Oxidation Reactions of Hydridotetrakis(diethoxyphenylphosphine)cobalt(II) Hexafluorophosphate: Preparation of Cationic Hydridocobalt(III) Complexes.

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The cobalt(II) hydride $[CoH\{PPh(OEt)_2\}_4][PF_6]$ is oxidised by $[Fe(\eta\text{-}C_5H_5)_2]^+$ in the presence of potential ligands L [MeCN, PhCN, $ClCH_2CN$, or $PPh(OEt)_2$] giving a series of cobalt(III) hydrides $[CoH\{PPh(OEt)_2\}_4L][PF_6]_2$, the first known cobalt complexes containing hydride or phosphorus ligands to carry a 2+ charge. Replacement of an aqua-ligand in an imperfectly characterised complex, possibly $[CoH(OH_2)\{PPh(OEt)_2\}_4][PF_6]_2$, by halide ions gives another series of Co^{III} complexes, $[CoH\{PPh(OEt)_2\}_4X][PF_6]$ (X = Cl, Br, or I).

The preparation of the paramagnetic cobalt(II) salt $[CoH\{PPh(OEt)_2\}_4][PF_6]$ and of similar salts with other phosphorus ligands, by one-electron oxidation reactions of cobalt(I) hydrides, have been described in a previous paper.[1] These complexes are some of the first paramagnetic transition-metal hydrides to be characterised.[2] This paper reports the results of attempts to oxidise $[CoH\{PPh(OEt)_2\}_4][PF_6]$ to Co^{III} species, using as oxidant ferrocenium hexafluorophosphate, $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$.

RESULTS

The cobalt(II) hydride did not react with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in dry dichloromethane or nitromethane. When an equivalent quantity of a potential two-electron ligand L was added the iron salt dissolved and the solution became yellow. The salts $[CoH\{PPh(OEt)_2\}_4L][PF_6]_2$ [L = MeCN, PhCN, $ClCH_2CN$, and $PPh(OEt)_2$] were isolated from these solutions: they are yellow air-stable diamagnetic solids, soluble in chlorinated solvents, acetone, and nitromethane, and insoluble in diethyl ether or light petroleum. They are the first known complexes of cobalt with hydride or phosphorus ligands to carry a 2+ charge.

When pyridine was used as a potential ligand an oil which could not be crystallised was isolated from the reaction mixture; when triphenylphosphine or pent-1-ene was used no reaction occurred. In the latter case no isomerisation of the olefin to pent-2-enes was observed. When carbon monoxide was used the five-co-ordinate complex $[Co(CO)\{PPh(OEt)_2\}_4][PF_6]$ was isolated; in this case, formal reduction in the oxidation state of the cobalt atom takes place. Unsuccessful attempts were made to decarbonylate this complex to produce the unknown $[Co\{PPh(OEt)_2\}_4][PF_6]$ by heating it in alcohols, as with $[Ir(CO)(dppe)_2][BF_4]$ [dppe = 1,2-bis(diphenylphosphino)ethane],[3] and to reoxidise it to a Co^{II} compound with more $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$. An analogous carbonylcobalt(I) complex with two dppe ligands has been prepared by a different route.[4]

The salt $[CoH\{PPh(OEt)_2\}_4][PF_6]$ and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ reacted in the presence of trace amounts of water giving a yellow material whose nature is discussed below. This material reacted in dichloromethane with the potential ligands L to give the Co^{III} complexes listed above, and with alkali-metal halides in alcohols giving another series of complexes of formula $[CoH\{PPh(OEt)_2\}_4X][PF_6]$ (X = Cl, Br, or I). The chloride of this series has been described [1] and the bromide and iodide may be prepared by oxidation of $[CoH\{PPh(OEt)_2\}_4][PF_6]$ with bromoform or iodine. Attempts to prepare similar complexes with X =

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H, PPh_2, or L-cysteinate by oxidation of $[CoH\{PPh(OEt)_2\}_4][PF_6]$ with hydrogen, tetraphenyldiphosphane, and L-cystine failed, no reaction taking place.

All of the complexes described above may also be prepared from $[CoH\{PPh(OEt)_2\}_4]$ by treating it with two equivalents of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ and one equivalent of L or X^-. When the hydride was treated with one equivalent only of the Fe^{III} salt it gave $[CoH\{PPh(OEt)_2\}_4][PF_6]$.

The complexes described above have been characterised by analyses, conductivity measurements, and spectral studies. The data obtained from conductivity measurements (including determinations of the molar conductivity of the salts at various concentrations [5]) clearly distinguish between 1 : 1 and 2 : 1 electrolytes. The i.r. spectra of the salts with nitrile ligands showed bands assignable to ν(C–N) and that of $[Co(CO)\{PPh(OEt)_2\}_4][PF_6]$ showed a strong band assignable to ν(C–O) at 1 945 cm^{-1}. Spectra of complexes with hydride ligands show bands due to ν(Co–H): in the case of complexes with doubly charged cations these are weak or not observed as in the case of the isoelectronic iron complexes (with different phosphorus ligands) studied by Bancroft.[6]

The ^1H n.m.r. spectra of these complexes showed signals due to protons on the phosphorus and nitrile ligands when these are present. The spectra of the hydrides also showed a 1 : 4 : 6 : 4 : 1 signal due to the proton bound to cobalt, which establishes that it is *cis* to four equivalent phosphorus ligands and hence *trans* to L or X. No signal due to the proton on cobalt in $[CoH\{PPh(OEt)_2\}_5][PF_6]_2$ (which should be a double quintet) could be seen; the other resonances in this spectrum were slightly broadened possibly due to paramagnetic impurities, and the signal due to the hydride proton was presumably so broadened that it was not detected.

