Paramagnetic Hydrido-complexes of Cobalt(II)

By **J. Roger Sanders,** Department of Chemistry, The University, Hull HU6 7RX

The preparation and characterisation of some hydrido-complexes of cobalt(II) of formula $[CoHL_4]^+X^-$ [L = $P(OEt)_2Ph$, $P(OMe)_2Ph$, or $P(OPh)_3$; X = PF_6 or BF_4] are described.

THIS paper describes some complexes of cobalt(II) with the general formula $[CoHL_4]^+X^-$ [L = $P(OEt)_2Ph$, $P(OMe)_2Ph$, or $P(OPh)_3$; X = PF_6 or BF_4], which are prepared by the reaction of the appropriate cobalt(I) hydride $CoHL_4$ with a stoicheiometric quantity of the appropriate triphenylmethyl (trityl) salt.

These complexes are green solids which are soluble in dichloromethane, nitromethane, and acetone, but insoluble in benzene or ether. They are almost instantly destroyed on exposure to air while in solution, and deterioration of the solids is noticeable after a few minutes exposure. Those compounds which contain $P(OMe)_2Ph$ ligands are especially unstable to air, and the tetrafluoroborate salts are less stable than their hexafluorophosphate analogues.

Conductivity measurements suggest that these compounds are 1 : 1 electrolytes in nitromethane solution and therefore contain monomeric cations. To confirm this, values of $\Lambda_0 - \Lambda_M$ for $[CoH\{P(OEt)_2Ph\}_4]^+BF_4^-$ were determined at concentrations over the range 10^{-4}—10^{-2}M.[1] The complexes have magnetic moments in the solid state with values corresponding to the presence of one unpaired electron, and measurements on $[CoH\{P(OEt)_2Ph\}_4]^+PF_6^-$ dissolved in dichloromethane suggest that this low-spin state is maintained in solution.

The presence of a hydride ligand in these compounds cannot be inferred from their elemental analyses because of the large number of hydrogen atoms in the other ligands. As the compounds are paramagnetic, their ^1H n.m.r. spectra show only broadened absorptions which may be assigned to the phosphorus ligand protons, and no absorption which may be assigned to a hydrogen bound to cobalt. The i.r. spectra of some complexes in the solid state and in solution show a weak absorption band in the 2000—1900 cm^{-1} region which may be tentatively assigned to ν(Co–H). It is noticeable that this band is absent from the spectra of the salts which contain $P(OPh)_3$ ligands; no band which may be assigned to ν(Co–H) has been found in the spectrum of $[CoH\{P(OPh)_3\}_4]$.[2]

The presence of a hydride ligand in these salts is confirmed by their reaction with the non-hydridic reducing agent sodium amalgam to give the corresponding cobalt(I) hydrides $CoHL_4$. The hydride $[CoH\{P(OPh)_3\}_4]$ may be isolated in almost 100% yield from this reaction; smaller yields of the other cobalt(I) hydrides were obtained, as they are much more soluble in non-polar solvents.

The presence of a hydride ligand in $[CoH\{P(OEt)_2Ph\}_4]^+PF_6^-$ is also confirmed by its reaction with carbon tetrachloride under mild conditions, when *trans*-$[CoHCl\{P(OEt)_2Ph\}_4]^+PF_6^-$ is produced in 80% yield. This compound is a yellow air-stable solid which has a 1 : 4 : 6 : 4 : 1 quintet absorption at τ 32·50 (J_{PH} 59 Hz) in its n.m.r. spectrum which may be assigned to the hydrogen bound to cobalt.

DISCUSSION

Trityl salts have been used to remove a hydride ligand as H^- from $[RuH_2(PPh_3)_4]$[3] and also to remove hydride anions from hydrocarbon ligands in π-complexes of various transition metals.[4] It was thought that the reaction of the hydrides $CoHL_4$ with trityl salts would produce salts containing the four-co-ordinate $[CoL_4]^+$ cations which might undergo oxidation–addition reactions like the cation $[Co(Ph_2PCH_2CH_2PPh_2)_2]^+$.[5] Instead, the trityl cation acts as a one-electron oxidising agent towards the hydrides $CoHL_4$ and does not cleave the cobalt–hydrogen bond. The Co–H bond in $[CoH\{P(OPh)_3\}_4]$ is known to be extremely inert compared to most transition-metal–hydrogen bonds: no data are available on the reactivity of the Co–H bonds in the other two cobalt(I) hydrides.

