

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

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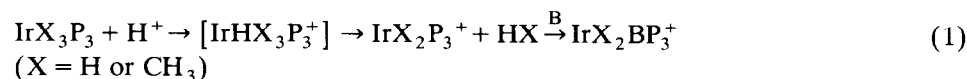
(Received August 9, 1991)

Abstract

Reaction of $\text{HBF}_4 \cdot \text{OEt}_2$ with $\text{IrH}_2(\text{MeCN})\text{P}_3^+$ (**1**) ($\text{P} = \text{PMe}_2\text{Ph}$) in the presence of MeCN gives rapid conversion to *cis,mer*- $\text{IrH}(\text{MeCN})_2\text{P}_3^{2+}$ and H_2 . The corresponding reaction with *cis,mer*- $\text{IrMe}_2(\text{MeCN})\text{P}_3^+$ is much slower, but gives the corresponding product, *cis,mer*- $\text{IrMe}(\text{MeCN})_2\text{P}_3^{2+}$. In the absence of added MeCN, $\text{HBF}_4 \cdot \text{OEt}_2$ transforms the dihydride cation **1** to equimolar *cis,mer*- $\text{IrH}(\text{MeCN})_2\text{P}_3^{2+}$ 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*- $\text{IrMe}(\text{Et}_2\text{O})(\text{MeCN})\text{P}_3^{2+}$, which is subsequently scavenged by adventitious water to yield *mer*- $\text{IrMe}(\text{H}_2\text{O})(\text{MeCN})\text{P}_3^{2+}$. The crystal structure of this aquo complex, as its BF_4^- salt, shows a chain of $\text{BF}_4^-/\text{IrMe}(\text{H}_2\text{O})(\text{MeCN})\text{P}_3^{2+}$ units held together by two hydrogen bonds to each water molecule. Crystallographic data for $[\text{IrMe}(\text{H}_2\text{O})(\text{NCMe})(\text{PMe}_2\text{Ph})_3](\text{BF}_4)_2$ (at -169°C): $a = 10.709(3)$ Å, $b = 15.645(4)$, $c = 10.481(2)$, $\beta = 106.49(1)^\circ$ 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].



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; Et₂O was dried with NaK/benzophenone. Methylene chloride-*d*₂ and NCCD₃ were dried over CaH₂ prior to use and stored in the glovebox. HBF₄ · OEt₂ (Aldrich, 85%) was used as received. IrH₃(PMe₂Ph)₃ and IrMe₃(PMe₂Ph)₃ were synthesized according to literature methods [1,6], starting from IrCl₃ · xH₂O. ¹H (360 MHz) and ³¹P (146 MHz) NMR were obtained on a Nicolet NT-360 instrument. Negative ³¹P NMR chemical shifts are upfield from external 85% H₃PO₄.

Synthesis of *cis,mer*-[IrH₂(NCMe)(PMe₂Ph)₃]BF₄ (1)

A 100 mL flask containing 150 mg (0.21 mmol) of [IrH₄P₃]BF₄ (generated [1] *in situ* from *fac*-IrH₃P₃ and HBF₄ · OEt₂) in 50 mL of CH₂Cl₂ 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 Et₂O 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, CD₂Cl₂): 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). ³¹P{¹H} NMR (24°C, CD₂Cl₂): δ –31.32 (d, *J*(PP) = 18 Hz, 2P), –39.67 (t, *J*(PP) = 18 Hz, 1P).

Synthesis of *cis,mer*-[IrH(NCMe)₂(PMe₂Ph)₃](BF₄)₂ (2)

A 100 mL flask containing 121 mg (0.164 mmol) of [IrH₂(NCMe)P₃]BF₄ in 50 mL of CH₂Cl₂ was charged with 0.5 mL (9.6 mmol) of acetonitrile and 20 mL of HBF₄ · OEt₂ (0.164 mmol). After stirring for 1 h, the volume was reduced to 5 mL *in vacuo*. To the concentrated solution, 40 mL of Et₂O 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, CD₂Cl₂): δ 7.5–7.0 (m, PPh), 2.72 (s, 3H), 2.36 (s, 3H), 1.64 (virtual triplet, 6H), 1.60 (virtual triplet, 6H), 1.46 (d, *J*(PMe) = 8 Hz, 6H), –20.25 (dt, *J*(PH) = 17, 14 Hz, 1H). ³¹P{¹H} NMR (CD₂Cl₂): δ –28.39 (d, *J*(PP) = 20 Hz, 2P), –41.12 (t, *J*(PP) = 20 Hz, 1P).

