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Protonation of cationic hydride and alkyl complexes of Ir(III)

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Abstract

Reaction of $HBF_4 \cdot OEt_2$ with $IrH_2(MeCN)P_3^+$ (**1**) ($P = PMe_2Ph$) in the presence of MeCN gives rapid conversion to *cis,mer*-$IrH(MeCN)_2P_3^{2+}$ and H_2. The corresponding reaction with *cis,mer*-$IrMe_2(MeCN)P_3^+$ is much slower, but gives the corresponding product, *cis,mer*-$IrMe(MeCN)_2P_3^{2+}$. In the absence of added MeCN, $HBF_4 \cdot OEt_2$ transforms the dihydride cation **1** to equimolar *cis,mer*-$IrH(MeCN)_2P_3^{2+}$ and $IrH_4P_3^+$; 0.5 mol of acid suffices to effect this reaction. In the absence of added MeCN, the protonation of the dimethyl cation leads to the ether complex *mer*-$IrMe(Et_2O)(MeCN)P_3^{2+}$, which is subsequently scavenged by adventitious water to yield *mer*-$IrMe(H_2O)(MeCN)P_3^{2+}$. The crystal structure of this aquo complex, as its BF_4 salt, shows a chain of BF_4^- /$IrMe(H_2O)(MeCN)P_3^{2+}$ units held together by two hydrogen bonds to each water molecule. Crystallographic data for $[IrMe(H_2O)(NCMe)(PMe_2Ph)_3](BF_4)_2$ (at −169°C): $a = 10.709(3)$ Å, $b = 15.645(4)$, $c = 10.481(2)$, $\beta = 106.49(1)°$ with $Z = 2$ in space group $P\bar{1}$.

Introduction

We have shown that protonation of neutral polyhydrides and polyalkyls is a useful technique to generate reactive, unsaturated metal monocations [1,2]. These species are created via facile dissociation of H_2 or CH_4 and are subsequently trapped by Lewis bases (B) to yield new stable cationic complexes [3–5].

$$IrX_3P_3 + H^+ \rightarrow [IrHX_3P_3^+] \rightarrow IrX_2P_3^+ + HX \xrightarrow{B} IrX_2BP_3^+ \quad (1)$$
$(X = H \text{ or } CH_3)$

The presence of additional alkyl or hydride ligands within these cations led us to consider the feasibility of further protonation to create multiply-charged unsaturated cations. The outstanding question we address here is whether monocations retain enough Brønsted basicity to be protonated by the available acids.

Experimental

General

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk technique. Solid transfers were accomplished in a Vacuum Atmospheres Corp. glovebox. Methylene chloride and acetonitrile were distilled under nitrogen from calcium hydride; Et_2O was dried with NaK/benzophenone. Methylene chloride-d_2 and $NCCD_3$ were dried over CaH_2 prior to use and stored in the glovebox. $HBF_4 \cdot OEt_2$ (Aldrich, 85%) was used as received. $IrH_3(PMe_2Ph)_3$ and $IrMe_3(PMe_2Ph)_3$ were synthesized according to literature methods [1,6], starting from $IrCl_3 \cdot xH_2O$. ^1H (360 MHz) and ^{31}P (146 MHz) NMR were obtained on a Nicolet NT-360 instrument. Negative ^{31}P NMR chemical shifts are upfield from external 85% H_3PO_4.

Synthesis of cis,mer-*[IrH$_2$(NCMe)(PMe$_2$Ph)$_3$]BF$_4$ (1)*

A 100 mL flask containing 150 mg (0.21 mmol) of $[IrH_4P_3]BF_4$ (generated [1] *in situ* from *fac*-IrH_3P_3 and $HBF_4 \cdot OEt_2$) in 50 mL of CH_2Cl_2 was charged with 0.5 mL (9.6 mmol) of acetonitrile. After stirring for 15 min, the volume was reduced to 5 mL *in vacuo*. To the concentrated solution, 40 mL of Et_2O was added, causing immediate precipitation of a yellow solid. The supernate was removed via cannula and the solid was dried *in vacuo*. Yield: 96%. ^1H NMR (24°C, CD_2Cl_2): δ +7.0–7.5 (m, PPh), 2.27 (s, 3H), 1.85 (overlapping virtual triplets, 12H), 1.27 (d, J(PMe) = 8 Hz, 6H), −11.56 (dtd, J(PH) = 127, 21, 5 Hz, 1H), −20.80 (dtd, J(PH) = 12, 16, 5 Hz, 1H). $^{31}P\{^1H\}$ NMR (24 °C, CD_2Cl_2): δ −31.32 (d, J(PP) = 18 Hz, 2P), −39.67 (t, J(PP) = 18 Hz, 1P).

