinic
space group, *Z*	$P\bar{1}$, $Z = 2$	$P\bar{1}$, $Z = 2$
a (Å)	10.608(2)	8.956(2)
b (Å)	12.543(2)	11.558(3)
c (Å)	13.029(2)	16.862(5)
α (deg)	65.67(2)	98.99(2)
β (deg)	82.31(2)	93.64(2)
γ (deg)	82.37(2)	111.50(2)
V (Å^3)	1559.6(5)	1590.1(7)
density (g/cm^3)	1.364	1.338
temp (K)	123(5)	123(5)
X-ray wavelength (Å)	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	0.686	0.673
2θ range (deg)	3.0−55.0	3.0−55.0
no. of reflcns collcd	7575	7803
no. of indept reflcns (R_{int})	7186 (0.033)	7333 (0.022)
no. of obsd reflcns ($F > 4.0\ \sigma(F)$)	5645	5958
L.S. parameters	391	353
$R(F)$, $R_w(F)$	0.039, 0.046	0.039, 0.042
$S(F)$	1.25	1.60

probability ellipsoids for some of the ring carbon atoms. The other two rings, (C(51)−C(56)) and (C(61)−C(66)), were modeled using rigid C_6H_5 groups with isotropic displacement parameters for the carbon atoms to define in each case two orientations for the ring. Phenyl hydrogen atoms for major and minor orientations were included in the rigid groups in calculated positions. The relative occupancy of the two orientations are, (C(51)−C(56):(C(51′)−C(56′) = 0.55:0.45 and (C(61)−C(66)):(C(61′)−C(66′)) = 0.53:0.47. For both structures the hydride hydrogen was located directly from the difference map and its positional parameters refined without constraints. Experimental data are given in Table 1.

Results and Discussion

As indicated above, the structures of both a trigonal bipyramidal form and a square-pyramidal form of the complex $HCo(CO)_2(PPh_3)_2$ have been determined. Atomic coordinates for **1**(**TBP**) and **1**(**SP**) are given in Tables 2 and 3. For the rigid groups esds are given only for the pivot atoms. Selected bond lengths and angles are in Table 4. The molecular structures of **1**(**TBP**) and **1**(**SP**) are shown in Figures 1 and 2, respectively. The TPB and SP arrangement of ligands are more clearly depicted in views of the core geometries in Figure 3.

Although a number of structures of the type $HCo(L)_n(PR_3)_{4-n}$ have been described, this is the first example to be structurally characterized where $n = 2$. In all previous $HCo(L)_n(PR_3)_{4-n}$ structures ($n = 0, 1, 3, 4$) the complex can (and indeed does) adopt a geometry with approximate C_{3v} symmetry in which the hydride lies *trans* to another ligand. Such geometries conform to either a trigonal bipyramidal description, or in some cases might be interpreted as a monocapped tetrahedral form with the (small) hydride ligand capping a "face" defined by three other ligands. These geometries for $HCoL_4$ complexes have been discussed in detail by Watkins and co-workers.[6]

In structure **1**(**TBP**) the trigonal bipyramidal arrangement of ligands places the hydride and one carbonyl ligand in the axial positions; the (larger) phosphine ligands occupy equatorial positions as has been previously observed for $HCo(L)(PR_3)_3$ complexes (e.g., $[HCo(CO)(PPh_3)_3]$;[6] $[HCo(N_2)(PPh_3)_3]$[7]). The equatorial ligands lie closer to the hydride ligand than to the other axial ligand as expected on steric grounds, and as observed for all other trigonal bipyramidal $HCo(L)_n(PR_3)_{4-n}$ complexes. [average H−Co−L_{eq} 82(2)° and C_{ax}−Co−L_{eq} 98(3)° for **1**(**TBP**)].

