The Crystal and Molecular Structure of Hydridotetrakis(diethyl phenylphosphonite)cobalt(I)†

By D. D. TITUS, A. A. ORIO,‡ R. E. MARSH, and HARRY B. GRAY*
(*Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California* 91109)

Summary An *X*-ray structure determination of the title compound shows that the co-ordination about the cobalt atom is approximately trigonal bipyramidal; n.m.r. data indicate that the complex is non-rigid in solution.

THE syntheses and n.m.r. spectra of $HCo[(PhO)_3P]_4$[1] and $HCo[(EtO)_3P]_4$[2] have been reported. Although $HCo[(EtO)_3P]_4$ has been assigned a square-pyramidal configuration on the basis of a temperature-independent high-field quintet,[2] the possibility of a distorted trigonal bipyramidal structure with a very low intramolecular rearrangement barrier is attractive.[1] We have found the latter possibility in the case of an analogous complex, $HCo[(Ph)P(OEt)_2]_4$, and report its preparation and structural characterization.

A mixture of cobaltous chloride, diethyl phenylphosphonite, and ethanol was treated with a concentrated ethanolic solution of sodium borohydride. After filtration, orange-yellow holohedral prisms separated from the solution (80% yield).

In the i.r. spectrum ν(Co–H) is observed as a weak band at 2017 cm^{-1} (Nujol mull). At room temperature, the high-field n.m.r. spectrum (methylcyclohexane solution) consists of a quintet (τ 24·5) with intensity ratios 1 : 4 : 6 : 4 : 1. At $-55°$, however, only a single broad band is observed (τ 24·5). The change in the spectrum at low temperature is consistent with a non-rigid model for the molecule.

Crystal data: $HCo[(Ph)P(OEt)_2]_4$; $M = 850$; triclinic; $a = 11{\cdot}932(2)$; $b = 12{\cdot}841(2)$; $c = 17{\cdot}680(2)$ Å; $\alpha = 95{\cdot}50(1)$; $\beta = 89{\cdot}75(1)$; $\gamma = 123{\cdot}09(1)°$; $U = 2255 \pm 1$ Å^3, $D_c = 1{\cdot}25$; $Z = 2$; space group $P\bar{1}$.

Intensities of 4294 independent reflections were recorded on a Datex-automated General Electric diffractometer, using Co-K_α radiation. The non-hydrogen atoms were located by Patterson and Fourier techniques, and least-squares refinements of the atomic parameters were carried out with all atoms vibrating anisotropically. The ethyl and phenyl hydrogen atoms were then positioned according to their known geometries. A difference Fourier map was calculated and the ligand hydrogen atom was observed as the most prominent feature of the map (0·36 e^-/Å^3), 1·54 Å from the cobalt atom. Positional parameters for the ligand hydrogen atom were refined in two subsequent cycles of least-squares refinement, yielding a position somewhat closer to the cobalt atom (Co–H 1·38 Å). As *X*-ray studies classically yield short bond lengths when hydrogen atoms are involved, the true internuclear distance is probably closer to the 1·54 Å distance derived from the difference Fourier parameters. At the end of the refinement, R stood at 0·050.

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† This research was supported by the National Science Foundation.

‡ On leave of absence from the Istituto di Chimica Generale, University of Padova.

The inner co-ordination sphere about the cobalt atom is represented in the Figure. Selected bond distances and angles are given in the Table. The configuration of the ligands about the cobalt atom is roughly trigonal bipyramidal, with the cobalt atom positioned 0·492 Å out of the equatorial plane defined by P(1), P(2), and P(3). Although the four phosphorus atoms are arranged nearly tetrahedrally the hydride ligand occupies a specific co-ordination site. A recent *X*-ray study of $HCo(PF_3)_4$ failed to give the hydrogen atom position, although a slight distortion of the CoP_4 structure from tetrahedral symmetry indicates that in this case also the hydrogen atom occupies a specific co-ordination site.[3] These observations are of interest in view of the fact that in *X*-ray structural studies of $HRh(PPh_3)_4$[4] and $HRh(PPh_3)_3(AsPh_3)$[5] a specific co-ordination position for the hydrogen atom could not be established.

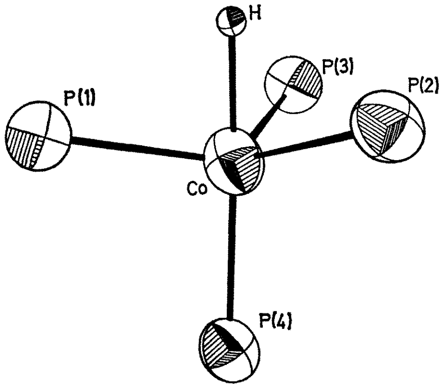

FIGURE. *The inner co-ordination sphere of the cobalt atom in* $HCo[(Ph)P(OEt)_2]_4$.

The approximately tetrahedral disposition of the four phosphorus ligands suggests strongly that the barrier to intramolecular rearrangement *via* a tetrahedral CoP_4 transition state would be extremely low. Presumably, in the transition state the hydrogen could tunnel between triangular face (edge) positions. The n.m.r. data require the barrier to be lower for $HCo[PhO)_3P]_4$ and $HCo[(EtO)_3P]_4$ than it is for $HCo[(Ph)P(OEt)_2]_4$, which implies that the solution ground-state CoP_4 geometries of the former two complexes are closer to a tetrahedral configuration.

TABLE

Bond distances		Bond angles	
Co–P(1)	2·115(2) Å	P(1)–Co–P(2)	124.1(1)°
Co–P(2)	2·103(2)	P(1)–Co–P(3)	115·4(1)
Co–P(3)	2·126(1)	P(1)–Co–P(4)	97·8(1)
Co–P(4)	2·128(1)	P(2)–Co–P(3)	104·5(1)
Co–H	1·38(54)[a]	P(2)–Co–P(4)	108·4(1)
		P(3)–Co–P(4)	104·9(1)
		P(4)–Co–H	173·5(2·0)

[a] See text.

There appear to be significant differences in the cobalt–phosphorus bond distances for $HCo[(Ph)P(OEt)_2]_4$, as was also noted previously in the case of $HCo(N_2)(PPh_3)_3$.[6] The Co–P bond distances in the present work are 0·06 to 0·10 Å shorter than those in $HCo(N_2)(PPh_3)_3$, consistent with the greater π-bonding capabilities of the $(Ph)P(OEt)_2$ ligand. The π-acceptor character of $(Ph)P(OEt)_2$, however, does not appear to match that of PF_3; the average Co–P distance in $HCo(PF_3)_4$ has been found[3] to be 2·052(5) Å.

(*Received, December 7th,* 1970; *Com.* 2119.)

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