Synthesis of cis,mer-*[IrH(NCMe)$_2$(PMe$_2$Ph)$_3$](BF$_4$)$_2$ (2)*

A 100 mL flask containing 121 mg (0.164 mmol) of $[IrH_2(NCMe)P_3]BF_4$ in 50 mL of CH_2Cl_2 was charged with 0.5 mL (9.6 mmol) of acetonitrile and 20 mL of $HBF_4 \cdot OEt_2$ (0.164 mmol). After stirring for 1 h, the volume was reduced to 5 mL *in vacuo*. To the concentrated solution, 40 mL of Et_2O was added, causing immediate precipitation of a white solid. The excess solvent was removed via cannula and the solid was dried *in vacuo*. Yield: 95%. ^1H NMR (24°C, CD_2Cl_2): δ 7.5–7.0 (m, PPh), 2.72 (s, 3H), 2.36 (s, 3H), 1.64 (virtual triplet, 6H), 1.60 (virtual triplet, 6 H), 1.46 (d, J(PMe) = 8 Hz, 6H), −20.25 (dt, J(PH) = 17, 14 Hz, 1H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −28.39 (d, J(PP) = 20 Hz, 2P), −41.12 (t, J(PP) = 20 Hz, 1P).

Synthesis of cis,mer-*[IrMe$_2$(NCMe)(PMe$_2$Ph)$_3$]BF$_4$ (3)*

To a Schlenk flask containing 30 mL of dry CH_2Cl_2 was added 150 mg (0.25 mmol) of $IrMe_3(PMe_2Ph)_3$; 28 μL (22 mg, 0.54 mmol) of acetonitrile was added via syringe followed by 31 μL (0.25 mmol) of $HBF_4 \cdot OEt_2$. The solution was stirred for 30 min and then pumped dry to yield a white solid which was then washed with 10 mL of Et_2O. The remaining white powder was pumped dry to yield 130 mg (0.16 mmol, 64% yield) of $[IrMe_2(NCMe)(PMe_2Ph)_3]BF_4$. $^{31}P\{^1H\}$ NMR in CD_2Cl_2: δ −35.4 (d, J(PP) = 16 Hz), −49.1 (t, J(PP) = 16 Hz). ^1H NMR in CD_2Cl_2: 1.39 (d, J(PMe) = 8 Hz), 1.51 (vt, J(PMe) = 3 Hz), 1.62 (vt, J(PMe′) = 3.5 Hz), 2.00 (s,

Table 1

Crystallographic data for $[IrMe(NCMe)(H_2O)(PMe_2Ph)_3](BF_4)_2$

Chemical formula	$C_{27}H_{41}B_2F_8NOP_3Ir$	Space group	$P\bar{1}$
a (Å)	10.709(3)	T (°C)	−169
b (Å)	15.645(4)	λ (Å)	0.71069
c (Å)	10.481(2)	$\rho_{calc.}$ (g cm^{-3})	1.708
β (deg)	106.49(1)	μ(Mo-K_α) (cm^{-1})	42.1
V (Å^3)	1661.41	R	0.0392
Z	2	R_w	0.0399
Formula weight	854.38		

$NCCH_3$), 0.24 (dt, J(PMe) = 7.9 Hz, J(PMe) = 5.0 Hz), 0.21 (apparent quartet, 7.6 Hz), 7.3 (phenyl multiplet).

Synthesis of mer-*$[Ir(Me)(NCMe)(H_2O)(PMe_2Ph)_3](BF_4)_2$*

To a Schlenk tube containing 10 mL of dry CH_2Cl_2 was added 94 mg (0.12 mmol) of $[IrMe_2(NCMe)(PMe_2Ph)_3]BF_4$; 30 μL (0.25 mmol) of $HBF_4 \cdot Et_2O$ was then added via syringe and the solution was allowed to stand without agitation for 4 days to give a colorless crystalline solid. No NMR data are available owing to the insolubility of the solid in THF, H_2O, $CHCl_3$ and CH_2Cl_2.

X-Ray diffraction study of mer-*$[IrMe(NCMe)(H_2O)(PMe_2Ph)_3](BF_4)_2$*

A crystal of suitable size was mounted using silicone grease and was transferred to a goniostat where it was cooled to −169°C for characterization [7] and data collection (Table 1). A systematic search of a limited hemisphere of reciprocal space revealed no symmetry or systematic absences. An initial choice of space group $P\bar{1}$ was confirmed by the successful solution of the structure.

The structure was solved by the usual combination of direct methods (MULTAN78) and Fourier techniques. The Ir and P positions were obtained from an initial E-map, and the remainder of the non-hydrogen atoms were found in subsequent iterations of least-squares refinement and difference Fourier calculations. After partial refinement of the non-hydrogen atoms, a difference Fourier map revealed many of the hydrogen atoms. All but the hydrogens of the water molecule were included in the calculated positions. In the final cycles of least-squares refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters and the hydrogen atoms were varied with isotropic thermal parameters. The final difference map had one Ir residual peak (1.6 e/Å^3) and some smaller peaks within the BF_4 groups. See Table 2 for the fractional coordinates and isotropic thermal parameters.