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients[a] (Å^2 × 10^3) for **1**(**TBP**)

	x	*y*	*z*	*U*(eq)
Co	2927(1)	8935(1)	8419(1)	16(1)
H	1895(30)	9349(27)	8937(26)	50
C(1)	3648(2)	9010(2)	9518(2)	23(1)
O(1)	4080(2)	9020(2)	10280(2)	34(1)
C(2)	4237(2)	8324(2)	7788(2)	22(1)
O(2)	5083(2)	7884(2)	7419(2)	35(1)
P(1)	1822(1)	7411(1)	8990(1)	16(1)
C(11)	1932(2)	6627(2)	8054(2)	19(1)
C(12)	2061(2)	5406(2)	8436(2)	25(1)
C(13)	2118(3)	4875(2)	7680(2)	31(1)
C(14)	2039(3)	5557(2)	6537(2)	31(1)
C(15)	1908(2)	6774(2)	6146(2)	27(1)
C(16)	1871(2)	7305(2)	6897(2)	23(1)
C(21)	2297(2)	6236(2)	10331(2)	19(1)
C(22)	3592(2)	6007(2)	10522(2)	27(1)
C(23)	3987(3)	5123(2)	11520(2)	33(1)
C(24)	3096(3)	4461(2)	12341(2)	30(1)
C(25)	1812(3)	4685(2)	12163(2)	25(1)
C(26)	1411(2)	5563(2)	11161(2)	22(1)
C(31)	91(2)	7622(2)	9308(2)	17(1)
C(32)	−796(2)	7216(2)	8885(2)	21(1)
C(33)	−2099(2)	7432(2)	9125(2)	27(1)
C(34)	−2533(2)	8036(2)	9802(2)	26(1)
C(35)	−1653(2)	8423(2)	10248(2)	24(1)
C(36)	−357(2)	8220(2)	10007(2)	21(1)
P(2)	2472(1)	10571(1)	6956(1)	16(1)
C(41)	2323(2)	10484(2)	5604(2)	18(1)
C(42)	3299(2)	9863(2)	5191(2)	24(1)
C(43)	3246(3)	9780(2)	4170(2)	26(1)
C(44)	2210(3)	10313(2)	3546(2)	29(1)
C(45)	1228(3)	10918(3)	3947(2)	36(1)
C(46)	1282(2)	11005(2)	4973(2)	28(1)
C(51)	996(2)	11471(2)	7086(2)	17(1)
C(52)	−109(2)	10914(2)	7628(2)	21(1)
C(53)	−1262(2)	11563(2)	7696(2)	25(1)
C(54)	−1333(2)	12778(2)	7228(2)	28(1)
C(55)	−248(3)	13341(2)	6684(2)	30(1)
C(56)	911(2)	12694(2)	6608(2)	25(1)
C(61)	3662(2)	11660(2)	6525(2)	18(1)
C(62)	3984(2)	12373(2)	5393(2)	25(1)
C(63)	4844(3)	13219(2)	5109(2)	29(1)
C(64)	5381(2)	13366(2)	5948(2)	29(1)
C(65)	5078(2)	12658(2)	7076(2)	26(1)
C(66)	4236(2)	11800(2)	7357(2)	22(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Structure **1**(**SP**) is more unusual. It is the first example of a square-pyramidal cobalt(I) hydride complex. The cobalt(II) hydride complex $[HCo(NCBH_3)(PPh_3)_3]$[8] is best described as SP, rather than TBP. The geometry of **1**(**SP**) is most apparent from the fact that no ligand lies *trans* to another ligand. The carbonyl ligand, C(1)−O(1), is in the axial position with interligand angles involving C(1) ranging from 102.5(1)° to 113.9(1)°. The two phosphine ligands are situated at opposite vertices in the "basal plane" [P(1)−Co−P(2) 139.8(1)°], as are the hydride ligand and the other carbonyl ligand, C(2)−O(2), [H−Co−C(2) 135.6(11)°].