Synthesis of *cis,mer*-[IrMe₂(NCMe)(PMe₂Ph)₃]BF₄ (3)

To a Schlenk flask containing 30 mL of dry CH₂Cl₂ was added 150 mg (0.25 mmol) of IrMe₃(PMe₂Ph)₃; 28 μL (22 mg, 0.54 mmol) of acetonitrile was added via syringe followed by 31 μL (0.25 mmol) of HBF₄ · OEt₂. The solution was stirred for 30 min and then pumped dry to yield a white solid which was then washed with 10 mL of Et₂O. The remaining white powder was pumped dry to yield 130 mg (0.16 mmol, 64% yield) of [IrMe₂(NCMe)(PMe₂Ph)₃]BF₄. ³¹P{¹H} NMR in CD₂Cl₂: δ –35.4 (d, *J*(PP) = 16 Hz), –49.1 (t, *J*(PP) = 16 Hz). ¹H NMR in CD₂Cl₂: 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 $[\text{IrMe}(\text{NCMe})(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3](\text{BF}_4)_2$

Chemical formula	$\text{C}_{27}\text{H}_{41}\text{B}_2\text{F}_8\text{NOP}_3\text{Ir}$	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)	$\rho_{\text{calc.}}$ (g cm^{-3})	1.708
β (deg)	106.49(1)	$\mu(\text{Mo-K}\alpha)$ (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, $J(\text{PMe}) = 7.9$ Hz, $J(\text{PMe}) = 5.0$ Hz), 0.21 (apparent quartet, 7.6 Hz), 7.3 (phenyl multiplet).

Synthesis of mer-[Ir(Me)(NCMe)(H₂O)(PMe₂Ph)₃](BF₄)₂

To a Schlenk tube containing 10 mL of dry CH_2Cl_2 was added 94 mg (0.12 mmol) of $[\text{IrMe}_2(\text{NCMe})(\text{PMe}_2\text{Ph})_3]\text{BF}_4$; 30 μL (0.25 mmol) of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ 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-[Ir(Me)(NCMe)(H₂O)(PMe₂Ph)₃](BF₄)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 ($1.6 \text{ e}/\text{\AA}^3$) 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 $\text{B}(41)\text{F}_4^-$ is ordered and not hydrogen bonded.

Synthesis of cis,mer-[Ir(Me)(NCMe)₂(PMe₂Ph)₃](BF₄)₂ (6)

One millimole of $[\text{Ir}(\text{Me})(\text{NCMe})(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3](\text{BF}_4)_2$ 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)(H₂O)(PMe₂Ph)₃(BF₄)₂

	<i>x</i>	<i>y</i>	<i>z</i>	10 <i>B</i> _{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)	11 917(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)	10 283(10)	1840(7)	9559(11)	26
C(17)	8369(13)	1144(8)	10 487(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)	11 027(14)	1161(8)	13 607(12)	43
C(22)	10 248(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)	10 974(10)	15
C(27)	9512(10)	3584(6)	11 680(10)	19
C(28)	9927(11)	3492(7)	13 019(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)	11 649(10)	19
C(32)	4992(9)	1773(6)	9298(10)	16
C(33)	4170(12)	1479(8)	10 010(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)

	<i>x</i>	<i>y</i>	<i>z</i>	10 <i>B</i> _{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*. ¹H NMR (CD₂Cl₂): 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-[IrMe₂(NCMe)(PMe₂Ph)₃]BF₄

[IrMe₂(NCMe)(PMe₂Ph)₃]BF₄ (53 mg, 0.066 mmol) was dissolved in 1 mL of CH₂Cl₂ and treated with 10 μ L (0.082 mmol) of HBF₄·OEt₂. The reaction was monitored by ³¹P{¹H} NMR. After 1 min, two new AM₂ patterns were evident, one of which (− 26.6 (d) and − 41.7 (t) ppm with *J* = 18) was due to IrMe(NCMe)(OEt₂)(PMe₂Ph)₃²⁺. The resonances of coordinated Et₂O in this ion at − 56°C in CD₂Cl₂ were at 4.19 ppm (q) and 1.36 ppm (t). The second AM₂ 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 AM₂ patterns remained. At 30 min, the spectrum was unchanged from that at 10 min.