The unit cell contains two independent BF_4^- ions; one of them (involving B34) hydrogen bonds to the water molecule and also shows a 60:40 disorder of two of its fluorines (F35 with F36 and F39 with F40). The other B(41)F_4^- is ordered and not hydrogen bonded.

Synthesis of cis,mer-*$[Ir(Me)(NCMe)_2(PMe_2Ph)_3](BF_4)_2$* ***(6)***

One millimole of $[Ir(Me)(NCMe)(H_2O)(PMe_2Ph)_3](BF_4)_2$ was covered with 15 mL of CH_2Cl_2; 200 μL (0.157 g, 3.83 mmol) of acetonitrile was introduced by syringe. The insoluble iridium salt soon dissolved to yield a clear, colorless

Table 2

Fractional coordinates [a] and isotropic thermal parameters [b] for $IrMe(NCMe)(H_2O)(PMe_2Ph)_3](BF_4)_2$

	x	y	z	$10\ B_{iso}$
Ir(1)	6980.9(4)	2314.2(3)	7751.2(4)	12
P(2)	5423(2)	3023(2)	6146(3)	14
P(3)	8628(3)	1442(2)	8982(3)	17
P(4)	7559(3)	3553(2)	9203(3)	14
O(5)	6346(6)	1111(4)	6385(7)	19
N(6)	5652(8)	2013(5)	8756(8)	17
C(7)	8284(9)	2461(7)	6661(10)	14
C(8)	4920(10)	2307(6)	4559(10)	18
C(9)	5919(10)	3961(7)	5615(11)	22
C(10)	3879(9)	3352(6)	6485(9)	11
C(11)	3086(10)	2696(7)	6627(11)	23
C(12)	11917(11)	2905(7)	6874(11)	26
C(13)	1497(11)	3763(8)	6998(11)	27
C(14)	2207(11)	4391(8)	6835(11)	28
C(15)	3413(11)	4192(7)	6585(10)	22
C(16)	10283(10)	1840(7)	9559(11)	26
C(17)	8369(13)	1144(8)	10487(12)	33
C(18)	8804(10)	412(7)	7979(10)	17
C(19)	8020(11)	−283(7)	7941(13)	29
C(20)	8151(12)	−1075(9)	7147(14)	42
C(21)	11027(14)	1161(8)	13607(12)	43
C(22)	10248(13)	488(8)	3601(11)	33
C(23)	9652(11)	297(7)	7200(11)	23
C(24)	6224(10)	4305(7)	9308(11)	21
C(25)	8741(9)	4195(7)	8890(11)	18
C(26)	8195(9)	3431(6)	10974(10)	15
C(27)	9512(10)	3584(6)	11680(10)	19
C(28)	9927(11)	3492(7)	13019(11)	24
C(29)	9106(11)	3237(7)	3676(10)	20
C(30)	7816(10)	3071(7)	2977(10)	22
C(31)	7368(9)	3178(7)	11649(10)	19
C(32)	4992(9)	1773(6)	9298(10)	16
C(33)	4170(12)	1479(8)	10010(12)	31
B(34)	6569(15)	−23(10)	3229(16)	36(3)
F(35)	5932(10)	−467(7)	4056(11)	32(2)
F(36)	5215(21)	7(14)	3148(22)	60(4)
F(37)	7361(7)	−662(5)	2944(7)	46(2)
F(38)	7193(6)	665(4)	4176(7)	36(2)
F(39)	5644(13)	152(9)	2217(13)	48(3)
F(40)	6340(20)	441(13)	1950(19)	49(4)
B(41)	2985(13)	3582(9)	1477(13)	24(3)
F(42)	4213(8)	3503(6)	1251(9)	61(2)
F(43)	3053(8)	4234(5)	2582(8)	54(2)
F(44)	2085(6)	3800(4)	390(6)	29(1)
F(45)	2706(6)	2812(4)	1801(6)	27(1)
H(46)	814(8)	203(5)	587(8)	44(4)
H(47)	808(9)	298(6)	630(9)	44(238)
H(48)	898(10)	238(6)	686(10)	65(27)
H(49)	429(17)	265(11)	393(17)	18(4)
H(50)	562(17)	205(12)	434(18)	61(2)
H(51)	441(11)	179(8)	471(11)	41(671)
H(52)	661(7)	380(5)	521(8)	32(43)

