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Halo-, Hydrido- and Dinitrogen-complexes of Iron(II) with Tritertiary Phosphines

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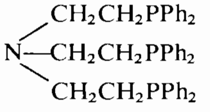
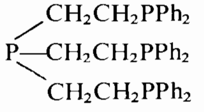
From the five-coordinate iron(II) complexes [FeXL] BPh_4, (L = tris(2-diphenylphosphinoethyl)amine, np_3, and tris(2-diphenylphosphinoethyl)phosphine, pp_3) hydrido and hydrido dinitrogen complexes have been obtained; these have formula [FeH(pp_3)]BPh_4 and [FeHN_2L]BPh_4 (L = np_3, pp_3). In the latter complexes the dinitrogen molecule may be replaced by other neutral ligands such as CO, CH_3CN, C_6H_5CN.

Introduction

The complexing properties of the potentially tetradentate tripod ligand tris(2-diphenylphosphinoethyl) amine, np_3, towards some


np_3


pp_3

3d metals have been the object of previous studies.[1] This ligand has been found to form four- and five-coordinate complexes with nickel and cobalt, the oxidation states of the metal being $+2^{1a}$, $+1^2$, 0^3. The most common geometries found for these compounds are trigonal bipyramidal, square pyramidal and trigonal pyramidal.

It seemed therefore also interesting to investigate the complexing ability of the ligand np_3 towards iron (II). The ligand np_3 reacts with iron(II) halides in presence of $NaBPh_4$ to give complexes of formula [FeX (np_3)]BPh_4 (X = Cl, Br, I), which are five-coordinate; with iron(II) thiocyanate a six-coordinate complex, Fe(np_3)$(NCS)_2$, is formed.

Since ligands containing tertiary phosphines have been found to favour the formation of hydride complexes containing bonded dinitrogen,[4] the possibility of similar behaviour for these five-coordinate complexes and for the analogous compound [FeX(pp_3)] BPh_4,[1b] where pp_3 is tris(2-diphenylphosphinoethyl) phosphine, has been investigated.

Reaction of $NaBH_4$ with [FeX(pp_3)]BPh_4 under argon gives a hydride compound of formula [FeH (pp_3)]BPh_4. If the reaction is carried out under nitrogen both [FeX(np_3)]BPh_4 and [FeX(pp_3)]BPh_4 give compounds of formula [FeHN_2L]BPh_4 (L = pp_3, np_3); in the latter compounds dinitrogen may be replaced by neutral ligand molecules such as CO, CH_3CN, C_6H_5CN.

Experimental

All reactions were carried out under pure dry nitrogen or argon; reagent grade solvents were used. Gas chromatographic determinations were made using a CARLO ERBA "Fractovap C". Magnetic susceptibilities, molecular weights and X-ray powder patterns were all obtained using the methods described elsewhere.[5]

Preparation of Complexes

[FeX(np_3)]BPh_4, X = Cl, Br, I

To a solution of the appropriate anhydrous ferrous salt (1.5 mmol) in absolute ethanol (30 ml) was added the ligand (1.5 mmol) in methylene chloride (20 ml) and then sodium tetraphenylborate (1.5 mmol) dissolved in absolute ethanol (30 ml). The complexes precipitated immediatly and were recrystallized from methylene chloride and absolute ethanol. Fe(np_3) $(NCS)_2$. A solution containing the ligand (1 mmol) in methylene chloride (20 ml) was added to a filtered solution of absolute ethanol (30 ml) where were dissolved anhydrous ferrous bromide (1 mmol) and potassium thiocyanate (2 mmol). Warming and evaporating the solvent precipitated a dark blue crystalline product which was recrystallized from methylene chloride and ethanol.

[FeH(pp_3)]BPh_4

Sodium borohydride (1.5 mmol) dissolved in absolute ethanol (20 ml) was added under argon to a suspension of [FeBr(pp_3)]BPh_4 in dry benzene (50 ml). The resulting solution was stirred for three hours, filtered, concentrated and the pale yellow product recrystallized from dry benzene and absolute ethanol.