The difference in geometry of **1**(**TBP**) and **1**(**SP**) might be expected to have some impact upon the Co-H distance, particularly as in **1**(**TBP**) the hydride lies *trans* to a carbonyl ligand. However, within the precision of this structure determination, the Co-H separations are not significantly different

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Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients[a] ($Å^2 \times 10^3$) for **1(SP)**

	x	*y*	*z*	*U*(eq)
Co	3644(1)	7653(1)	7166(1)	14(1)
H	4918(37)	7259(28)	7445(18)	50
C(1)	2570(3)	6679(2)	6224(1)	20(1)
O(1)	1834(2)	6054(2)	5624(1)	32(1)
C(2)	2889(3)	8802(2)	7548(1)	21(1)
O(2)	2396(2)	9549(2)	7811(1)	34(1)
P(1)	5921(1)	8953(1)	6923(1)	15(1)
C(11)	7106(3)	8275(2)	6283(1)	18(1)
C(12)	8654(3)	9019(3)	6136(2)	27(1)
C(13)	9493(3)	8486(3)	5629(2)	35(1)
C(14)	8824(3)	7223(3)	5269(2)	38(1)
C(15)	7305(3)	6481(3)	5411(2)	34(1)
C(16)	6451(3)	7008(2)	5918(2)	25(1)
C(21)	5858(3)	10253(2)	6439(1)	17(1)
C(22)	4409(3)	10136(2)	6012(1)	19(1)
C(23)	4338(3)	11080(2)	5614(1)	23(1)
C(24)	5706(3)	12144(2)	5628(2)	27(1)
C(25)	7159(3)	12285(2)	6059(2)	28(1)
C(26)	7235(3)	11352(2)	6468(2)	25(1)
C(31)	7335(3)	9804(2)	7843(1)	17(1)
C(32)	7104(3)	10803(2)	8327(1)	22(1)
C(33)	8057(3)	11402(2)	9065(2)	28(1)
C(34)	9259(3)	11006(3)	9331(2)	29(1)
C(35)	9491(3)	10012(2)	8857(1)	26(1)
C(36)	8533(3)	9405(2)	8117(1)	21(1)
P(2)	2696(1)	6455(1)	8015(1)	14(1)
C(41)	2483(3)	4804(2)	7719(1)	16(1)
C(42)	1309(3)	3809(2)	7970(2)	23(1)
C(43)	1247(3)	2581(2)	7765(1)	24(1)
C(44)	2340(3)	2325(2)	7310(2)	30(1)
C(45)	3502(4)	3301(3)	7050(2)	48(1)
C(46)	3556(3)	4527(2)	7247(2)	33(1)
C(51)	3959	6958	9018	17(1)
C(52)	4083(6)	6110(2)	9499(2)	23(1)
C(53)	5022	6563	10257	25(1)
C(54)	5839	7864	10534	22(1)
C(55)	5715	8712	10053	22(1)
C(56)	4775	8259	9296	19(1)
C(51′)	3768	6939	9054	17(1)
C(52′)	3459(7)	6104(3)	9593(2)	24(1)
C(53′)	4327	6492	10368	26(2)
C(54′)	5505	7715	10604	32(2)
C(55′)	5814	8550	10064	22(1)
C(56′)	4946	8162	9289	19(1)
C(61)	710	6292	8282	17(1)
C(62)	−410(3)	6288(3)	7667(2)	22(1)
C(63)	−1969	6158	7822	31(1)
C(64)	−2408	6031	8593	26(1)
C(65)	−1288	6035	9208	29(1)
C(66)	271	6165	9053	21(1)
C(61′)	563	6252	8138	17(1)
C(62′)	−558(4)	5813(4)	7438(2)	25(1)
C(63′)	−2168	5652	7490	28(1)
C(64′)	−2658	5929	8241	26(1)
C(65′)	−1537	6368	8941	26(1)
C(66′)	73	6529	8889	23(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthongalized $\mathbf{U}_{ij}$ tensor.

from each other. Comparison with other structures of the type $HCo_n(PR_3)_{4-n}$, as shown in Table 5, indicates that the Co-H distances determined for **1** lie at the shorter end of the range of values determined for related cobalt hydride complexes. It should be noted, however, that hydrogen positions determined by X-ray diffraction freqently result in short M−H distances.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **1(TBP)** and **1(SP)**