Table 2 (continued)

	x	y	z	10 B_{iso}
H(53)	520(13)	418(8)	498(13)	32(19)
H(54)	621(10)	439(7)	638(11)	32(3)
H(55)	1019(8)	225(5)	1043(8)	104(23)
H(56)	1083(9)	134(6)	1002(9)	107(22)
H(57)	1056(12)	198(8)	893(12)	97(39)
H(58)	750(19)	86(14)	1021(21)	20(15)
H(59)	902(18)	70(13)	1068(19)	23(3)
H(60)	848(16)	164(15)	1108(18)	29(3)
H(61)	649(7)	473(5)	992(8)	15(3)
H(62)	593(7)	452(5)	850(8)	14(42)
H(63)	556(9)	402(6)	954(9)	20(10)
H(64)	845(11)	427(8)	795(12)	25(3)
H(65)	962(11)	393(8)	893(11)	13(3)
H(66)	885(13)	467(10)	956(14)	17(3)
H(67)	351(9)	125(6)	958(9)	91(36)
H(68)	477(7)	110(5)	1061(7)	102(21)
H(69)	411(8)	186(6)	1074(9)	37(3)
H(70)	346(9)	217(8)	650(10)	30(3)
H(71)	1152(12)	250(8)	705(12)	55(31)
H(72)	79(8)	391(6)	724(9)	19(7)
H(73)	197(8)	497(6)	689(9)	17(3)
H(74)	393(12)	458(9)	645(12)	55(3)
H(75)	736(11)	−27(8)	845(12)	52(2)
H(76)	758(14)	−144(10)	722(15)	82(24)
H(77)	1087(11)	164(7)	1413(11)	48(15)
H(78)	961(9)	55(6)	409(10)	29(3)
H(79)	1016(8)	75(6)	716(9)	19(3)
H(80)	995(10)	372(7)	1119(10)	35(3)
H(81)	1085(8)	365(5)	1355(8)	11(37)
H(82)	937(8)	316(5)	465(8)	18(26)
H(83)	723(10)	309(7)	348(11)	41(3)
H(84)	655(9)	314(7)	1129(10)	31(3)

[a] Fractional coordinates are $\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for hydrogen atoms. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given by W.C. Hamilton, Acta Crystallogr., 12 (1959) 609.

solution. After 1 h, the solvent was removed *in vacuo*. ^{1}H NMR (CD_2Cl_2): 2.63 (s, NCMe, 3H), 2.02 (s, NCMe, 3H), 1.75 (vt, J(PMe) = 3.7 Hz), 1.73 (d, J(PMe) = 10.5 Hz), 1.68 (vt, J(PMe) = 3.7 Hz), 0.64 (dt, IrMe, J(PH) = 6.5 Hz, J(PH) = 3.4 Hz, 3H).

Acidolysis of cis,mer-*[$IrMe_2(NCMe)(PMe_2Ph)_3$]BF_4*

[$IrMe_2$(NCMe)($PMe_2Ph)_3$]BF_4 (53 mg, 0.066 mmol) was dissolved in 1 mL of CH_2Cl_2 and treated with 10 μL (0.082 mmol) of $HBF_4 \cdot OEt_2$. The reaction was monitored by $^{31}P\{^1H\}$ NMR. After 1 min, two new AM_2 patterns were evident, one of which (−26.6 (d) and −41.7 (t) ppm with $J = 18$) was due to IrMe(NCMe)(OEt_2)($PMe_2Ph)_3^{2+}$. The resonances of coordinated Et_2O in this ion at −56°C in CD_2Cl_2 were at 4.19 ppm (q) and 1.36 ppm (t). The second AM_2 pattern had peaks at −34.9 (d) and −46.4 (t) with $J = 21$ Hz. After 10 min, all starting material was gone and only the above AM_2 patterns remained. At 30 min, the spectrum was unchanged from that at 10 min.

Synthesis of cis,mer-*[Ir(PMe$_2$Ph)$_3$(NCMe)(NCCD$_3$)(Me)](BF$_4$)$_2$*

A small amount of [IrMe(NCMe)(H$_2$O)(PMe$_2$Ph)$_3$](BF$_4$)$_2$ was dissolved in CD$_3$CN. After 28 h, the ^{1}H NMR showed: 1.95 (s, NCMe), 1.72 (vt, J(PMe) = 4 Hz), 1.71 (d, J(PMe) = 11 Hz), 1.64 (vt, J(PMe) = 4 Hz), 0.59 (dt, J(PH) = 6 Hz, J(PH) = 3.5 Hz).