Synthesis of cis,mer-[Ir(PMe₂Ph)₃(NCMe)(NCCD₃)(Me)](BF₄)₂

A small amount of [IrMe(NCMe)(H₂O)(PMe₂Ph)₃](BF₄)₂ was dissolved in CD₃CN. After 28 h, the ¹H 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

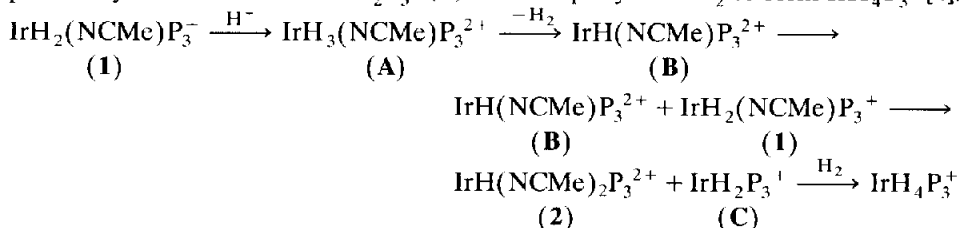
Characterization of cis,mer-[IrX(NCMe)₂P₃](BF₄)₂ (X = H, CH₃; P = PMe₂Ph)

Addition of excess HBF₄·OEt₂ to a CH₂Cl₂/CH₃CN solution of *cis,mer*-[IrH₂(NCMe)P₃](BF₄)₂ (**1**) results in visible gas evolution. After 15 min at 25°C, addition of Et₂O causes precipitation of a colorless solid. The ³¹P{¹H} NMR of this material in CD₂Cl₂ shows an AB₂ pattern. The ¹H 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)₂P₃](BF₄)₂ (**2**), containing an 18-electron dication. Treatment of IrH₃P₃ with 2.0 equiv. of HBF₄·OEt₂ in CH₂Cl₂/CH₃CN also yielded complex **2**.

Addition of excess HBF₄·OEt₂ to a CH₂Cl₂/CH₃CN solution of *cis,mer*-[IrMe₂(NCMe)P₃](BF₄)₂ (**3**) causes no visible gas evolution. After 24 h at 25°C, addition of Et₂O causes precipitation of a colorless solid. The ³¹P{¹H} NMR of this powder in CD₂Cl₂ shows an AB₂ pattern. The ¹H 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*(PCH₃) = 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)₂P₃](BF₄)₂ (**6**). Treatment of IrMe₃P₃ with 2.5 equiv. of HBF₄·OEt₂ in CH₂Cl₂/NCMe also yielded complex **6**.

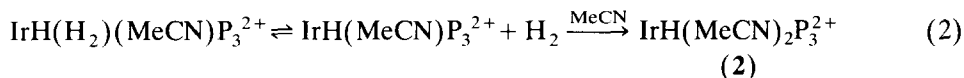
Mechanism of acidolysis of cis,mer-IrH₂(NCMe)P₃⁺ in the absence of MeCN

Protonation of *cis,mer*-IrH₂(NCMe)P₃⁺ (**1**) with 1 equiv. of HBF₄·OEt₂ in CD₂Cl₂ at 25°C occurs rapidly (within 1 s) and a visible amount of gas (H₂) is liberated. The ¹H and ³¹P{¹H} NMR spectra reveal the presence of equimolar amounts of IrH(NCMe)₂P₃²⁺ (**2**), IrH₄P₃⁺ and unreacted HBF₄·OEt₂. These data suggest that an IrH₃(NCMe)P₃²⁺ (**A**) species loses H₂ to create an unsaturated IrH(NCMe)P₃²⁺ transient (**B**), which scavenges 1 equiv. of acetonitrile from IrH₂(NCMe)P₃⁺ (**1**) to yield **2** and IrH₂P₃⁺ (**C**). The unsaturated hydride **C** then scavenges H₂ to generate IrH₄P₃⁺ (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 HBF₄·OEt₂. The products of this reaction are equimolar **2** and IrH₄P₃⁺. It has previously been shown that IrH₂P₃⁺ (**C**) reacts rapidly with H₂ to form IrH₄P₃⁺ [4].