	1(TBP)	**1(SP)**
Co−H	1.37(3)	1.45(4)
Co−C(1)	1.751(3)	1.781(2)[a]
Co−C(2)	1.767(3)[b]	1.755(3)
Co−P(1)	2.185(1)	2.153(1)
Co−P(2)	2.200(1)	2.145(1)
C(1)−O(1)	1.154(4)	1.148(3)
C(2)−O(2)	1.146(3)	1.151(4)
P(1)−C(11)	1.841(3)	1.843(3)
P(1)−C(21)	1.843(2)	1.834(3)
P(1)−C(31)	1.836(2)	1.827(2)
P(2)−C(41)	1.837(3)	1.829(2)
P(2)−C(51)	1.837(2)	1.856(4)
P(2)−C(51′)		1.840(4)
P(2)−C(61)	1.846(2)	1.812(3)
P(2)−C(61′)		1.867(4)
H−Co−C(1)	80(2)	111(1)
H−Co−P(1)	82(2)	72(1)
H−Co−P(2)	83(1)	73(1)
H−Co−C(2)	177(1)	136(1)
C(1)−Co−P(1)	112.6(1)	107.5(1)
P(1)−Co−P(2)	122.6(1)	139.8(1)
P(2)−Co−C(1)	118.8(1)	102.5(1)
C(2)−Co−C(1)	100.2(1)	113.9(1)
C(2)−Co−P(1)	94.9(1)	96.6(1)
C(2)−Co−P(2)	99.5(1)	95.1(1)
Co−C(1)−O(1)	176.5(2)	177.9(2)
Co−C(2)−O(2)	177.1(2)	178.8(2)

[a] Apical Co−C distance. [b] Axial Co−C distance.

Complexes of the type HML_4 (M = Co, Rh, Ir) have received much attention in efforts to understand the role of such species as catalysts in the hydroformylation reaction.[22] A number of groups have investigated the use of chelating diphosphine ligands in controlling the geometry of HML_4 complexes. One might at first anticipate that complexes of the form $HM(P\text{-}P)_2$, where P-P is a bidentate diphosphine, would adopt square pyramidal geometries with the hydride ligand in the axial position. However, crystal structures show that in the solid state complexes of this type tend to adopt distorted TBP coordination geometries with the hydride presumed to be in an equatorial site (for example, see $HRh\{P(C_2F_5)_2CH_2CH_2P(C_2F_5)_2\}_2$,[23] and $HIr(dppe)_2$,[24] dppe = bis(diphenylphosphinoethane)). Presumably, square-pyramidal complexes are disfavored by steric interactions between the phoshine substituents.

Allogons of 5-Coordinate Metal Complexes. A survey of structures of the type HML_4, M= Co, Rh, Ir, revealed only one other complex for which the square-pyramidal and trigonal bipyramidal allogons have been structurally characterized. [HIr-

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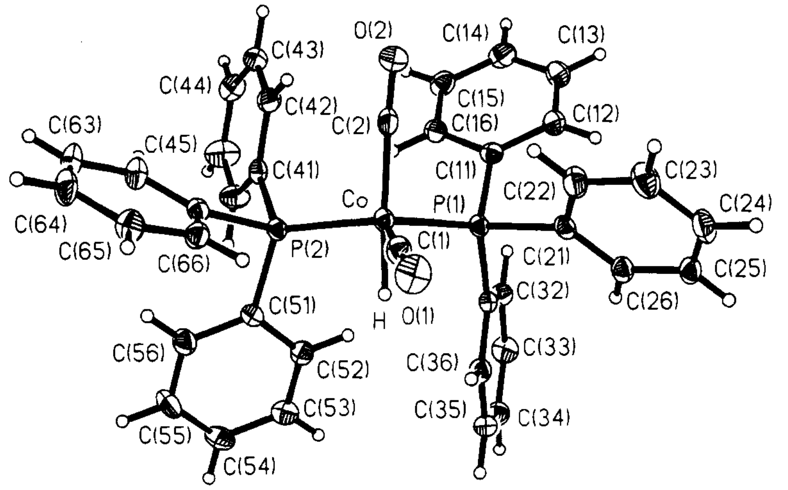

Figure 1. Molecular structure of $[HCo(CO)_2(PPh_3)_2]$, (**1(TBP)**) shown with 50% probability ellipsoids for non-hydrogen atoms. Hydrogen atoms are represented by spheres of arbitrary radius.