Results

Characterization of cis,mer-*[IrX(NCMe)$_2$P$_3$](BF$_4$)$_2$ (X = H, CH$_3$; P = PMe$_2$Ph)*

Addition of excess HBF$_4$ · OEt$_2$ to a CH$_2$Cl$_2$/CH$_3$CN solution of *cis,mer*-[IrH$_2$(NCMe)P$_3$]BF$_4$ (**1**) results in visible gas evolution. After 15 min at 25°C, addition of Et$_2$O causes precipitation of a colorless solid. The ^{31}P{^{1}H} NMR of this material in CD$_2$Cl$_2$ shows an AB$_2$ pattern. The ^{1}H NMR spectrum reveals two virtual triplets (6H each) and a doublet (6H) in the PMe spectral region. A hydride resonance is detected at −20.2 ppm (doublet of triplets, 1H). Two singlets at 2.72 and 2.36 (3H each) are attributed to two chemically inequivalent acetonitrile ligands. These data are consistent with the formulation *cis,mer*-[IrH(NCMe)$_2$P$_3$](BF$_4$)$_2$ (**2**), containing an 18-electron dication. Treatment of IrH$_3$P$_3$ with 2.0 equiv. of HBF$_4$ · OEt$_2$ in CH$_2$Cl$_2$/CH$_3$CN also yielded complex **2**.

Addition of excess HBF$_4$ · OEt$_2$ to a CH$_2$Cl$_2$/CH$_3$CN solution of *cis,mer*-[IrMe$_2$(NCMe)P$_3$]BF$_4$ (**3**) causes no visible gas evolution. After 24 h at 25°C, addition of Et$_2$O causes precipitation of a colorless solid. The ^{31}P{^{1}H} NMR of this powder in CD$_2$Cl$_2$ shows an AB$_2$ pattern. The ^{1}H NMR spectrum reveals two virtual triplets (6H each) and a doublet (6H) in the PMe spectral region. A methyl resonance is detected at 0.64 ppm (triplet of doublets, J(PCH$_3$) = 6.5, 3.5 Hz, 3H). Singlets at 2.63 and 2.02 ppm (3H each) are attributed to two chemically inequivalent acetonitrile ligands. These data are consistent with a *cis,mer* configuration for [IrMe(NCMe)$_2$P$_3$](BF$_4$)$_2$ (**6**). Treatment of IrMe$_3$P$_3$ with 2.5 equiv. of HBF$_4$ · OEt$_2$ in CH$_2$Cl$_2$/NCMe also yielded complex **6**.

Mechanism of acidolysis of cis,mer-*IrH$_2$(NCMe)P$_3^+$ in the absence of MeCN*

Protonation of *cis,mer*-IrH$_2$(NCMe)P$_3^+$ (**1**) with 1 equiv. of HBF$_4$ · OEt$_2$ in CD$_2$Cl$_2$ at 25°C occurs rapidly (within 1 s) and a visible amount of gas (H$_2$) is liberated. The ^{1}H and ^{31}P{^{1}H} NMR spectra reveal the presence of equimolar amounts of IrH(NCMe)$_2$P$_3^{2+}$ (**2**), IrH$_4$P$_3^+$ and unreacted HBF$_4$ · OEt$_2$. These data suggest that an IrH$_3$(NCMe)P$_3^{2+}$ (**A**) species loses H$_2$ to create an unsaturated IrH(NCMe)P$_3^{2+}$ transient (**B**), which scavenges 1 equiv. of acetonitrile from IrH$_2$(NCMe)P$_3^+$ (**1**) to yield **2** and IrH$_2$P$_3^+$ (**C**). The unsaturated hydride **C** then scavenges H$_2$ to generate IrH$_4$P$_3^+$ (Scheme 1). The sequence of events occurring in Scheme 1 is further corroborated when 2.0 equiv. of **1** are reacted with 1 equiv. of HBF$_4$ · OEt$_2$. The products of this reaction are equimolar **2** and IrH$_4$P$_3^+$. It has previously been shown that IrH$_2$P$_3^+$ (**C**) reacts rapidly with H$_2$ to form IrH$_4$P$_3^+$ [4].

$$\underset{(\mathbf{1})}{IrH_2(NCMe)P_3^+} \xrightarrow{H^-} \underset{(\mathbf{A})}{IrH_3(NCMe)P_3^{2+}} \xrightarrow{-H_2} \underset{(\mathbf{B})}{IrH(NCMe)P_3^{2+}} \longrightarrow$$

$$\underset{(\mathbf{B})}{IrH(NCMe)P_3^{2+}} + \underset{(\mathbf{1})}{IrH_2(NCMe)P_3^+} \longrightarrow$$

$$\underset{(\mathbf{2})}{IrH(NCMe)_2P_3^{2+}} + \underset{(\mathbf{C})}{IrH_2P_3^+} \xrightarrow{H_2} IrH_4P_3^+$$