Scheme 1

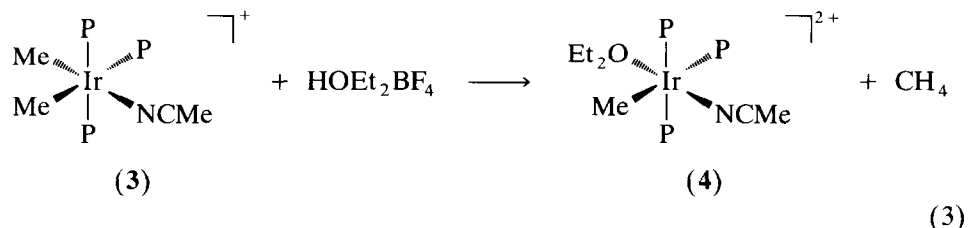
In an attempt to detect the trihydride transient **A**, **1** and $\text{HBF}_4 \cdot \text{OEt}_2$ were flame sealed in an NMR tube in CD_2Cl_2 under excess (approx. 4 equiv.) H_2 at -196°C . The NMR tube was placed in an NMR probe pre-cooled to -80°C for ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR data acquisition. No resonances consistent with an $\text{IrH}_3(\text{NCMe})\text{P}_3^{2+}$ formulation were observed after four ^1H NMR pulses. Only **1**, **2**, IrH_4P_3^+ , H_2 and $\text{HBF}_4 \cdot \text{OEt}_2$ were present in solution. Since this reaction is so fast, we propose that $\text{IrH}_3(\text{MeCN})\text{P}_3^{2+}$ is actually the dihydrogen complex $\text{IrH}(\text{H}_2)(\text{MeCN})\text{P}_3^{2+}$ (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.



*Mechanism of acidolysis of cis,mer-IrMe₂(NCMe)P₃⁺ (**3**) in the absence of MeCN*

The mechanism of production of $\text{IrMe}(\text{NCMe})_2\text{P}_3^{2+}$ (**6**) by acidolysis of **3** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ can be understood based on experiments executed in the absence of MeCN. Protonation of **3** with $\text{HBF}_4 \cdot \text{OEt}_2$ (1.5 equiv.) in CD_2Cl_2 at 25°C is conveniently monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR. Within the first minute after acidolysis, the $^{31}\text{P}\{^1\text{H}\}$ 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 $\text{HBF}_4 \cdot \text{OEt}_2$ (1.5 equiv.) and placed in a pre-cooled NMR probe at -55°C . From -50°C to -10°C only unreacted **3** and $\text{HBF}_4 \cdot \text{OEt}_2$ are present in solution. However, at -10°C , by $^{31}\text{P}\{^1\text{H}\}$ 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 ($J(\text{PCH}_3) = 36$ 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.



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

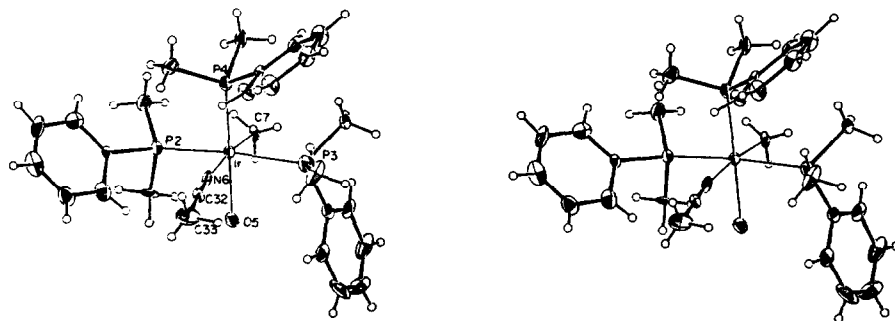


Fig. 1. Stereo ORTEP drawing of $\text{IrMe}(\text{H}_2\text{O})(\text{MeCN})(\text{PMe}_2\text{Ph})_3^{2+}$, showing selected atom labelling. Hydrogens of the water ligand (O5) were not located.