[FeHN_2(pp_3)]BPh_4

It was prepared as [FeH(pp_3)]BPh_4 using a nitrogen atmosphere in place of argon.

[FeHN$_2$(np$_3$)]BPh$_4$

To a solution of [FeX(np$_3$)]BPh$_4$, X = Cl, Br, I (1 mmol) in methylene chloride (30 ml) was added the stoichiometric amount of sodium borohydride dissolved in absolute ethanol (25 ml). By evaporation under nitrogen precipitated crystals which may be purified by recrystallization from a dilute solution of methylene chloride and absolute ethanol.

[FeHCO(pp$_3$)]BPh$_4$ and [FeHCO(np$_3$)]BPh$_4$

These compounds were prepared in the same manner as the analogous dinitrogen complexes but under carbon monoxide.

The other complexes of iron(II) were obtained by replacing dinitrogen with the appropriate neutral ligand added in excess to the hydride dinitrogen complex dissolved in methylene chloride under argon.

Deuterated compounds were prepared similarly to the hydride complexes using deuterated solvents and sodium tetradeuteroborate.

Results and Discussion

[FeX(np$_3$)]BPh$_4$Complexes

Analyses and some other physical properties of these compounds are given in Table I. The complexes are crystalline, air-stable, solids which decompose slowly in solution; all are high-spin with room temperature magnetic moments ranging between 5.19 and 5.29 B.M. X-ray powder photographs of [FeX(np$_3$)]BPh$_4$ complexes are identical and in fact indistinguishable from the corresponding cobalt(II) complexes. A complete X-ray structural analysis of the latter compounds has shown them to be distorted trigonal bipyramidal[6] and similar geometries are therefore implied for the present iron(II) complexes. The electronic spectra both solid and 1,2-dichloroethane solution and the conductivity data are also all in agreement with this hypothesis.

The compounds [FeX(np$_3$)]BPh$_4$ are 1 : 1 electrolytes in nitroethane and 1,2-dichloroethane solutions. Their diffuse reflectance and 1,2-dichloroethane solution spectra, which are practically identical (Table II) show two intense bands: one in the region 8.0–9.0 kK attributable to the $^5E'' \rightarrow {}^5A'$ transition and the other in the region above 5.0 kK corresponding to the $^5E'' \rightarrow {}^5E'$ transition in D_{3h} simmetry. Bands of weak intensity which occur at higher frequencies are not well resolved and are thought to be due to transitions from the quintuplet state to the first excited triplet stated.

The magnetic moments of the present iron(II) complexes and of other previously reported iron(II) complexes with tetradentate ligands having essentially tri-

TABLE I. Physical Constants and Analytical Data.

