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Iridium(III) Complex Containing a Unique Bifurcated Hydrogen Bond Interaction Involving Ir−H···H(N)···F−B atoms. Crystal and Molecular Structure of [IrH(η^1-SC$_5$H$_4$NH)(η^2-SC$_5$H$_4$N)(PPh$_3$)$_2$](BF$_4$)·0.5C$_6$H$_6$

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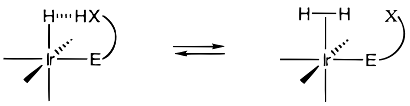
A synthetic route to a new iridium(III) complex containing a novel proton hydride bonding interaction has been established. *fac*-IrH$_3$(PPh$_3$)$_3$ reacts with 2-mercaptopyridine HSpy (Spy = 2-SC$_5$H$_4$N) to give the known dihydride Ir(H)$_2$(η^2-Spy)(PPh$_3$)$_2$ **8**. Ir(H)$_2$(η^2-Spy)(PPh$_3$)$_2$ reacts with HSpy·HBF$_4$ to give [IrH(η^1-SC$_5$H$_4$NH)(η^2-SC$_5$H$_4$N)(PPh$_3$)$_2$](BF$_4$) **9** which possesses a unique bifurcated hydrogen bonding interaction involving Ir−H···H(N)···F−B atoms with the distances of 2.0(1) Å for the H···H unit and of 2.0(1) Å for the F···H unit in the crystalline state. In solution the N−H···H−Ir interaction is maintained according to ^{1}H T_1(min) and nOe measurements. Isotope shifts in the chemical shifts of the hydride and one phosphorus of **9** have been observed in ^{1}H and ^{31}P{^{1}H} NMR spectra of [IrH(η^1-SC$_5$H$_4$ND)(η^2-SC$_5$H$_4$N)(PPh$_3$)$_2$](BF$_4$), **9**-d_1, prepared by the reaction of **9** with MeOD or CF$_3$CO$_2$D. The crystal and molecular structure of [IrH(η^1-SC$_5$H$_4$NH)(η^2-SC$_5$H$_4$N)(PPh$_3$)$_2$](BF$_4$)·0.5C$_6$H$_6$ **9** has been solved by X-ray analysis: monoclinic space group $P2_1/c$ with a = 17.723(3) Å, b = 10.408(1) Å, c = 26.073(4) Å, β = 108.08(1)°, V = 4572.0(11) Å^3, and Z = 4. The known complex *fac*-IrH$_3$(PPh$_3$)$_3$, **7**, is made by a new and improved method by reacting *mer*-IrHCl$_2$(PPh$_3$)$_3$ with NaOEt and H$_2$(g). VT-^{1}H NMR spectra (+90 to −80 °C) of the hydrides of **7** reveal that the J_{AA} and J_{AX} couplings change in the AA′A″XX′X″ pattern (A = ^{1}H, X = ^{31}P) but that the complex is not fluxional. The T_1(min) value of 0.144 s for the hydrides of **7** at −60 °C (300 MHz) indicates that the shortest H-H distances are about 1.8 Å.

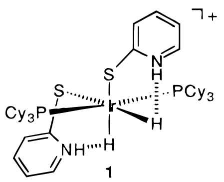
Introduction

A new intramolecular proton-hydride interaction was discovered recently by Crabtree's group[1] and us.[2] Such H···H interactions are potentially important as intermediates in the base-promoted heterolytic splitting of dihydrogen.[3]



So far complexes of the types **1**, **2**, **4**, and **5** have proton−hydride interactions at about 1.7−1.9 Å in solution as well as in the solid state. An iridium hydroxy complex **3** has been proposed to contain an Ir−H···H−O interaction at the longer H−H distance of 2.40(1) Å as determined in a single crystal neutron diffraction study.[4]

We have suggested[2a] that the H/D exchange between **1** and D$_2$ gas occurs via the intramolecular proton (NH) transfer to hydride to give a dihydrogen tautomer. In the presence of the H-bond acceptor THF, the NH groups of **1** are not correctly positioned for formation of such a dihydrogen tautomer and no H/D exchange is possible.



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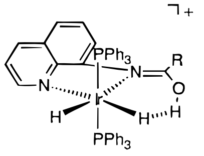

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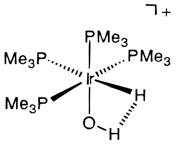

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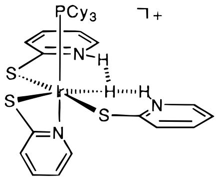

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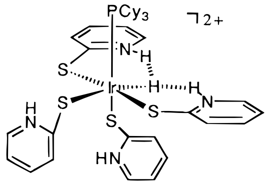

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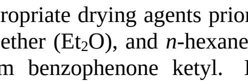
Here we report the preparation and characterization of an iridium(III) complex **9** containing a unique bifurcated hydrogen bonding interaction involving hydride, proton, nitrogen, and a fluorine atom of tetrafluoroborate anion.