Scheme 1

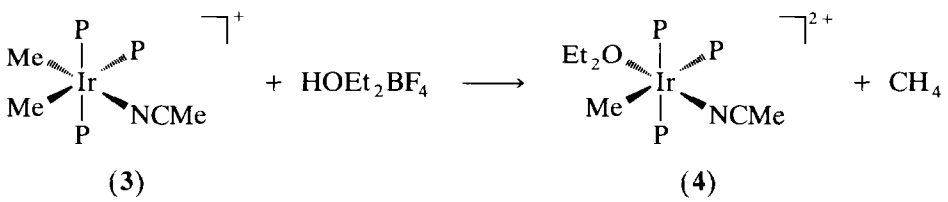
In an attempt to detect the trihydride transient **A**, **1** and $HBF_4 \cdot OEt_2$ were flame sealed in an NMR tube in CD_2Cl_2 under excess (approx. 4 equiv.) H_2 at −196°C. The NMR tube was placed in an NMR probe pre-cooled to −80°C for ^1H and $^{31}P\{^1H\}$ NMR data acquisition. No resonances consistent with an $IrH_3(NCMe)P_3^{2+}$ formulation were observed after four ^1H NMR pulses. Only **1**, **2**, $IrH_4P_3^+$, H_2 and $HBF_4 \cdot OEt_2$ were present in solution. Since this reaction is so fast, we propose that $IrH_3(MeCN)P_3^{2+}$ is actually the dihydrogen complex $IrH(H_2)(MeCN)P_3^{2+}$ (rather than an Ir^V trihydride) and that it rapidly dissociates H_2. Taken together, these results readily explain the reaction mechanism when acidolysis is executed in the presence of added MeCN.

$$IrH(H_2)(MeCN)P_3^{2+} \rightleftharpoons IrH(MeCN)P_3^{2+} + H_2 \xrightarrow{MeCN} \underset{(2)}{IrH(MeCN)_2P_3^{2+}} \qquad (2)$$

Mechanism of acidolysis of cis,mer-*$IrMe_2(NCMe)P_3^+$ (3) in the absence of MeCN*

The mechanism of production of $IrMe(NCMe)_2P_3^{2+}$ (**6**) by acidolysis of **3** in CH_2Cl_2/CH_3CN can be understood based on experiments executed in the absence of MeCN. Protonation of **3** with $HBF_4 \cdot OEt_2$ (1.5 equiv.) in CD_2Cl_2 at 25°C is conveniently monitored by $^{31}P\{^1H\}$ NMR. Within the first minute after acidolysis, the $^{31}P\{^1H\}$ NMR spectrum shows **3** (67%) and another AB_2 spin system **4** (33%). After 3 min, the spectrum reveals **3** (50%), **4** (40%) and a new AB_2 pattern, **D** (10%). Only **4** (67%) and **D** (33%) are present in solution after 0.5 h.

In an attempt to identify species **4** and **D**, a CD_2Cl_2 solution of **3** was protonated at 25°C with $HBF_4 \cdot OEt_2$ (1.5 equiv.) and placed in a pre-cooled NMR probe at −55°C. From −50°C to −10°C only unreacted **3** and $HBF_4 \cdot OEt_2$ are present in solution. However, at −10°C, by $^{31}P\{^1H\}$ NMR, a detectable amount of **4** is observed in the presence of **3**. At this temperature, the ^1H NMR spectrum of **4** shows two virtual triplets and a doublet in the PMe spectral region. A doublet of triplets ($J(PCH_3) = 36$ and 6 Hz) at 0.80 ppm indicates that the methyl ligand is *trans* to the unique phosphine (i.e., large coupling constant). A sharp singlet at 2.29 is assigned to a coordinated acetonitrile ligand. Also evident in this spectrum are signals due to coordinated Et_2O (shifted downfield relative to free Et_2O). Thus, protonation of **3** and subsequent loss of CH_4 creates unsaturation, allowing Et_2O to coordinate.



(3) (4)

(3)

Upon warming the solution to 5°C, complex **D** is observed to appear in the $^{31}P\{^1H\}$ NMR spectrum. If this solution is left undisturbed for 48 h, colorless crystals precipitate from the CD_2Cl_2 solution. The $^{31}P\{^1H\}$ NMR spectrum of the supernatant solution reveals the exclusive presence of **4**. Since the disappearance of **D**

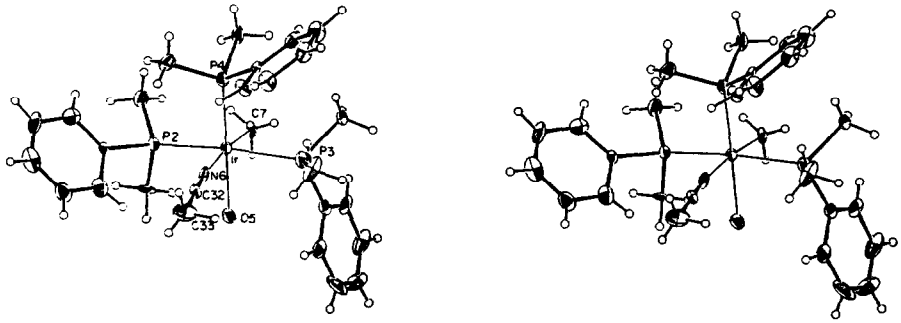


Fig. 1. Stereo ORTEP drawing of $IrMe(H_2O)(MeCN)(PMe_2Ph)_3^{2+}$, showing selected atom labelling. Hydrogens of the water ligand (O5) were not located.

coincided with formation of crystalline material, we felt that we could identify **D** by a single-crystal X-ray diffraction of these crystals.