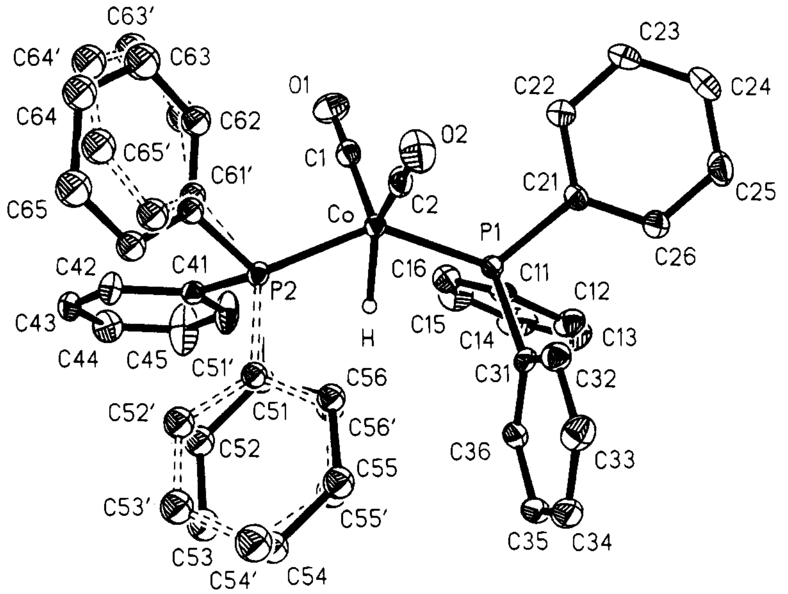

Figure 2. Molecular structure of $[HCo(CO)_2(PPh_3)_2]$ (**1(SP)**) shown with 50% probability ellipsoids for non-hydrogen atoms. The minor orientations for the disordered phenyl rings are represented by dashed lines. Phenyl hydrogen atoms are not shown, and the hydride hydrogen atom is represented by a sphere of arbitrary radius.

$(NO)(PPh_3)_3]ClO_4$ has been reported to exist in three crystalline forms (green, brown, and black) which exhibit different vibrational frequencies for the nitrosyl stretching vibration.[25] The structures of the black and brown forms have been determined and exhibit approximately TBP[26] and SP geometries,[27] respectively. The hydride ligand was not located in either of these structures, but the coordination geometry can be inferred from the other interligand angles. The TBP (black) form clearly has the (larger) phosphine ligands in the equatorial positions, which places the nitrosyl and hydride ligands trans to each other in the axial positions. Waters and co-workers describe the structure of the brown form of $[HIr(NO)(PPh_3)_3]ClO_4$ as exhibiting a distorted TBP coordination geometry with two phosphine ligands in the axial positions.[27] However, the angle between the two "axial" ligands is 141.6(2)° indicating that the distortion is a very large one. It seems that a better description of the coordination geometry would be square-pyramidal, with the nitrosyl ligand in the axial position, and the "missing" hydride occupying the basal vertex opposite from P(2), i.e., a geometry similar to that of **1(SP)**. Of course, it is well known that for many 5-coordinate transition metal complexes, there is only a small difference between the thermodynamic stability of the TBP and SP coordination geometries, and furthermore often only a small energy barrier to interconversion.[28] Indeed, in some cases, the energy differences are small enough that in the solid state packing forces can have a significant effect upon the preferred geometry.

In solution, an equilibrium typically exists between different TBP and SP isomers which interconvert rapidly. ^1H NMR spectra for **1** in acetone-d_6 solution show a triplet in the hydride region, δ −10.47 with $^2J_{PH}$ 40.6 Hz at 293 K, which persists with little variation over the temperature range 193−293 K (data at 193 K are δ −10.10 with $^2J_{PH}$ 41.7 Hz.). Spectra taken in toluene-d_8 over the same temperature range show no significant difference from the acetone spectra. These spectra are of course consistent with either a static TBP geometry or a static SP geometry as long as the two phosphine ligands occupy equivalent sites. However, the most probable explanation is a

