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SOME DICATIONIC HYDRIDE COMPLEXES OF IRIDIUM *

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Summary

A series of cationic iridium hydride complexes of the type $[Ir(P_2)_2HL][BF_4]_2$ ($P_2 = Ph_2PCH_2CH_2PPh_2$; L = $(CH_3)_2CO$, C_5H_5N, CH_3CN, Et_3N, Me_2PhN, CO, PF_3, or Me_2NPF_2; $P_2 = Ph_2P(CH_2)_3PPh_2$; L = C_5H_5N) have been synthesised and their stereochemistry in solution determined by NMR spectroscopy

Introduction

There has been recent interest [1—3] in the stereochemistry of cationic and coordinate hydride complexes of iridium containing chelating biphosphine ligands. In connection with a study of the factors affecting the ease of insertion of acetylenes into transition metal hydride complexes [4] we have synthesised $[Ir\{Ph_2P(CH_2)_nPPh_2\}_2H][BF_4]_2$ (n = 2, 3) and a series of complexes of the type $[Ir\{Ph_2P(CH_2)_nPPh_2\}_2H(L)][BF_4]_2$ and determined their structure in solution by NMR spectroscopy.

Results and discussion

The known cationic iridium hydride complex $[Ir(dppe)_2HCl][BF_4]$ (I) [dppe (dppe = 1,2-bis(diphenylphosphine)ethane, $Ph_2P(CH_2)_2PPh_2$) was prepared by the addition of HBF_4 to $[Ir(dppe)_2Cl]$ *** rather than via addition of HCl to $[Ir(dppe)_2][BF_4]$ [5]. I undergoes slow chloride abstraction on treatment with $AgBF_4$ to form the five-coordinate complex $[Ir(dppe)_2H][BF_4]_2$ (II). The small steric requirements of the hydride ligand and the positive charge on the iridium enables a series of six-coordinate complexes, III—X, of the type $[Ir(dppe)_2H(L)]$-

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[***] The analoguos hexafluorophosphate salt has been prepared by a similar route [3].

$[BF_4]_2$, to be obtained by treatment of II with the appropriate donor ligand L, viz. eq. 1.

$$[Ir(dppe)_2Cl] \xrightarrow{HBF_4} [Ir(dppe)_2HCl][BF_4] \xrightarrow{AgBF_4} \underset{(II)}{[Ir(dppe)_2H][BF_4]_2} \xrightarrow{L} \underset{(III-X)}{[Ir(dppe)_2H(L)][BF_4]_2} \quad (1)$$

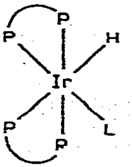
(III, L = $(CH_3)_2CO$; IV, L = C_5H_5N; V, L = CH_3CN; VI, L = $(C_2H_5)_3N$; VII, L = $(CH_3)_2(C_6H_5)N$; VIII, L = CO; IX, L = PF_3; X, L = PF_2NMe_2)

The five-coordinate complex $[Ir(dppp)_2H][BF_4]_2$ XI (dppp = 1,2-bis(diphenylphosphine)propane, $Ph_2P(CH_2)_3PPh_2$) was similarly prepared from $[Ir(dppp)_2HCL[BF_4]$ [3], but addition of donor ligands proved to be more difficult, presumably due to the larger steric requirements of the dppp ligand and only one example, viz. $[Ir(dppp)_2H(C_5H_5N)][BF_4]_2$ (XII), was characterised satisfactorily.

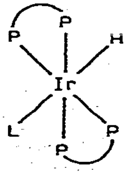
While there have been several reports of dicationic iridium monohydrides in the literature [1,2,6,7], the method outlined above seems to be the most versatile for the preparation of this type of complex. The formulation of all the new complexes is confirmed by elemental analysis, IR, and NMR spectroscopy, while conductivity measurements on solutions of the complexes in nitromethane confirm the presence of 2 : 1 electrolytes. The data are given in Tables 1 and 2.