Compound	Colour	Λ_M[a] (cm^2 ohm^{-1} mol^{-1})	Anal %						μ_{eff} (B.M.)
			Calcd.			Found			
			C	H	N	C	H	N	
[FeCl(NP$_3$)]BPh$_4$[b]	leaf yellow	22(A) 46(B)	74.5	5.9	1.3	74.2	5.8	1.4	5.20
[FeBr(NP$_3$)]BPh$_4$[c]	dark yellow	21(A) 46(B)	71.5	5.6	1.2	71.5	5.8	1.1	5.19
[FeI(NP$_3$)]BPh$_4$[d]	dark yellow	19(A) 47(B)	68.6	5.4	1.2	68.6	5.6	1.2	5.29
Fe(NP$_3$)(NCS)$_2$[e]	dark bleu		64.3	5.1	5.1	64.4	5.2	5.2	diam.
[FeH(PP$_3$)]BPh$_4$[f]	yellow	24(A)	75.7	6.1		75.8	6.4		diam.
[FeHN$_2$(PP$_3$)]BPh$_4$[g]	yellow	24(A)	73.8	5.9	2.6	73.6	6.2	2.3	diam.
[FeHCH$_3$CN(PP$_3$)]BPh$_4$	senape	23(A)	75.0	6.2	1.3	74.7	6.6	1.3	diam.
[FeHC$_6$H$_5$CN(PP$_3$)]BPh$_4$	dark red	26(A)	76.2	6.0	1.2	75.6	5.9	1.1	diam.
[FeHCO(PP$_3$)]BPh$_4$[h]	green	22(A)	74.8	5.9		74.1	5.8		diam.
[FeDCO(PP$_3$)]BPh$_4$	yellow green	23(A)	73.7	5.7		73.5	5.8		diam.
[FeHN$_2$(NP$_3$)]BPh$_4$[i]	yellow green	23(A)	74.9	6.0	3.9	74.5	6.0	3.9	diam.
[FeDN$_2$(NP$_3$)]BPh$_4$	pale brown	20(A)	74.9	6.1	3.9	74.9	6.3	3.8	diam.
[FeHCH$_3$CN(NP$_3$)]BPh$_4$	cream	20(A)	76.2	6.2	2.6	76.4	6.3	2.5	diam.
[FeHC$_6$H$_5$CN(NP$_3$)] BPh$_4$ · 1.5CH$_2$Cl$_2$[l]	ocre	23(A)	71.0	5.7	2.2	71.5	6.0	2.3	diam.
[FeHCO(NP$_3$)]BPh$_4$ · 2CH$_2$Cl$_2$[m]	green	21(A)	67.5	5.5	1.1	66.8	5.7	1.1	diam.
[FeDCO(NP$_3$)]BPh$_4$	green	23	76.0	5.9	1.3	75.5	5.7	1.1	diam.

[a] Molar conductance of *ca.* 10^{-3} *M* soln. in A, 1,2-dichloroethane and B, nitroethane at 20° C. [b] Calcd.: Fe, 5.3%; P, 8.7%; found: Fe, 5.2%; P, 8.7%. [c] Calcd.: P, 8.4%; found: P, 8.3%. [d] Calcd.: Fe, 4.8%; P, 8.0%; I, 11.0%; found: Fe, 4.7%; P, 8.2%; 1, 10.9%. [e] Calcd.: Fe, 6.8%; mol. wt. 825; found: Fe, 6.9%; mol. wt. 800. [f] Calcd.: Fe, 5.3%; P, 11.8%; found: Fe, 5.2%; P, 11.4%. [g] Calcd.: Fe, 5.2%; found: Fe, 5.1%. [h] Calcd.: Fe, 5.2%; found: Fe, 5.0%. [i] Calcd.: Fe, 5.3%; P, 8.8%; found: Fe, 5.2%; P, 8.7%. [l] Calcd.: Cl, 8.4%; found: 8.6%. [m] Calcd.: Fe, 4.5%; Cl, 11.5%; found: Fe, 4.4%; Cl, 13.2%.

TABLE II. Spectroscopic Data for $[FeX(np_3)]BPh_4$ Complexes.

Compound	State	Absorption max. (kK) (ε_{molar} for soln. in parentheses)
$[FeCl(np_3)]BPh_4$	[a]	<5.0; 8.4; 17.9 sh
	$(CH_2Cl)_2$	<5.0; 8.9(66); 19.7 sh
$[FeBr(np_3)]BPh_4$	[a]	<5.0; 9.2; 17.5 sh
	$(CH_2Cl)_2$	<5.0; 8.7(59); 19.9 sh
$[FeI(np_3)]BPh_4$	[a]	<5.0; 7.7; 18.2 sh
	$(CH_2Cl)_2$	<5.0; 8.3(58); 14.2(13)
$Fe(np_3)(NCS)_2$	[a]	17.4; 23.5
	$(CH_2Cl)_2$	17.3(395); 24.1(483)

[a] Diffuse reflectance spectrum.

gonal bipyramidal geometry[1,7] show the same type of correlation between the overall nucleophilic reactivity constants, Σn^0, and the electronegativity, $\Sigma\chi$, of the donor atoms and the spin state of the central ion which was earlier described for five-coordinate complexes of nickel(II) and cobalt(II) (Table III).[8]

It is noteworthy that the cross-over point falls at higher Σn^0 values for iron(II) than for nickel(II), whose analogous complexes have a cross-over point when $\Sigma n^0 = 33$.