Experimental Section

All preparations were carried out under an atmosphere of dry argon using conventional Schlenk techniques. All the solvents were distilled under argon over appropriate drying agents prior to use. Tetrahydrofuran (THF), diethyl ether (Et$_2$O), and *n*-hexane were dried over and distilled from sodium benzophenone ketyl. Ethanol (EtOH) and dichloromethane were distilled from magnesium ethoxide and calcium hydride, respectively. Deuterated solvents were dried over Linde type 4 Å molecular sieves and degassed prior to use. Triphenylphosphine, 2-mercaptopyridine, and an 85% solution of HBF$_4$·Et$_2$O complex were

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Table 1. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters for **9**

empirical formula	$C_{49}H_{43}BF_4IrN_2P_2S_2{\cdot}0.5C_6H_6$
M_r	1064.92
cryst class	monoclinic
space group	$P2_1/c$
a, Å	17.723(3)
b, Å	10.408(1)
c, Å	26.073(4)
β, deg	108.08(1)
V, Å^3	4572.0(11)
Z	4
D_{calc}, M gm^{-3}	1.547
μ(Mo Kα), mm^{-1}	3.134
F(000)	2124
θ range for data collcn, deg	2.56−27.00
T, K	173(2)
min., max. transm[a]	0.5297, 0.7937
no. of reflcns collcd	10290
no. of indep reflcns	9964
R_{int}	0.0453
no. of obsd. data [$I > 2\sigma(I)$]	6153
R1 [$I > 2\sigma(I)$][b]	0.0468
wR2 (all data)[c]	0.1156
params refined	556

[a] Absorption correction using SHELXA-90 in SHELXL-93.[6] [b] $R1 = \sum(F_o - F_c)/\sum F_o$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

purchased from Aldrich Chemical Co., Inc. Iridium trichloride hydrate was obtained from Johnson-Matthey Co. Sodium ethoxide was generated in the reaction of sodium metal with water-free ethanol under argon and dried to white powder before use.

NMR spectra were obtained on a Varian Unity-400, operating at 400.0 MHz for ^{1}H and 161.98 MHz for ^{31}P, or on a Varian Gemini-300, operating at 300.0 MHz for ^{1}H and 121.45 MHz for ^{31}P. All ^{31}P NMR spectra were obtained with proton decoupling unless otherwise stated. ^{31}P NMR chemical shifts were measured relative to H_3PO_4 as external reference. ^{1}H NMR chemical shifts were measured relative to deuterated solvent peaks or tetramethylsilane. Variable temperature T_1 measurements were made at 400 MHz using the inversion recovery method. Second order spectra were simulated using the program LAOCN-5.[5] IR spectra were recorded on a Nicolet 550 Magna-IR spectrometer. Fast atom bombardment mass spectrometry (FAB MS) was carried out with a VG 70-250S instrument using a 3-nitrobenzyl alcohol (NBA) matrix. All FAB MS samples were dissolved in acetone and placed in the matrix under a blanket of nitrogen. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Ontario, Canada.

X-ray Structural Determination. Intensity data for **9** were collected on an Siemens P4 diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The ω scan technique was applied with variable scan speeds. Intensities of three standards measured every 97 reflections showed no decay. Data were corrected for Lorentz and polarization effects and for absorption.[6] The Ir atom position was solved by the Patterson method, and other non-hydrogen atoms were located by successive difference Fourier syntheses. Non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2 (negative intensities included). Hydrogen atoms were positioned on geometric grounds (C−H 0.96 Å, U_{iso} = 0.029(3) Å^2). The N−H hydrogen and the Ir-hydride hydrogen were refined with isotropic thermal parameters. Crystal data, data collection, and least-squares parameters are listed in Table 1. All calculations were done and diagrams created using SHELXL-93[6] and SHELXTL/PC[7] on a 486-66 personal computer. A view of complex **9**, including the crystallographic labeling scheme is shown in Figure 1.

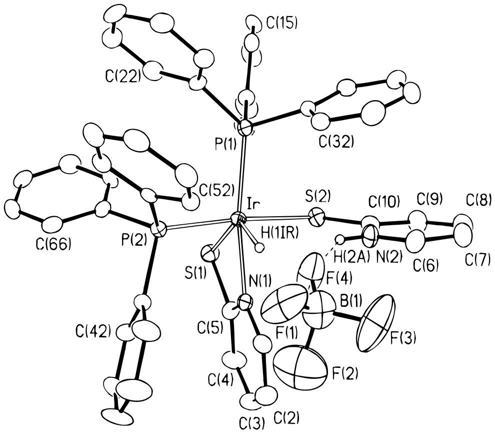

Figure 1. Structure of the cation and anion of **9** which also shows the N−H···F−B interaction. The hydrogen on the nitrogen of the pyridiniumthiolate and the hydride ligand are well defined in Fourier difference maps.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **9**