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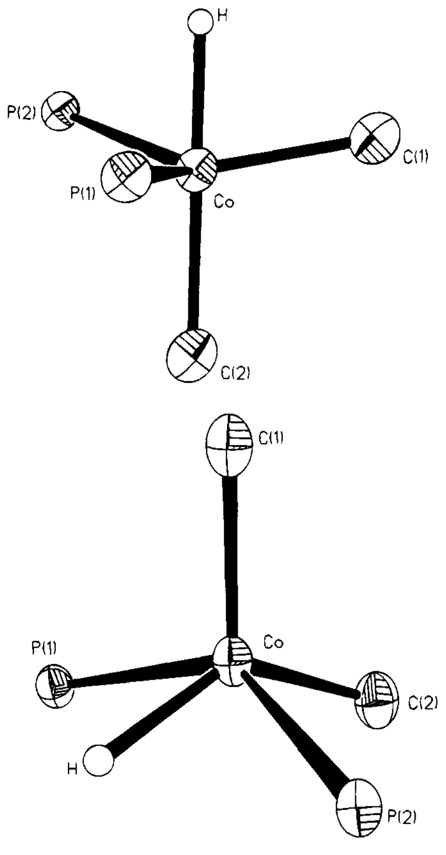

Figure 3. Core geometries of **1(TBP)** and **1(SP)**.

Table 5. Comparison of Geometries of $[HCo(L)_n(PR_3)_{4-n}]^{m+}$ Structures ($n = 0-4$, $m = 0, 1$) Determined by X-ray Diffraction

complex	Co–H separation (Å)	CSD REFCODE[a]	ref
$[HCo(CO)_2(PPh_3)_2]$ (TBP form)	1.37(3)	this work	
$[HCoN(CH_2CH_2PPh_2)_3]{\cdot}C_4H_8O$	1.38[b]	PPEHCO	9
$[HCo\{PPh(OEt)_2\}_4]$	1.38(54)[c]	HEPPCO	10
$\{HCo(CO)(PPh_3)_3]$	1.41(9)	CAHCOP	6
$[HCo(NCBH_3)(PPh_3)_3]$[d,e]	1.42	BOBMEK10	8
$\{HCo(dppp)_2]{\cdot}C_6H_6$	1.42(3)	DOBNIR	11
$[HCo(CO)_3(PCy_3)]$	1.43(3)	VAFDIP	12
$[HCoP(CH_2CH_2PPh_2)_3]{\cdot}Me_2CO$	1.43(6)	COHPPP	13
$[HCo(CO)_2(PPh_3)_2]$ (SP form)	1.45(4)	this work	
$[HCoN(CH_2CH_2PPh_2)_3]$	1.45(5)	HPAMCO10	14
$[HCoP(CH_2CH_2PPh_2)_3]BPh_4$[d]	1.53	HPEPCO	15
$[HCo(PMe_3)_3]_2(\mu\text{-}N_2)$	1.56[a]	VIJDUN	16
$[HCo(CO)_4]$	1.56(3)	*f*	17
$[HCoP(o\text{-}C_6H_4PPh_2)_3]$	1.60(16)	HPHPCO10	18
$[HCo(CO)(PPh_3)_3]{\cdot}Et_2O$	1.64[g]	CUCHAJ	19
$[HCo(N_2)(PPh_3)_3]$	1.64(11), 1.67(12)	PPHCHN10	7
$[HCo(N_2)(PPh_3)_3]{\cdot}Et_2O$	*h*	COTTPP	20
$[HCo(PEt_3)\{(PPh_2CH_2)_3\text{-}CCH_3\}]BPh_4$[c]	1.71(10)	FEYCUH	21

[a] Reference code for the Cambridge Structural Database (see: Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.*, **1983**, *16*, 146). [b] Hydrogen position not refined; distance from CSD listed. [c] Hydride hydrogen located from Fourier map at 1.54 Å from Co; authors suggest that this a more reasonable Co–H distance than that obtained from refinement of the hydrogen position. [d] Cobalt is in oxidation state (II). [e] Geometry is closer to SP than TBP. [f] Structure determined by electron diffraction study. [g] Treatment of hydride hydrogen unknown; distance from CSD is listed. [h] Hydride ligand not located, but geometry is confirmed as TBP as in the unsolvated structure (PPHCHN10).

rapid equilibrium between various TBP and SP geometries. The pathways for interconversion between these geometries have been the subject of much attention. Auf der Heyde has recently reviewed the many studies of the pathways for ligand and geometry interconversion, and for ligand substitution, involving five-coordinate metal complexes.[29] The review focuses on the application of the Structure Correlation Method[30] to this problem as well as drawing comparisons with results of theoretical calculations.