The i.r. spectrum of the material obtained from the reaction of $[CoH\{PPh(OEt)_2\}_4][PF_6]$ with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in the presence of water (which may be called the aqua-material) showed two bands at 3 570 and 3 485 cm^{-1} which may be assigned to ν(O–H) of an aqua-ligand. When D_2O was used instead of H_2O in the preparation of this material the spectrum showed bands at 2 650 and 2 555 cm^{-1} which may be assigned to ν(O–D) of a D_2O ligand, so that ν(O–H)/ν(O–D) is 1.35 for the higher-frequency band and 1.36 for the other band. The n.m.r. spectrum of the aqua-material showed a signal of intensity 1 : 10 relative to that due to the 20 Ph protons of the phosphorus ligands: this signal was absent in the spectrum of the deuteriated material and may be assigned to the two protons of an aqua-ligand. In view of these measurements and of analytical and conductivity data, it is tempting to assign the structure $[CoH(OH_2)\{PPh(OEt)_2\}_4][PF_6]_2$ to this material which would make it the only complex known containing hydride, aqua-, and phosphorus ligands.

However, no evidence of the presence of a hydride ligand was found in the n.m.r. spectrum of this material, even though it is diamagnetic and the spectrum was examined at −90 °C. The only evidence that this material is a hydride is that it reacts with ligands L in dichloromethane to give $[CoH\{PPh(OEt)_2\}_4L][PF_6]_2$ in which the presence of a hydride ligand is clearly established. In an attempt to determine whether a signal due to a hydride proton in the spectrum of the aqua-material is broadened due to exchange between this proton and protons of the aqua-ligand, equal quantities of the aqua- and D_2O materials were treated in n.m.r. tubes with acetonitrile in dichloromethane. The signal due to the hydride proton in $[CoH(NCMe)\{PPh(OEt)_2\}_4][PF_6]_2$ was in each case of intensity 1 : 20 relative to that of the Ph protons. This suggests that no exchange of the kind described above takes place. Conductivity data appear to rule out the possibility that a dissociation of the ion $[CoH(OH_2)\{PPh(OEt)_2\}_4]^{2+}$ to $[Co(OH_2)\{PPh(OEt)_2\}_4]^+$ and a solvated proton is occurring. No evidence of either intramolecular proton exchange or dissociation has been found in studies of the only known metal hydride containing an aqua-ligand, $[RhH(NH_3)_4(OH_2)][SO_4]$, and in the spectrum of this complex the signal due to the proton bound to rhodium is in the usual range for signals due to hydride ligands.[7] It must therefore be concluded that the assignment of any structure containing a hydride proton to the aqua-material is extremely tentative.

DISCUSSION

Several Fe^{II} complexes of formulae $[FeH(X)Z_4]$ or $[FeH(L)Z_4]^+$ (X = Cl, Br, I, or SCN; L = N_2, CO, phosphorus ligand, nitrile, or isonitrile; Z = phosphorus ligand) have been prepared. Some of these are isoelectronic with the Co^{III} complexes described in this work (though with different Z ligands) but bear a lower positive charge. Most of these Fe^{II} complexes have been prepared by ligand-replacement reactions involving no change in the oxidation state of the iron atom, but very recently the iron(I) hydride $[FeH(dppe)_2]$ was oxidised to Fe^{II} and Fe^{III} cationic complexes by trityl or silver(I) perchlorate.[8] These reactions are very similar to those reported in the present work; it is noticeable that the $[FeH(dppe)_2]^+$ system is able to accept N_2 and CO ligands while the isoelectronic but more highly charged $[CoH\{PPh(OEt)_2\}_4]^{2+}$ system cannot accept an N_2 ligand and in accepting a CO ligand is converted into a cation of a lower oxidation state of cobalt.

The use of the ferrocenium cation as a one-electron oxidant in a non-polar solvent has the advantage over Ag^+ in that its reduction product, ferrocene, is fairly inert and readily soluble in all organic solvents. The same advantages may be claimed for the trityl cation, but its use was avoided in the present work because it is potentially capable of abstracting hydride ions from metal complexes.[9]

EXPERIMENTAL

Preparations were carried out under N_2 in dried solvents. Microanalyses, conductivity measurements, and spectroscopic studies were carried out as described.[1] The Table gives analytical and other data for all the new complexes.

Ferrocenium Hexafluorophosphate.—Ferrocene (1.86 g) in dichloromethane was added to triphenylmethyl hexafluorophosphate (3.88 g) also in dichloromethane. Dark blue crystals formed immediately in >90% yield and were filtered off and washed with dichloromethane and diethyl ether.