Ir−N(1)	2.080(6)	Ir−P(2)	2.291(2)
Ir−P(1)	2.304(2)	Ir−S(2)	2.394(2)
Ir−S(1)	2.535(2)	Ir−H(1Ir)	1.72(11)
S(2)−C(10)	1.730(8)	S(1)−C(5)	1.741(7)
P(1)−C(11)	1.828(7)	P(1)−C(21)	1.831(7)
P(1)−C(31)	1.843(7)	P(2)−C(41)	1.826(7)
P(2)−C(61)	1.827(7)	P(2)−C(51)	1.833(7)
N(1)−C(5)	1.352(10)	N(1)−C(1)	1.320(9)
N(2)−C(10)	1.354(10)	N(2)−C(6)	1.349(10)
N(2)···F(4)	2.778(8)	N(2)−H(2A)	0.94(8)
C(2)−C(3)	1.393(11)	C(1)−C(2)	1.374(10)
C(4)−C(5)	1.412(10)	C(3)−C(4)	1.391(11)
C(7)−C(8)	1.370(11)	C(6)−C(7)	1.344(11)
C(9)−C(10)	1.383(10)	C(8)−C(9)	1.381(12)
B(1)−F(4)	1.316(13)	B(1)−F(3)	1.36(2)
B(1)−F(1)	1.326(14)	B(1)−F(2)	1.48(2)
F(4)···H(1Ir)	2.30(11)	F(4)···H(2A)	1.96(8)
H(1Ir)···H(2A)	2.05(13)		

N(1)−Ir−P(2)	90.1(2)	N(1)−Ir−P(1)	170.7(2)
P(2)−Ir−P(1)	99.07(7)	N(1)−Ir−S(2)	85.2(2)
P(2)−Ir−S(2)	175.03(7)	P(1)−Ir−S(2)	85.2(2)
N(1)−Ir−S(1)	66.4(2)	P(2)−Ir−S(1)	93.87(7)
P(1)−Ir−S(1)	114.26(6)	S(2)−Ir−S(1)	82.95(7)
N(1)−Ir−H(1Ir)	69(4)	P(2)−Ir−H(1Ir)	82(4)
P(1)−Ir−H(1Ir)	111(4)	S(2)−Ir−H(1Ir)	98(4)
S(1)−Ir−H(1Ir)	135(4)	F(4)···H(1Ir)−Ir	164(6)
C(5)−S(1)−Ir	77.7(3)	C(10)−S(2)−Ir	114.4(3)
C(11)−P(1)−C(21)	100.3(3)	C(11)−P(1)−C(31)	104.1(3)
C(21)−P(1)−C(31)	104.4(3)	C(11)−P(1)−Ir	116.5(2)
C(21)−P(1)−Ir	122.0(2)	C(31)−P(1)−Ir	107.7(2)
C(51)−P(2)−Ir	114.7(2)	C(41)−P(2)−Ir	112.3(2)
C(1)−N(1)−C(5)	120.2(6)	C(61)−P(2)−Ir	119.0(2)
C(5)−N(1)−Ir	104.7(5)	C(1)−N(1)−Ir	134.9(5)
C(10)−N(2)−H(2A)	127(5)	C(6)−N(2)−C(10)	123.5(7)
N(1)−C(1)−C(2)	122.6(7)	C(6)−N(2)−H(2A)	110(5)
C(4)−C(3)−C(2)	121.5(7)	C(1)−C(2)−C(3)	117.8(7)
N(1)−C(5)−C(4)	121.8(7)	C(3)−C(4)−C(5)	116.1(8)
C(4)−C(5)−S(1)	127.3(6)	N(1)−C(5)−S(1)	110.9(5)
N(2)−C(10)−S(2)	122.7(6)	C(9)−C(10)−S(2)	121.3(6)
F(4)−B(1)−F(1)	118.9(12)	F(4)−B(1)−F(3)	114.1(11)
F(1)−B(1)−F(3)	116.4(10)	F(4)−B(1)−F(2)	99.6(10)
F(1)−B(1)−F(2)	102.7(11)	F(3)−B(1)−F(2)	100.4(11)
H(1Ir)···F(4)−B(1)	149(3)	H(1Ir)···F(4)···H(2A)	57(3)
F(4)···H(2A)−N(2)	144(7)	H(2A)···F(4)−B(1)	148.1(24)