The hydride resonances of the two five-coordinate complexes II and XI appear as a quintet in the ^1H NMR spectrum, while a singlet is observed in the $\{^1H\}-^{31}P$ spectrum both at room temperature and at −80°C (Table 1). Although the elemental analyses show that the solid complexes do not contain solvent, it is possible that a solvent molecule is coordinated in solution, giving a six-coordinate complex. The equivalence of the phosphorus atoms can arise by solvent exchange and phosphorus site exchange. The complexes could also be five-coordinate in solution, for although structural details on five-coordinate iridium (III) monohydrides are scarce, the iridium(I) hydrides, such as $HIr(PF_3)_4$, have been shown by NMR spectroscopy to have equivalent phosphorus atoms [8,9].

For six-coordinate complexes there are two possible structures:



cis



trans

Until recently, the appearance of the hydride resonance as a quintet in octahedral complexes of the type $Ir(P_2)_2HX$, has been taken as an indication of *trans*-geometry [1,4]. It has been shown, however, that while the hydride resonance of $[Ir(dppp)_2HCl][PF_6]$ is a quintet and the $\{^1H\}-^{31}P$ spectrum at room temperature is a singlet, the spectra are in fact temperature dependent [3]. The low temperature phosphorus spectrum is a doublet of triplets clearly showing a *cis*-geometry with the H and Cl atoms still undergoing site equilibration. The situation for $[Ir(dppe)_2HCl][PF_6]$ was less clear, since the $\{^1H\}-^{31}P$ spec-

TABLE 1

^{1}H AND ^{31}P NMR DATA FOR $[Ir(P\text{--}P)_2H(L)][BF_4]_2$ COMPLEXES

Complex	(P—P)	L	τ(M--H) [a]	δ(P) [b]	^2J(HIrP) [c]	^2J(PIrP) [c]	Other ^{1}H resonances
II	dppe	—	29.3	120.6	12		
III	dppe	$(CH_3)_2CO$	29.1	114.7	12		τ 8.80s $(C\underline{H}_3)_2CO$
IV	dppe	C_5H_5N	29.6	113.1	13		
V	dppe	CH_3CN	29.0	115.0	13		τ 8.13s $C\underline{H}_3CN$
VI	dppe	$(C_2H_5)_3N$	29.3	119.7 127.0	108(P_{trans}) 12.0(P_{cis})	6.7	τ_A 8.62t, τ_B 6.8q, J(AB) = 8 Hz $(CH_3^ACH_2^B)_3N$
VII	dppe	$(CH_3)_2C_6H_5N$	29.7	119.2 126.5	112(P_{trans}) 13.2(P_{cis})	4.9	τ 6.72s $(C\underline{H}_3)_2PhN$
VIII	dppe	CO	19.6	117.0	12.7		
IX [d]	dppe	PF_3	n.o. [f]	121.9		22	
X [e]	dppe	$PF_2N(CH_3)_2$	n.o.	119.1		27	τ 7.35m $(C\underline{H}_3)_2NPF_2$
XI	dppp		29.4	174.3	12		
XII	dppp	C_5H_5N	n.o.	167.2 185.6		19.5	

[a] In ppm rel. TMS. [b] In ppm rel. TMP. [c] In Hz. [d] φ_F 14.8 (rel. CCl_3F); ^1J(PF) 1338 Hz; ^3J(FH) 36.6 Hz; $\delta(PF_3)$ 61.3 ppm. [e] φ_F 20.1 (rel. CCl_3F); ^1J(PF) = 1222 Hz; ^3J(FH) 35.6 Hz; $\delta(PF_2NMe_2)$ = 89.0 ppm. [f] n.o. not observed.