Fe(np$_3$)(NCS)$_2$

The complex is monomeric in 1,2-dichloroethane and nitroethane solutions and is diamagnetic in the solid state. The reflectance spectrum of this compound is almost identical to its absorption spectrum in 1,2-dichloroethane solution, the absorption bands occurring at similar frequencies to those previously reported for octahedral diamagnetic iron(II) complexes containing similar ligands.[5,7a] The infrared spectra in nujol mull and in 1,2-dichloroethane solution exhibit two bands at 2110 and 2100 cm^{-1} in the $C\equiv N$ stretching region. Therefore a *cis*-octahedral geometry containing nitrogen bonded thiocyanathes may be assigned to the complex $Fe(np_3)(NCS)_2$.

Hydride Complexes

The complexes $[FeX(pp_3)]BPh_4$ react in solution under argon with sodium borohydride to give a compound of formula $[FeH(pp_3)]BPh_4$. The same reaction under nitrogen atmosphere yields the complex $[FeHN_2(pp_3)]BPh_4$. Both these complexes are air-sensitive crystalline solids, decomposing in a few days even when stored in argon or nitrogen atmosphere. The complexes are almost insoluble in non polar organic solvents and only slightly soluble in tetrahydrofuran, absolute ethanol, 1,2-dichloroethane. When gently warmed in chloroform or methylene chloride these compounds react to form $[FeCl(pp_3)]BPh_4$.

By thermal decomposition and by reaction with hydrochloric acid and iodine in tetrahydrofuran all the compounds evolve hydrogen or hydrogen and nitrogen respectively; gas chromatographic determinations of gases evolved have given ratios of 1 for H/Fe, N_2/Fe and H/N_2.

The compound $[FeHN_2(np_3)]BPh_4$ is obtained in a manner similar to that for the formation of the analogous pp_3 derivative. The np_3 analogue is more stable, less reactive and is decomposed by chloroform, and methylene chloride only after refluxing in these solvents. Only nitrogen is evolved on thermal decomposition.

All the pp_3 and np_3 complexes are diamagnetic in the solid state and 1:1 electrolytes in 1,2-dichloroethane solution. Their electronic spectra show only one band in the crystal field region ranging from 24.7 kK to 27.0 kK. Infrared spectra show one band of medium intensity in the region 1915–1945 cm^{-1}, attributable to the Fe–H stretching mode. This band is not present in the analogous deuterated complexes, which were prepared for comparison purposes.

It was not possible to record the n.m.r. spectra because the complexes were insufficiently soluble. The formula of the complexes $[FeHN_2L]BPh_4$, L = pp_3 and np_3, appear to suggest these compounds are similar to the six-coordinate hydrido complexes, $[FeHN_2L_2]^+$, where L = dppe[9] or depe[10], which have the same set of donor atoms. Unfortunately the hypothesis of six-coordinate iron(II) in the present compounds cannot be confirmed either from their diamagnetism or from their electronic spectra, which are all similar to that of the complex $[FeH(pp_3)]BPh_4$ in which it seems likely that hydrogen ion occupies a coordination position left vacant by a halogen ion and which therefore contains five-coordinate iron(II).

TABLE III.