Synthesis of crude *mer*-$IrHCl_2(PPh_3)_3$, 6. $IrCl_3{\cdot}3H_2O$ (1.0 g, 2.84 mmol) was suspended in EtOH (15 mL) in a Schlenk flask containing a stirring bar under argon. To this was slowly added concentrated hydrochloric acid (1.8 mL) while the suspension was stirred. Heating at reflux for 5 h produced a dark greenish yellow solution. This was then cooled to room temperature, and then 3 equiv of triphenylphosphine (1.49 g, 5.68 mmol) was added. The solution was again refluxed for a further 12 h to produce a pale yellow precipitate. After the solution was cooled to 0 °C, the product was filtered in air and washed

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Table 3. Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [$Å^2 \times 10^3$] for **9**[a]

	x	*y*	*z*	*U*(eq)
Ir	2404(1)	1468(1)	788(1)	16(1)
S(1)	1808(1)	−760(2)	735(1)	24(1)
S(2)	1253(1)	2066(2)	1027(1)	22(1)
P(1)	3117(1)	2108(2)	1648(1)	17(1)
P(2)	3434(1)	803(2)	497(1)	17(1)
N(1)	1606(3)	1035(6)	36(2)	20(1)
N(2)	1249(4)	4385(7)	551(3)	27(2)
C(1)	1325(4)	1658(8)	−425(3)	25(2)
C(2)	741(5)	1161(8)	−858(3)	29(2)
C(3)	430(5)	−38(9)	−796(3)	34(2)
C(4)	707(5)	−725(9)	−316(3)	32(2)
C(5)	1320(4)	−139(8)	98(3)	24(2)
C(6)	1016(5)	5607(8)	418(3)	30(2)
C(7)	426(5)	6119(8)	574(3)	32(2)
C(8)	43(5)	5375(9)	849(3)	34(2)
C(9)	288(5)	4124(9)	978(3)	32(2)
C(10)	924(4)	3616(8)	845(3)	23(2)
C(11)	2942(4)	1208(7)	2203(3)	20(2)
C(12)	2408(5)	212(8)	2110(3)	27(2)
C(13)	2250(6)	−459(9)	2528(3)	38(2)
C(14)	2656(6)	−74(8)	3060(3)	36(2)
C(15)	3186(5)	906(8)	3157(3)	28(2)
C(16)	3341(4)	1573(8)	2740(3)	23(2)
C(21)	4203(4)	2167(7)	1876(3)	20(2)
C(22)	4622(5)	1038(7)	2064(3)	26(2)
C(23)	5458(5)	1021(8)	2213(3)	29(2)
C(24)	5878(5)	2110(9)	2191(3)	29(2)
C(25)	5467(5)	3240(8)	2024(3)	30(2)
C(26)	4634(4)	3287(7)	1861(3)	24(2)
C(31)	2811(4)	3761(7)	1742(3)	19(2)
C(32)	2937(5)	4733(8)	1417(3)	26(2)
C(33)	2632(5)	5960(8)	1432(4)	39(2)
C(34)	2187(5)	6222(8)	1759(3)	40(2)
C(35)	2068(5)	5253(9)	2098(3)	36(2)
C(36)	2373(5)	4052(8)	2086(3)	29(2)
C(41)	3114(4)	435(7)	−224(3)	17(2)
C(42)	2758(4)	−754(8)	−389(3)	25(2)
C(43)	2492(5)	−1089(8)	−927(3)	32(2)
C(44)	2585(6)	−244(9)	−1310(3)	42(2)
C(45)	2921(6)	948(9)	−1162(3)	43(2)
C(46)	3196(5)	1284(8)	−616(3)	34(2)
C(51)	4217(4)	2003(7)	566(3)	16(2)
C(52)	3986(4)	3267(7)	413(3)	20(2)
C(53)	4540(5)	4204(8)	445(3)	27(2)
C(54)	5353(5)	3909(8)	640(3)	27(2)
C(55)	5594(5)	2676(8)	795(3)	29(2)
C(56)	5027(4)	1729(7)	762(3)	22(2)
C(61)	3959(4)	−678(7)	771(3)	17(2)
C(62)	3864(4)	−1248(7)	1232(3)	22(2)
C(63)	4291(5)	−2340(8)	1447(3)	29(2)
C(64)	4776(5)	−2893(8)	1195(3)	30(2)
C(65)	4869(5)	−2355(8)	732(3)	28(2)
C(66)	4461(5)	−1253(8)	521(3)	27(2)
B(1)	2210(9)	5303(13)	−532(6)	59(4)
F(1)	2891(3)	5504(8)	−630(2)	86(3)
F(2)	1797(6)	4386(10)	−963(3)	126(3)
F(3)	1686(4)	6290(7)	−643(3)	100(3)
F(4)	2212(4)	4626(6)	−105(2)	68(2)
C(1S)	659(12)	1218(22)	−2236(9)	50(11)
C(2S)	−45(14)	778(18)	−2599(9)	26(7)
C(3S)	−568(11)	1641(22)	−2936(8)	49(10)
C(4S)	−386(11)	2943(21)	−2911(8)	4(5)
C(5S)	319(13)	3382(18)	−2547(9)	85(16)
C(6S)	842(11)	2520(24)	−2210(9)	26(7)
C(7S)	40(15)	1503(19)	−2683(10)	89(17)
C(8S)	−525(11)	2379(22)	−2972(7)	9(5)
C(9S)	−441(11)	3677(20)	−2841(8)	25(7)
C(10S)	207(13)	4099(19)	−2421(9)	40(9)
C(11S)	772(11)	3224(25)	−2132(8)	38(9)
C(12S)	688(13)	1926(23)	−2263(9)	33(8)
H(1IR)	2367(64)	2675(108)	333(42)	94(39)
H(2A)	1682(45)	4188(74)	429(29)	22(21)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