TABLE 2

PHYSICAL PROPERTIES OF $[Ir(P—P)_2H(L)][BF_4]_2$ COMPLEXES

Complex	(P—P)	L	Colour	M.p. (°C)	Λ [f]	Analysis found (calcd.) (%)			ν(Ir—H) (cm⁻¹)
						C	H	N	
II	dppe		White	194—197	164	53.1 (53.7)	4.36 (4.24)		2240
III	dppe	$(CH_3)_2CO$ [a]	White	221(dec.)	156	53.8 (54.1)	4.57 (4.54)		2305
IV	dppe	C_5H_5N	Orange	134(dec.)	191	55.4 (55.5)	4.37 (4.34)	0.99 (1.12)	2233
V	dppe	CH_3CN [b]	White	223	148	53.4 (53.8)	4.48 (4.35)	1.2 (1.16)	2228
VI	dppe	$(C_2H_5)_3N$	Yellow	196(dec.)	143	54.3 (55.1)	5.13 (5.10)	1.24 (1.11)	2238
VII	dppe	$(CH_3)_2C_6H_5N$	Yellow	201(dec.)	170	55.7 (56.1)	4.81 (4.71)	1.16 (1.09)	2240
VIII	dppe	CO [c]	White	228	191	52.8 (53.4)	4.24 (4.14)		2163
IX	dppe	PF_3 [d]	White	174(dec.)	169	49.7 (49.9)	4.05 (3.95)		2120
X	dppe	PF_2NMe_2 [e]	White	183(dec.)	151	50.4 (50.8)	4.22 (4.34)	1.07 (1.10)	2098
XI	dppp		Yellow	225	162	54.4 (54.4)	5.09 (4.48)		2225
XII	dppp	C_5H_5N	Orange	162(dec.)	175	55.3 (55.7)	4.79 (4.60)	0.93 (1.10)	2225

[a] ν(C=O) 1713 cm^{-1}. [b] ν(C≡N) 1632 cm^{-1}. [c] ν(C≡O) 2057 cm^{-1}. [d] ν(P—F) 878, 893, 910 cm^{-1}. [e] ν(P—F) 796 cm^{-1}. [f] S cm^2 mol^{-1}.

trum is a singlet even at low temperature, but a similar intramolecular site exchange is believed to occur. The isonitrile complex $[Ir(dppe)_2H(p\text{-}CH_3C_6H_4NC)][ClO_4]_2$ has the *cis*-structure, while $[Ir(dppe)_2H(CH_3NC)][BF_4]_2$, prepared as the *cis*-isomer, can subsequently be thermally converted to the *trans*-isomer, so it seems that these two complexes are stereochemically rigid. The complex $[Ir(dmpe)_2H(CO)]^{2+}$ shows a quintet for the hydride resonance, but from the data reported it is not clear whether it is *trans* or stereochemically non-rigid.

The complexes VI, VII and XII can definitely be assigned a *cis*-structure, since their $\{^1H\}—^{31}P$ NMR spectra appear as two 1 : 2 : 1 triplets.

In the $\{^1H\}—^{31}P$ NMR spectra of the two fluorophosphine complexes IX and X, the resonances of the diphosphines appear as doublets and the fluorophosphine resonances occur as a quartet of quintets (IX) and a triplet of quintets (X), suggesting *trans*-structures. This is confirmed by their ^{19}F NMR spectra which both show $^3J(FH)$ ca. 36 Hz, which is in the expected range for hydride and fluorphosphine ligands occupying mutually *trans*-positions [10]. The $\{^1H\}—^{31}P$ NMR spectrum of the carbonyl complex VIII appears as a singlet and the similarity of the metal—H stretching frequency to that of XI and X suggests that it also has a *trans*-geometry.

The metal—hydrogen stretching band in the IR of VIII is considerably more intense than that for the other complexes and the carbonyl stretching mode is rather weak, both indicative of vibrational coupling between the hydride and carbonyl groups. It has been shown [1] for other iridium carbonyl hydrides that coupling only takes place when the groups are *trans*. The solution and solid state IR spectra are identical, indicating that the *trans*-structure persists in solution. As expected, the Ir—H and C≡O stretching vibrations in VIII are slightly higher than those observed previously [1] for the complex $[IrH(CO)(dmpe)_2]^{2+}$ (dmpe = $Me_2PCH_2CH_2PMe_2$).

For the remaining complexes III, IV and V, the structural evidence is less clear. While they all show a quintet hydride resonance and a singlet in their $\{^1H\}$—^{31}P NMR spectra, the hydride resonance frequency and the metal—hydride stretching frequency in the IR are similar to those complexes having a *cis*-, rather than a *trans*-structure. Although the $\{^1H\}$—^{31}P spectra remain unchanged at low temperatures, we suggest from the above evidence that these complexes are stereochemically non-rigid in solution similar to $[Ir(dppe)_2HCl][PF_6]$ [3]. This non-rigidity may be due at least in part to dissociation of the ligand L in solution.