Several complexes containing five-co-ordinate cobalt(II) cations are known. Those which have ligands with highly electronegative donor atoms like N, O, Cl, are high spin, while those containing ligands with phosphorus donor atoms are usually low spin with one unpaired electron.[6,7] The low spin character of the cobalt(II) complexes described in this paper, which contain one hydride and four phosphorus ligands, fits into this pattern. Both trigonal-bipyramidal and square-pyramidal shapes have been found for five-co-ordinate low-spin cobalt(II) cations, but all *X*-ray studies on five-co-ordinate transition-metal species containing one hydride and four phosphorus ligands have shown them to have a shape of a distorted trigonal bipyramid with the hydride ligand axial and the equatorial phosphorus ligands displaced towards it.[8] It seems likely that the cations of the salts described here have this shape also.

Hydride complexes of transition metals usually react with carbon tetrachloride to replace a hydride ligand with a chloride ligand, although vigorous conditions are some-

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times needed, *e.g.* with $[CoH\{P(OPh)_3\}_4]$.[2] The reaction between $[CoH\{P(OEt)_2Ph\}_4]^+PF_6^-$ and CCl_4 where the Co–H bond is untouched is therefore unusual. However, unlike all other transition metal hydrides so far reported, the compounds $[CoHL_4]^+X^-$ are paramagnetic with a 17-electron cation, and the reaction with CCl_4 converts this into an 18-electron cation. The conditions used are too mild to allow further reactions to occur.

EXPERIMENTAL

Preparations were carried out under argon in dried solvents. Compounds were dried and decomposition points measured *in vacuo*. Microanalyses, conductivities, and spectral measurements were carried out as described.[3] Magnetic susceptibilities were measured by the Gouy method and corrected for the diamagnetic contribution by measurements on the hydrides $CoHL_4$ and calculations of the diamagnetic susceptibilities for PF_6^- and BF_4^- anions.

Analytical and other data

Compound	Found (required)			Decomp. point	$\Lambda_{0·001}$ [a]	$\mu_{eff.}$ B.M.	ν(Co–H) [b]
	C	H	P				
$[CoH\{P(OEt)_2Ph\}_4]^+PF_6^-$	47·8 (48·2)	5·9 (6·0)	14·5 (15·6)	191—192	69	2·04	1947m
$[CoH\{P(OEt)_2Ph\}_4]^+BF_4^-$	51·0 (51·2)	6·2 (6·4)	11·8 (13·2)	172—175	70	2·12	1940w
$[CoH\{P(OMe)_2Ph\}_4]^+PF_6^-$	42·9 (43·4)	5·5 (5·6)		182—184	75	2·4 [c]	1951m
$[CoH\{P(OMe)_2Ph\}_4]^+BF_4^-$	45·7 (46·5)	5·4 (5·3)		132—135	60	*d*	1935w
$[CoH\{P(OPh)_3\}_4]^+PF_6^-$	60·3 (59·8)	4·2 (4·2)		143—146	89	1·96	*e*
$[CoH\{P(OPh)_3\}_4]^+BF_4^-$	61·4 (62·3)	4·6 (4·3)		110—111	67	2·19	*e*
trans-$[CoHCl\{P(OEt)_2Ph\}_4]^+PF_6^-$	46·0 (46·4)	6·0 (5·9)	15·1 (15·0)	124—127	78		1979m

[a] In ohm^{-1}, in $MeNO_2$ at 20°. [b] In cm^{-1}, as Nujol mulls. [c] The high value is probably due to partial decomposition of the sample during packing. [d] The crystals of this compound were too sticky to be packed in a reproducible way. [e] See text. [f] Also analysed for Cl: 3·6 (3·4%).

The Table gives analytical and other data for all new compounds.

Hydridotetrakis(diethoxyphenylphosphine)cobalt(II) *Hexafluorophosphate.*—$[CoH\{P(OEt)_2Ph\}_4]$ [9] (4·25 g) was added to Ph_3CPF_6 (1·95 g) in dichloromethane (10 ml). A dark green colour developed immediately. Ether was added to precipitate a green solid which was recrystallised in 70% yield from dichloromethane–ether and dried overnight at 100°.

The other cobalt(II) salts were prepared by the same method, but in lower yields (50—60%).

trans-*Hydridochlorotetrakis(diethoxyphenylphosphine)-cobalt*(III) *Hexafluorophosphate.*—Carbon tetrachloride (2 ml) was added to $[CoH\{P(OEt)_2Ph\}_4]^+PF_6^-$ (1·6 g) in dichloromethane (4 ml) at 20°. No change in colour was seen. After 3 h ether was added giving a yellow precipitate which was recrystallised from dichloromethane–ether in 80% yield, and dried overnight at 75°.

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