Perhaps the most obvious comparison with the structure(s) of $HCo(CO)_2(PPh_3)_2$ which should be sought is that with the congeners $HRh(CO)_2(PPh_3)_2$ and $HIr(CO)_2(PPh_3)_2$. Although both complexes are known, the structure of only the latter has been reported. It is interesting to note that three crystalline forms (one orthorhombic and two monoclinic) of $HIr(CO)_2(PPh_3)_2$ have been reported as arising from a *single* solution.[31] The structure of only the orthorhombic form has been determined.[31] Although this form of $HIr(CO)_2(PPh_3)_2$ exhibits a TBP coordination geometry, it differs from that of **1(TBP)** in that a phoshine (rather than a carbonyl) ligand lies *trans* to the hydride in an axial position (P–Ir–H = 175°). It would of course be interesting to see whether the monoclinic crystalline forms consist of a different TBP isomer or an SP allogon. In this regard it is interesting to note that the two monoclinic unit cells have volumes which are respectively 0.5% smaller and 1.5% larger than that of the orthorhombic unit cell at 295 K. For comparison, the unit cell of **1(SP)** is 2.0% larger than of **1(TBP)** at 123 K. However, one should not jump to the conclusion that the molecular volume (and by implication the resultant unit cell volume) should be larger for the square-pyramidal allogon. Presumably the disorder in **1(SP)** resulting from more than one conformation of one PPh_3 ligand is associated with an increased effective molecular volume.

Other examples of five-coordinate metal complexes which exist as TBP and SP allogons have been isolated and crystallographically characterized. However, the structures of $HCo(CO)_2(PPh_3)_2$ are the first examples of two allogons that have been crystallized separately and whose geometries do not arise from an interaction with other species that are also present in the crystal structure. For example, crystalline tris(ethylenediamine)chromium(III) pentacyanonickelate(II) sesquihydrate, $[Cr(en)_3][Ni(CN)_5]{\cdot}1.5H_2O$, contains both square-pyramidal and slightly distorted trigonal bipyramidal $Ni(CN)_5^{3-}$ anions.[32] Both types of anion are involved in hydrogen bonding to water molecules in the structure. The low spin d^7 complex $[Co(dppe)_2Cl]^+$ cation crystallizes in two forms as its trichlorostannate(II) salt. The green form contains TBP cations and the red form contains SP cations.[33] However, the green form also differs from the red form in that it contains one molecule of chlorobenzene per cation.

Allogons of Metal Complexes with Other Coordination Numbers. The formation of allogons is not confined to the five-coordinate metal complexes. In fact it is perhaps better documented in tetracoordinate metal complexes. In a series of papers Venanzi and co-workers examined the effect of varying the ligands attached to 4-coordinate Ni(II) complexes upon the magnetic moment of the complex in solution.[34] From these measurements, inferences about the nickel coordination geometry could be made based on the fact the d^8 Ni(II) metal centers should be paramagnetic with two unpaired electrons when situated in a tetrahedral ligand field and diamagnetic when situated in a square planar ligand field. Their work also

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suggested that individual allogons might be isolated in the solid state. The study of structures of four-coordinate Ni(II) complexes will be the subject of the next paper in this series.[35]

Conclusions

X-ray crystal structures of both the trigonal bipyramidal and square pyramidal forms of $HCo(CO)_2(PPh_3)_2$ have been determined. This is the first example we are aware of in which two allogons of a neutral five coordinate metal complex have been structurally characterized. Neither structure contains solvent of crystallization. This suggests that packing forces between the $HCo(CO)_2(PPh_3)_2$ molecules are sufficient to cause the molecules to favor one geometry or the other. Hence the diffence in energy between the two molecular geometries is presumably very small.

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Supplementary Material Available: Tables of crystallographic data, positional and anisotropic displacement parameters, and interatomic distances and angles (16 pages). Ordering information is given on any current masthead page.

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