Structure of $[IrMe(NCMe)(H_2O)P_3](BF_4)_2$ (5)

The X-ray diffraction study shows that the dication (Fig. 1) has a mer arrangement of phosphines with the methyl ligand trans to MeCN. The geometry at iridium is approximately octahedral, with all *cis* angles from 85 to 95° and *trans* angles from 169 to 177° (see Table 3). The Ir–P distance *trans* to the aquo ligand (2.26 Å) is distinctly shorter than those *trans* to phosphine (2.37 Å). The Ir–CH_3 distance here (2.081(10) Å) is distinctly shorter than that (2.160(9) Å) in *fac*-$IrMe_3(PMe_2Ph)_3$. As shown in Fig. 2, both protons on the aquo ligand are involved in hydrogen bonding (O–F = 2.59–2.70 Å), each to a different (but symmetry-related) BF_4^- ion. Since two fluorines of each $B(34)F_4^-$ are involved in hydrogen bonding, the crystal structure is composed of infinite chains of $(BF_4H_2OIr(NCMe)Me(PMe_2Ph)_3^+$ cations, together with isolated $B(41)F_4^-$ anions. Since this structure involves hydrogen bonding to both protons on the aquo ligand, it supports the

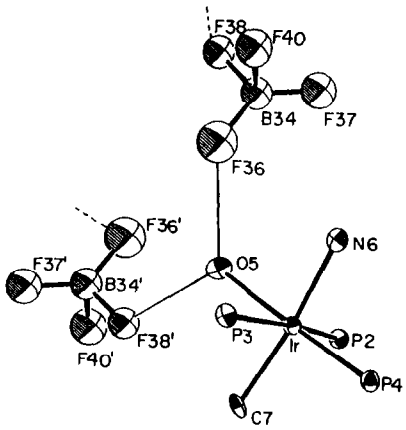


Fig. 2. Drawing of the hydrogen bonding of the $IrMe(H_2O)(MeCN)(PMe_2Ph)_3^{2+}$ *unit* with two symmetry-related BF_4^- ions. Hydrogens of the water ligand (O5) were not located. Dotted lines show connection to symmetry-related iridium aquo cations.

Table 3

Selected bond distances (Å) and angles (deg) for $[IrMe(NCMe)(H_2O)(PMe_2Ph)_3](BF_4)_2$

Ir(1)–P(2)	2.3714(27)
Ir(1)–P(3)	2.3702(28)
Ir(1)–P(4)	2.2615(28)
Ir(1)–O(5)	2.189(7)
Ir(1)–N(6)	2.110(9)
Ir(1)–C(7)	2.081(10)
N(6)–C(32)	1.136(11)
O(5)–F(35)	2.587(9)
O(5)–F(36)	2.683(9)
O(5)–F(38)′	2.695(9)
P(2)–Ir(1)–P(3)	168.80(9)
P(2)–Ir(1)–P(4)	93.55(10)
P(2)–Ir(1)–O(5)	86.16(18)
P(2)–Ir(1)–N(6)	95.34(22)
P(2)–Ir(1)–C(7)	86.38(27)
P(3)–Ir(1)–P(4)	95.21(10)
P(3)–Ir(1)–O(5)	85.41(18)
P(3)–Ir(1)–N(6)	91.34(22)
P(3)–Ir(1)–C(7)	86.01(27)
P(4)–Ir(1)–O(5)	177.35(19)
P(4)–Ir(1)–N(6)	91.98(24)
P(4)–Ir(1)–C(7)	94.3(3)
O(5)–Ir(1)–N(6)	85.4(3)
O(5)–Ir(1)–C(7)	88.3(3)
N(6)–Ir(1)–C(7)	173.4(4)
F(35)–O(5)–F(38)′	109.29(10)
F(36)–O(5)–F(38)′	116.97(11)
N(6)–C(32)–C(33)	178.8(11)

general contention that hydrogen bonding occurs in such a way that every proton forms a hydrogen bond.