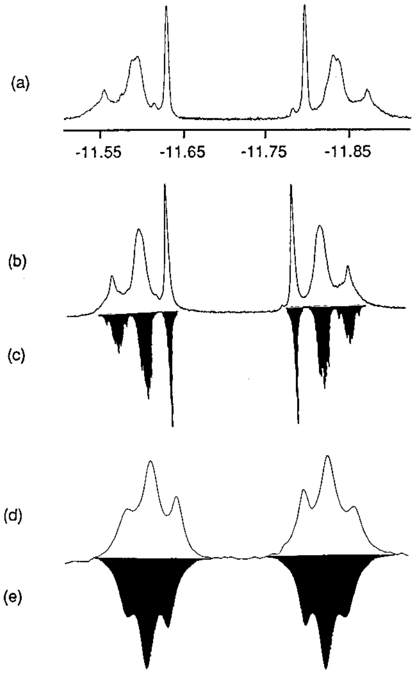


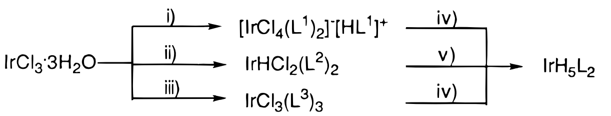
Figure 2. ^1H NMR spectra at 500 MHz of the hydride resonance of *fac*-Ir(H)$_3$(PPh$_3$)$_3$ in toluene-d_8: (a) spectrum at 90 °C; (b) spectrum at 25 °C; (c) simulation of b; (d) spectrum at −40 °C; (e) simulation of d.

with two portions of cold ethanol and dried *in vacuo*. The product was a pale yellow powder containing a mixture of a major (*mer*-IrHCl$_2$(PPh$_3$)$_3$ **6**) and minor species. Yield: 2.3 g (77% based on *mer*-IrHCl$_2$(PPh$_3$)$_3$). This was used without further purification as indicated below. Spectroscopic data for *mer*-IrHCl$_2$(PPh$_3$)$_3$ follow. NMR (CD$_2$Cl$_2$, δ): $^{31}P\{^1H\}$, −8.9 (d, J_{PP} = 13.3 Hz), −29.1 (t, J_{PP} = 13.3 Hz); ^1H, −13.88 (dt, 1H, $^2J_{PH(cis)}$ = 16.4 Hz, $^2J_{PH(trans)}$ = 162 Hz, Ir−*H*), 6.8−8.0 {m, 45H, P(C$_6$*H*$_5$)$_3$}. NMR (CDCl$_3$, δ) for the minor species: $^{31}P\{^1H\}$, 6.7 (d, J = 13.5 Hz, Int. = 0.02 relative to total intensity of 3 in complex **6**), −1.8 (d, J = 16.4 Hz, Int. = 0.1), −6.8 (t, J = 16.4 Hz, Int. = 0.04); ^1H, −19.16 (quartet, J = 14.1 Hz, Int. = 0.14 relative to intensity of one hydride in complex **6**). MS(FAB), *m*/*z*: calculated for $C_{54}H_{46}{}^{35}Cl_2{}^{193}IrP_3$, 1050; observed, 1049 (M$^+$ − H), 1015 (M$^+$ − Cl), 979 (M$^+$ − 2Cl).