Complex	Set	Σn^0	$\Sigma\chi$	Spin State	Ref.
$[FeBr(nn_3)]^+$	N_4Br	16.58	15.02	H.S.	7b
$[FeX(np_3)]^+$	NP_3Cl	32.51	12.08	H.S.	
	NP_3Br	33.65	11.99	H.S.	
	NP_3I	34.89	11.46	H.S.	
$[FeX(pp_3)]^+$	P_4Cl	38.20	11.07	L.S.	1b
	P_4Br	39.34	10.98	L.S.	
$[FeI(QP)]^+$	P_4I	41.18	10.45	L.S.	7a

TABLE IV. I.r. Bands (cm^{-1}) for Hydride Complexes.

Compound	Solvent	ν(Fe–H)	ν(L)
$[FeH(pp_3)]BPh_4$	nujol	1940	
$[FeHN_2(pp_3)]BPh_4$	nujol	1945	2100
$[FeHCH_3CN(pp_3)]BPh_4$	nujol	1945	2220
$[FeHC_6H_5CN(pp_3)]BPh_4$	nujol	1940	2190
$[FeHCO(pp_3)]BPh_4$	nujol	1915sh	1930
$[FeDCO(pp_3)]BPh_4$	nujol		1930
$[FeHN_2(np_3)]BPh_4$	nujol	1925	2090
$[FeHN_2(np_3)]BPh_4$	CH_2Cl_2	1920	2085
$[FeDN_2(np_3)]BPh_4$	nujol		2090
$[FeHCH_3CN(np_3)]BPh_4$	nujol	1930	2215
$[FeHC_6H_5CN(np_3)]BPh_4 \cdot 1.5CH_2Cl_2$	nujol	1920	2190
$[FeHCO(np_3)]BPh_4 \cdot 2CH_2Cl_2$	nujol	1915sh	1935
$[FeHCO(np_3)]BPh_4 \cdot 2CH_2Cl_2$	CH_2Cl_2	1915sh	1935
$[FeDCO(np_3)]BPh_4$	nujol		1935
$[FeDCO(np_3)]BPh_4$	CH_2Cl_2		1935

The complexes $[FeHN_2(L)]BPh_4$, L = pp_3, np_3, quickly react with some neutral ligands, L′, such as carbon monoxide, acetonitrile, benzonitrile releasing the coordinated molecular nitrogen:

$$[FeHN_2(L)]BPh_4 + L' \rightarrow [FeHL'(L)]BPh_4 + N_2$$

In contrast to the original dinitrogen compounds, these new derivatives are fairly stable at room temperature in an inert atmosphere and are not decomposed by air. The carbon monoxide adducts are the least reactive of all and in fact they are only not decomposed by refluxing in chloroform or methylene chloride. This stability of the compounds appear to confirm the order of stability with molecular ligands $CO \gg CH_3CN \simeq C_6H_5CN$, an order which has been already proposed for other hydride and dinitrogen complexes of iron (II)[9,10].

Infrared Spectra

The most significant infrared absorption are reported in Table IV. The bands have been assigned on the basis of previous assignements.[9,10] Infrared spectra were recorded in methylene chloride solution only for some compounds, because of their low solubility in all solvents. The more significant absorptions measured in this medium, $\nu(N_2)$, ν(CO), *etc.*, do not differ by more than 5 cm^{-1} from their value in nujol mull. Qualitative arguments based on differences in nujol mull spectra for various complexes are, therefore, unlikely to be markedly affected by solid-state effects. Passing from pp_3 to np_3 derivatives, the Fe–H stretching frequencies are lowered by about 25 cm^{-1}; in the case of carbon monoxide compounds the ν(Fe–H) could not be distinguished from ν(CO), both absorptions occurring in the region from 1915 to 1945 cm^{-1}. The shifts in stretching frequencies of the neutral ligands nitrogen, carbon monoxide, methylcyanide, phenylcyanide are small in each case and it has not been possible to correlate these shifts with the stability and reactivity of these compounds. This shows that the substitution of the apical phosphorus with a nitrogen atom in the ligand L leaves unchanged the ligand site in both the systems $[FeH(pp_3)]^+$ and $[FeH(np_3)]^+$ towards the neutral ligands.

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