It was noted, particularly for complexes II and IV, that precipitation of a complex from solution in dichloromethane led to a partial loss of L. For all the complexes, examination of the $\{^1H\}$—^{31}P spectra of solutions which had been standing for several hours showed the presence of $[(P—P)_2Ir]^+$ and $[(P—P)_2Ir(H)]^{2+}$, as well as $[(P—P)_2Ir(H)L]^{2+}$ (P—P = dppe or dppp).

The stereochemistry of the complexes $[Ir(dppe)_2H(L)][BF_4]_2$ appears to be governed initially by electronic effects, ligands with a high *trans*-effect adopting a *trans*-H—L geometry. For the remaining complexes the two with the bulkiest ligands have a static *cis*-structure. The others appear to be stereochemically non-rigid in solution, due at least in part, to ligand dissociation. The complex $[Ir(dppp)_2H(C_5H_5N)][BF_4]_2$ having a static *cis*-structure and $[Ir(dppe)_2H(C_5H_5N)][BF_4]_2$ being stereochemically non-rigid in solution seems a further illustration [4] of the fact that rearrangement barriers decrease with decreasing ring size, as observed by Caulton and Miller [3].

Experimental

Manipulations were carried out under dry nitrogen using Schlenk techniques. Solvents were rigorously dried before use. ^1H NMR spectra were recorded on a Varian T60 instrument operating at 60 MHz, using tetramethylsilane as an external standard. ^1H, ^{19}F and ^{31}P spectra were recorded on a Jeol PFT100 instrument operating at 94.1 MHz and 40.49 MHz respectively. Trimethylphosphite was the external standard for the phosphorus spectra and CCl_3F or C_6F_6 internal standards for the fluorine spectra. IR spectra were run on a Perkin—Elmer 457 spectrometer (4000—250 cm^{-1}). Elemental analyses for carbon and hydrogen were carried out by Mr. and Mrs. A.G. Olney of this laboratory. The iridium complex $[Ir(dppe)_2HCl][BF_4]$ was prepared by the literature method for $[Ir(dppe)_2HCl][PF_6]$ using HBF_4/etherate in place of aqueous HPF_6. The analogous complex $[Ir(dppp)_2HCl][BF_4]$ was similarly prepared.

Preparation of $[Ir(dppe)_2H][BF_4]_2$

In a typical experiment, $AgBF_4$ (0.083 g, 0.43 mmol) was dissolved in acetone and added to a solution of $[Ir(dppe)_2HCl][BF_4]$ (0.474 g, 0.43 mmol) in dichloromethane. The mixture was stirred overnight in the dark and the AgCl produced filtered off. The solvent was removed and the resulting light-yellow solid washed well with hexane and recrystallised from a dichloromethane/hexane mixture giving $[Ir(dppe)_2H][BF_4]_2$ (II).

Reactions of $[Ir(dppe)_2H][BF_4]_2$ (I) with various donor ligands, L

The results are recorded in Table 2 and the experimental methods summarised below:

(a) L = acetone. Recrystallisation of II from a dichloromethane/acetone/hexane mixture gave complex III.

(b) L = acetonitrile. Recrystallisation of II from an acetonitrile/diethyl ether mixture gave complex V.

(c) L = pyridine, triethylamine, or *N,N*-dimethylaniline. A solution of II in dichloromethane was stirred (15 min) with an equimolar amount of the appropriate ligand. Recrystallisation from a dichloromethane/ether mixture gave IV, VI, or VII respectively.

(d) L = trifluorophosphine or dimethylaminodifluorophosphine. The reactions were carried out in sealed Pyrex ampoules with a solution of II in dichloromethane being shaken (1 h) with an equimolar amount of the ligand. Recrystallisation from dichloromethane/ether gave IX or X.

(e) L = CO. Carbon monoxide was bubbled (10 min) into a stirred solution of II in dichloromethane. The solvent was removed and the resulting white solid recrystallised from dichloromethane/hexane, giving VIII.

Reaction of $[Ir(dppp)_2HCl][BF_4]$ with $AgBF_4$ in a similar manner to that outlined above, gave $[Ir(dppp)_2H][BF_4]_2$, (XI).

A solution of XI in dichloromethane was stirred (15 min) with an equimolar amount of pyridine. Recrystallisation from a dichloromethane/hexane mixture gave XII.

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