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 $[\text{IrMe}(\text{NCMe})(\text{H}_2\text{O})\text{P}_3](\text{BF}_4)_2$ (**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–CH₃ distance here (2.081(10) Å) is distinctly shorter than that (2.160(9) Å) in *fac*- $\text{IrMe}_3(\text{PMe}_2\text{Ph})_3$. 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 $\text{B}(34)\text{F}_4^-$ are involved in hydrogen bonding, the crystal structure is composed of infinite chains of $(\text{BF}_4\text{H}_2\text{OIr}(\text{NCMe})\text{Me}(\text{PMe}_2\text{Ph})_3)^+$ cations, together with isolated $\text{B}(41)\text{F}_4^-$ anions. Since this structure involves hydrogen bonding to both protons on the aquo ligand, it supports the

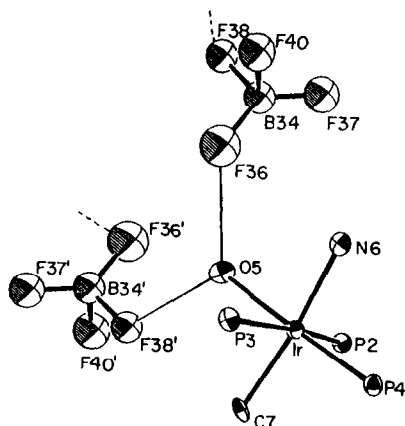


Fig. 2. Drawing of the hydrogen bonding of the $\text{IrMe}(\text{H}_2\text{O})(\text{MeCN})(\text{PMe}_2\text{Ph})_3^{2+}$ unit with two symmetry-related BF_4^- ions. Hydrogens of the water ligand (O5) were not located. Dotted lines show connection to symmetry-related iridium aquo cations.

Table 3

Selected bond distances (Å) and angles (deg) for $[\text{IrMe}(\text{NCMe})(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3](\text{BF}_4)_2$

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.

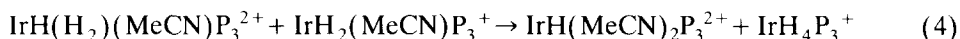
Reactivity of $[\text{IrMe}(\text{NCMe})(\text{H}_2\text{O})\text{P}_3](\text{BF}_4)_2$ (**5**)

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 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solution. An NMR tube charged with a CD_3CN solution of **5** monitored by ^1H NMR (25°C) shows a quantitative yield of $\text{IrMe}(\text{NCCD}_3)(\text{NCMe})\text{P}_3^{2+}$. This isotopomer has only the upfield protio CH_3CN resonance.

Discussion

There are two relevant comparison compounds for the structure of $[\text{IrMe}(\text{NCMe})(\text{H}_2\text{O})(\text{PMe}_2\text{Ph})_3](\text{BF}_4)_2$ reported here. $[\text{trans-Ir}(\text{H})(\text{Cl})(\text{CO})(\text{H}_2\text{O})(\text{PPh}_3)_2](\text{BF}_4)_2$ exhibits [8] hydrogen bonding between H_2O and BF_4^- with O/F distances of 2.62 and 2.86 Å; the Ir–OH₂ distance is 2.252(7) Å, with water *trans* to hydride. $[\text{trans,mer-IrCl}_2(\text{OH}_2)(\text{PMe}_2\text{Ph})_3]\text{ClO}_4$, 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 CH₃. 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, H₂ and CH₄, control the subsequent events. Dihydrogen is a competent ligand, and so it can undergo redistribution with MeCN from starting reagent.



Since CH₄ appears not to be a competent ligand, the slowly formed transient unsaturated dication $\text{IrMe}(\text{MeCN})\text{P}_3^{2+}$ scavenges Et₂O, yielding compound **4**, and this Et₂O is subsequently replaced by adventitious water from the HBF₄·OEt₂. 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 $\text{IrMe}(\text{NCMe})(\text{H}_2\text{O})\text{P}_3^+$, or it is a precursor to **5** in being an isomeric form, or due to BF₄[−] or CH₂Cl₂ coordinated in place of the Et₂O ligand of **4**.

The Brønsted basicity of monocations has its limits. Thus, we find (³¹P NMR) no change over 90 h when 1.1 mol of HBF₄·OEt₂ is added to 1 mol of $\text{IrMe}_2(\text{CO})\text{P}_3^+$ in CD₂Cl₂ 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).

Acknowledgement

This work was supported by the National Science Foundation. We thank Johnson Matthey Corp. for material support and Scott Horn for skilled technical assistance.

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.