Synthesis of *fac*-Ir(H)$_3$(PPh$_3$)$_3$, 7. The crude *mer*-IrHCl$_2$(PPh$_3$)$_3$ (1.0 g, *ca.* 0.63 mmol) and a large excess of dried sodium ethoxide (0.8 g, 12 mmol) were suspended in THF (15 mL) in a Schlenk flask containing a stirring bar under dihydrogen gas. After 30 min the stirred solution became orange-yellow and over a period of 24 h slowly turned pale yellow. All the solvent was then evaporated to dryness. To the residue obtained was added a sufficient amount (*ca.* 20 mL) of degassed distilled water to dissolve up sodium salts and this was stirred for 30 min before filtering under argon. The product was washed under argon twice with water (*ca.* 5 mL) and then cold ethanol (*ca.* 1 mL) and dried *in vacuo*. Finally the pale yellow powder was similarly washed with ether several times (3 × 5 mL) until filtrate was clear and the product was gray-white (0.95 g, 76%). NMR (CDCl$_3$, δ): $^{31}P\{^1H\}$, 30.05 (s); ^1H, −12.25 (AA′A″XX′X″, simulated, see Figure 2, Ir−*H*), 6.8−7.8 (m, 45H, P(C$_6$*H*$_5$)$_3$). MS(FAB), *m*/*z*: calculated for $C_{54}H_{48}{}^{193}IrP_3$, 982; observed, 982 (M$^+$), 979 (M$^+$ − 3H).

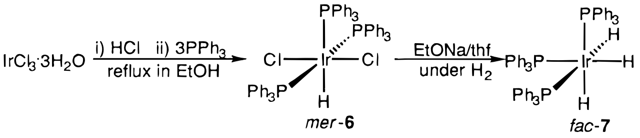
Synthesis of Ir(H)$_2$(η^2-SC$_5$H$_4$N)(PPh$_3$)$_2$, 8. *fac*-Ir(H)$_3$(PPh$_3$)$_3$ (1.0 g, 1.02 mmol) and excess 2-mercaptopyridine (0.218 g, 1.96 mmol) in benzene (15 mL) were placed in a Schlenk flask containing a magnetic stirring bar under argon. This was stirred and refluxed for 12 h and then the solvent was evaporated *in vacuo* to dryness. The residue was redissolved in CHCl$_3$ and filtered through Celite. Following removal of the solvent, the resulting powder was stirred for *ca.* 15 min with ether (*ca.* 5 mL) several times until the filtrate turned from yellow to colorless and then dried to give a yellowish white powder. Yield: 0.75 g, 89% based on *mer*-Ir(H)$_3$(PPh$_3$)$_3$. Anal. Calcd for C$_{41}$H$_{36}$IrNP$_2$S + CHCl$_3$: C, 53.22; H, 3.94; N, 1.48. Found: C, 53.78; H, 4.11; N, 1.74. IR(Nujol): ν(Ir−H) 2157 (w), 2111 (m) cm^{-1}. NMR: $^{31}P\{^1H\}$

Scheme 1[a]



Key: (i) HCl/EtOH/L^1; (ii) HCl/EtOH/L^2; (iii) HCl/EtOH/L^3; (iv) $LiAlH_4$/THF; (v) EtONa/THF; $L^1 = P^iPr_3$, $L^2 = PCy_3$, $L^3 = PPh_2Me$.

Scheme 2



(C_6D_6, δ), 21.3 (s); ^1H (CD_2Cl_2, δ), −21.0 (td, 1H, $J_{PH} = 16.6$ Hz, $J_{HH} = 6.8$ Hz, Ir*H*), −21.17 (td, 1H, $J_{PH} = 17.5$ Hz, $J_{HH} = 6.8$ Hz, Ir*H*), 5.80 (br t, 1H, $J = 6.4$ Hz, SC_5H_4N), 5.98 (br d, 1H, $J = 8.2$ Hz, SC_5H_4N), 6.51 (br d, 1H, $J = 5.5$ Hz, SC_5H_4N), 6.65 (br t, 1H, $J = 7.7$ Hz, SC_5H_4N), 7.0−7.9 {m, 30H, P*Ph*$_3$}, MS(FAB), *m/z*: calculated for $C_{41}H_{36}{}^{193}IrNP_2S$, 829; observed, 829 ($M^+$), 827 ($M^+ - 2H$).

Synthesis of *cis*-$[IrH(\eta^1\text{-}SC_5H_4NH)(\eta^2\text{-}SC_5H_4N)(PPh_3)_2](BF_4)$, 9. $Ir(H)_2(\eta^2\text{-}SC_5H_4N)(PPh_3)_2$ (100 mg, 0.12 mmol) and 1.5 equiv of 2-mercaptopyridine (20 mg, 0.18 mmol) were dissolved in dichloromethane (5 mL) in a Schlenk flask under argon. While the solution was being stirred, 85% $HBF_4{\cdot}Et_2O$ (*ca.* 80 μL) was slowly added through a septum using a syringe. After 10 min the solution was filtered through Celite under Ar. The solvent was then evaporated *in vacuo* to dryness. To the residue was added 5 mL of ether, and this mixture was swirled until the precipitation of a pale yellow powder. The powder was washed with ether (*ca.* 3 mL) twice more before drying to give a pale yellow powder. Yield: (110 mg, 89%). Anal. Calcd for $C_{46}H_{40}BF_4IrN_2P_2S_2 + CH_2Cl_2$: C, 50.8; H, 3.81; N, 2.52. Found: C, 49.45; H, 3.96; N, 2.88. IR(Nujol): ν(N−H) 3236 (m), ν(Ir−H) 2214 (m) cm^{-1}. NMR (CD_2Cl_2, δ): $^{31}P\{^1H\}$, −11.4 (d, $J_{PP} = 16.3$ Hz), 10.6 (d, $J_{PP} = 16.3$ Hz); ^1H, −17.82 (dd, 1H, $J_{HP} = 14.3$ Hz, Ir*H*), 6.3−8.8 (m, overlapping, 9H, SC_5H_4N and SC_5H_4NH), 7.0−7.6 (m, overlapping, 30H, P*Ph*$_3$), 12.03 (br s, 1H, N*H*). MS(FAB), *m/z*: calculated for $C_{46}H_{40}{}^{193}IrN_2P_2S_2$, 939; observed, 939 ($M^+$), 828 ($M^+ - HSC_5H_4N$).