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Analytical and spectroscopic data

Complex	Analysis [a]/%			Decomposition temperature (θ_c/°C)	Λ [b] S mol^{-1}	$\tilde{\nu}$(Co–H) [c] cm^{-1}	τ(Co–H) [d]	J_{PH} Hz
	C	H	Other					
$[Fe(\eta\text{-}C_5H_5)_2][PF_6]$	36.2	3.0		>250				
	(36.3)	(3.0)						
trans-$[CoH(NCMe)\{PPh(OEt)_2\}_4][PF_6]_2$	42.6	5.1	N 1.3	125—127	146	1 990vw	29.23	53
	(42.6)	(5.3)	(1.2)					
trans-$[CoH(NCPh)\{PPh(OEt)_2\}_4][PF_6]_2$	45.1	5.4	N 1.2	127—128	149	1 990vw	28.57	49
	(45.3)	(5.4)	(1.1)					
trans-$[CoH(NCCH_2Cl)\{PPh(OEt)_2\}_4][PF_6]_2$	41.9	5.5	N 1.0	105—106	160	1 995vw	28.78	51
	(41.5)	(5.1)	(1.1)					
$[CoH\{PPh(OEt)_2\}_5][PF_6]_2$	44.3	5.5	P 16.2	97—98	141	1 968m	*e*	*e*
	(44.7)	(5.7)	(17.0)					
trans-$[CoH(OH_2)\{PPh(OEt)_2\}_4][PF_6]_2$ [f]	41.6	5.7	P 12.5	97—99	148	*e*	*e*	*e*
	(41.5)	(5.5)	(16.0)					
$[Co(CO)\{PPh(OEt)_2\}_4][PF_6]$	47.9	5.8	P 15.7	193—194	76			
	(48.0)	(6.0)	(15.1)					
trans-$[CoBr(H)\{PPh(OEt)_2\}_4][PF_6]$	44.5	5.6	Br 7.4	119—121	74	1 994m	29.50	60
	(44.7)	(5.7)	(7.4)					
trans-$[CoH(I)\{PPh(OEt)_2\}_4][PF_6]$	42.3	5.4	I 11.3	132—133	76	1 978m	26.30	55
	(42.5)	(5.4)	(11.3)					

[a] Calculated values are given in parentheses. [b] For 10^{-3}M solutions in $MeNO_2$ at 20 °C. [c] In Nujol mulls. [d] In CH_2Cl_2. [e] See text. [f] Assumed structure (see text).

trans-*(Acetonitrile)tetrakis(diethoxyphenylphosphine)hydridocobalt*(III) *Hexafluorophosphate.*—Ferrocenium hexafluorophosphate (0.57 g) and acetonitrile (0.07 g) were added to $[CoH\{PPh(OEt)_2\}_4][PF_6]$ (1.70 g) in dichloromethane (5 cm^3) giving a clear yellow solution. Diethyl ether was added giving an oil which solidified on shaking and was recrystallised in 70% yield from dichloromethane–methanol by gradual addition of diethyl ether. Similar procedures were used to prepare complexes containing benzonitrile, chloroacetonitrile, and $PPh(OEt)_2$ ligands in place of acetonitrile. In the preparation of the analogous aqua-complex the reactants were shaken for 15 min to obtain the yellow solution from which the complex was obtained on gradual addition of diethyl ether.

Carbonyltetrakis(diethoxyphenylphosphine)cobalt(I) *Hexafluorophosphate.*—Carbon monoxide was bubbled through dichloromethane (10 cm^3) containing $[CoH\{PPh(OEt)_2\}_4][PF_6]$ (1.70 g) and $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.57 g) until a yellow solution formed; methanol was then added giving yellow crystals in 80% yield.

trans-*Bromotetrakis(diethoxyphenylphosphine)hydridocobalt*(III) *Hexafluorophosphate.*—(*a*) Bromoform (1 cm^3) was added to $[CoH\{PPh(OEt)_2\}_4][PF_6]$ (0.68 g) in dichloromethane (2 cm^3). After 15 h, diethyl ether was added giving yellow crystals in 80% yield. (*b*) Lithium bromide (0.2 g) was added to $[CoH(OH_2)\{PPh(OEt)_2\}_4][PF_6]_2$ (0.5 g) in methanol (5 cm^3). After 15 min solvent was removed *in vacuo* and the bromo-complex recrystallised from dichloromethane–diethyl ether.

trans-*Tetrakis(diethoxyphenylphosphine)hydridoiodocobalt*(III) *Hexafluorophosphate.*—(*a*) Iodine (0.10 g) was added to $[CoH\{PPh(OEt)_2\}_4][PF_6]$ (0.80 g) in dichloromethane (3 cm^3) giving immediately a red solution which deposited red crystals in 90% yield on addition of diethyl ether. (*b*) The iodo-complex could also be prepared by method (*b*) for the bromo-complex, using sodium iodide in place of LiBr. By use of lithium chloride the corresponding chloro-complex [1] is obtained.

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