Reactivity of $[IrMe(NCMe)(H_2O)P_3](BF_4)_2$ (5)

Compound **5** is insoluble in D_2O and in those organic solvents with which it does not react. This insolubility must originate from the hydrogen bonding present in the solid state. Neither does it dissolve in THF in the presence of CO or of 4-picoline. However, **5** readily dissolves (with reaction) in neat acetonitrile or a CH_2Cl_2/CH_3CN solution. An NMR tube charged with a CD_3CN solution of **5** monitored by ^1H NMR (25°C) shows a quantitative yield of $IrMe(NCCD_3)(NCMe)P_3^{2+}$. This isotopomer has only the upfield protio CH_3CN resonance.

Discussion

There are two relevant comparison compounds for the structure of $[IrMe(NCMe)(H_2O)(PMe_2Ph)_3](BF_4)_2$ reported here. [*trans*-$Ir(H)(Cl)(CO)(H_2O)(PPh_3)_2](BF_4)_2$ exhibits [8] hydrogen bonding between H_2O and BF_4^- with O/F distances of 2.62 and 2.86 Å; the Ir–OH_2 distance is 2.252(7) Å, with water *trans* to hydride. [*trans,mer*-$IrCl_2(OH_2)(PMe_2Ph)_3]ClO_4$, with water *trans* to phosphine, shows [9] an Ir/O distance of 2.189(6) Å, identical to the value reported here.

Of primary value in the present study is the ability to compare protonolysis of analogous compounds which differ only in the group protonated, H or CH_3. Both protonolysis reactions are noteworthy in showing Brønsted basicity for a cation, which would normally be anticipated to have minimal basicity [10]. The methyl compound reacts more slowly than the hydride. The unsaturated elimination products are rapidly and efficiently scavenged by MeCN. In the absence of such a good ligand, the ligating power of the elimination products, H_2 and CH_4, control the subsequent events. Dihydrogen is a competent ligand, and so it can undergo redistribution with MeCN from starting reagent.

$$IrH(H_2)(MeCN)P_3^{2+} + IrH_2(MeCN)P_3^{+} \rightarrow IrH(MeCN)_2P_3^{2+} + IrH_4P_3^{+} \qquad (4)$$

Since CH_4 appears not to be a competent ligand, the slowly formed transient unsaturated dication $IrMe(MeCN)P_3^{2+}$ scavenges Et_2O, yielding compound **4**, and this Et_2O is subsequently replaced by adventitious water from the $HBF_4 \cdot OEt_2$. Since compound **5**, once formed (consider the hydrogen bonded chain structure) is completely insoluble in those solvents in which it is formed, we are somewhat reluctant to assert that **5** is identical with the species **D**. Either **D** is the aquo cation $IrMe(NCMe)(H_2O)P_3^{+}$, or it is a precursor to **5** in being an isomeric form, or due to BF_4^- or CH_2Cl_2 coordinated in place of the Et_2O ligand of **4**.

The Brønsted basicity of monocations has its limits. Thus, we find (^{31}P NMR) no change over 90 h when 1.1 mol of $HBF_4 \cdot OEt_2$ is added to 1 mol of $IrMe_2(CO)P_3^{+}$ in CD_2Cl_2 at 25°C.

Supplementary material. Full crystallographic details, anisotropic thermal parameters, and observed and calculated structure factors (11 pages) are available from one of the authors (KGC).

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References

1 L.F. Rhodes, J.D. Zubkowski, K. Folting, J.C. Huffman and K.G. Caulton, Inorg. Chem., 21 (1982) 4185.
2 J.W. Bruno, J.C. Huffman and K.G. Caulton, J. Am. Chem. Soc., 106 (1984) 1663.
3 E.G. Lundquist, K. Folting, J.C. Huffman and K.G. Caulton, Organometallics, 9 (1990) 2254.
4 E.G. Lundquist, K. Folting, W.E. Streib, J.C. Huffman, O. Eisenstein and K.G. Caulton, J. Am. Chem. Soc., 112 (1990) 855.
5 D.J. Rauscher, E.G. Thaler, J.C. Huffman and K.G. Caulton, Organometallics, 10 (1991) 2209.
6 D.E. Westerberg, L.F. Rhodes, J. Edwin, W.E. Geiger and K.G. Caulton, Inorg. Chem., 30 (1991) 1107.
7 J.C. Huffman, L.N. Lewis and K.G. Caulton, Inorg. Chem., 19 (1980) 2755.
8 H. Bauer, U. Nagel and W. Beck, J. Organomet. Chem., 290 (1985) 219.
9 A.J. Deeming, G.P. Proud, H.M. Davies and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1986) 2545.
10 For other examples of protonation of a cationic metal hydride, see: M.L.H. Green, L.C. Mitchard and W.E. Silverthorn, J. Chem. Soc., Dalton Trans., (1974) 1361; J. Halpern, D.P. Riley, A.S.C. Chan and J.J. Pluth, J. Am. Chem. Soc., 99 (1977) 8055.