Results and Discussion

Crude *mer*-$IrHCl_2(PPh_3)_3$ **6**,[8,9] has been prepared from the reaction of a refluxing ethanolic solution of iridium trichloride with concentrated hydrochloric acid and triphenylphosphine under argon. The major product is *mer*-$IrHCl_2(PPh_3)_3$ **6** with three *mer*-phosphine ligands and two *trans* chlorides, based on the $^{31}P\{^1H\}$ and proton NMR spectra. In fact, this type of reaction has been used before,[10−12] but the products depended on the kind of phosphine ligand. For example, iridium(III) complexes $[IrCl_4(P^iPr_3)_2][HP^iPr_3]$, **10**,[10] $IrHCl_2(PCy_3)_2$, **11**,[11] and $IrCl_3(PPh_2Me)_3$, **12**,[12] have been obtained in such reactions. All of these complexes have been used as precursors to iridium pentahydrides according to Scheme 1. However, the reaction of **6** under reducing condition (NaOEt/THF/H_2) produced the trihydride **7** instead of the pentahydride complex $IrH_5(PPh_3)_2$, **13** (Scheme 2). This product has been assigned as an iridium(III) complex possessing three triphenylphosphine ligands and three hydrides based on the characteristic FAB mass spectrum. The singlet at δ 30.05 in the $^{31}P\{^1H\}$ NMR spectrum (25 °C) and the AA′A″XX′X″ pattern of the hydride resonances indicate that this complex has facial arrangement of hydrides and has the formula *fac*-$IrH_3(PPh_3)_3$, **7**. Therefore in the process of hydride addition, a rearrangement of the phosphine groups occurs from *mer*-[Ir] to *fac*-[Ir] under mild conditions. Even though this type of complex is known,[8,9,13,14] NMR data have not been completely reported. The observed variable temperature ^1H NMR spectra of **7** in the hydride region are shown in Figure 2. Approximate simulations of both the spectrum (500 MHz) of **7** in toluene-d_8 at 25 °C by use of parameters $J_{PH(trans)} = +120$ Hz, $J_{PH(cis)} = -18$ Hz, $J_{HH(cis)} = -3.5$ Hz, and $J_{PP(cis)} = -3.2$ Hz and the spectrum of −40 °C, by use of $J_{PH(trans)} = +120$ Hz, $J_{PH(cis)} = -14$ Hz, $J_{HH(cis)} = 0$ Hz, and $J_{PP(cis)} = -3.2$ Hz are also shown in Figure 2; the signs of these *J* values might all be reversed because no absolute sign determination has been done. The same spectrum was obtained at 300 MHz. This fact along with the lack of significant change of pattern when the sample is warmed to 90 °C suggests that this is not a fluxional process. Instead it can be interpreted as a change in structure of the molecule with increasing temperature which results in an increase in J_{PH} and J_{HH} coupling constants. Large increases in J_{HH} of hydride with temperature have been attributed to a quantum exchange coupling phenomenon.[15] However the small change in J_{HH} with temperature in the present system is not consistent with this. The T_1 at room temperature was reported previously.[14b] The T_1(min) value for the hydride was 0.144 s at −60 °C (300 MHz). This is consistent with a trihydride structure with H−H distances of about 1.83 Å.[16]

In general, preparation of iridium polyhydrides (i.e., trihydride, or pentahydride) involves one step,[8,13] two steps,[9,11,12,14a] or several steps[18] with commercially available appropriate iridium precursors. It normally requires reaction with a large excess of $NaBH_4$ or $LiAlH_4$ as hydride source and the yield is often low. In the case of iridium trihydrides there is the possibility of obtaining isomeric mixtures (i.e., *mer*-[Ir] and *fac*-[Ir]).[8,13,14a] The method of Scheme 2 has several advantages: convenience of making and handling sodium ethoxide, the relatively high yield, and the production of a single isomer under mild conditions.

Complex **7** reacts readily with 2-mercaptopyridine (HSpy) in boiling benzene to give the dihydride complex possessing a chelating Spy ligand, $Ir(H)_2(\eta^2\text{-}SC_5H_4N)(PPh_3)_2$, **8** (eq 1). This

$$\underset{\textbf{7}}{fac\text{- or }mer\text{-}IrH_3(PPh_3)_3} + HSpy \rightarrow \underset{\textbf{8}}{Ir(H)_2(\eta^2\text{-}Spy)(PPh_3)_2} + PPh_3 + H_2 \quad (1)$$

was formulated on the basis of the two characteristic hydride resonances of two doublets of triplets {−21.0, −21.17 ppm (td,

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[8] (a) Levison, J. J.; Robinson, S. D. *J. Chem. Soc. A* **1970**, 2947. (b) Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 843. (c) Geoffroy, G. L.; Pierantozzi, R. *J. Am. Chem. Soc.* **1976**, *98*, 8054.

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[11] Brinkmann, S.; Morris, R. H.; Ramachandran, R. Unpublished data.

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[14] (a) Chatt, J.; Coffey, R. S.; Shaw, B. L. *J. Chem. Soc.* **1965**, 7391. (b) Ammann, C.; Isaia, F.; Pregosin, P. S. *Magn. Reson. Chem.* **1988**, *26*, 236.

[15] (a) Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1990**, *9*, 2643. (b) Heinekey, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 6074.

[16] To obtain this distance the T_1(min) value is corrected for the contributions by other hydrogens on the PPh_3 groups.[17] Then it is assumed that two hydride nuclei on an equilateral triangle relax the third by the dipolar mechanism.

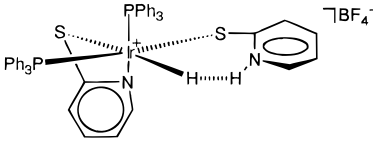
[17] Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

[18] Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205.

J_{PH} = 17.5 Hz, J_{HH} = 6.8 Hz)} in the ^{1}H NMR spectrum (CD_2Cl_2) and a singlet (21.3 ppm) in the $^{31}P\{^1H\}$ NMR (C_6D_6), along with microanalysis and FAB mass spectrum. This complex has been previously prepared from *mer*-$Ir(H)_3(PPh_3)_3$ and characterized by X-ray analysis.[19] An analogous complex of **7** containing bis(tricyclohexylphosphine) ligands has been conveniently prepared from the corresponding iridium(V) pentahydride complex.[20]

$$IrH_5(PCy_3)_2 + HSpy \rightarrow Ir(H)_2(\eta^2\text{-}Spy)(PCy_3)_2 + 2H_2 \quad (2)$$

Complex **8** reacts with 1 equiv of 2-mercaptopyridine and a strong acid ($HBF_4{\cdot}Et_2O$) in CH_2Cl_2 for 15 min at 20 °C to form after isolation a pale yellow, air stable microcrystalline solid (89%). This is identified as an iridium(III) monocationic complex **9** containing two *cis* phosphine ligands, which are *cis* to the hydride according to the spectroscopic studies: the hydride resonance at −17.82 ppm as a doublet of a doublet and the phosphorus resonances at −11.4 and 10.6 ppm as two doublets with a coupling constant of 16.3 Hz. The proton NMR spectrum of **9** in CD_2Cl_2 also contains a broad singlet at 12.03 ppm due to the proton on the pyridinium ring which is bound to iridium in a monodentate fashion via a sulfur atom. The proposed structure of **9** in solution is consistent with that obtained by X-ray analysis.



9

The presence of the Ir−H···H−N interaction in **9** in solution was deduced by use of the powerful NMR tools of VT−T_1 and NOE measurements. The proton on the pyridinium ring has a minimum T_1 of 0.235 s and the hydride of 0.266 s at 233 K (400 MHz). The Ir−H···H−N distance is calculated by use of these T_1(min) values and the method reported previously[1] to be 1.82 ± 0.05 Å which is close to the one (2.05(13) Å) obtained from the X-ray derived structure (see later). In an NOE experiment, a 12% enhancement for the resonance of the pyridinium proton in CD_2Cl_2 is achieved by selective irradiation at hydride. An attempt to disrupt the Ir−H···H−N interaction by introducing the H-bond acceptor $OPPh_3$ failed. In this attempt a CD_2Cl_2 solution of **9** containing excess $OPPh_3$ gave a similar enhancement (14%) for the NH resonance when the hydride is irradiated in a similar NOE experiment. Perhaps an H···F hydrogen bond between the NH group of the pyridinium ring and one of the fluorines of the BF_4^- group as seen in the solid state (Figure 1) prevents the $OPPh_3$ from approaching the NH group. The N−H and Ir−H vibrational modes of **9** in Nujol appear as broad peaks at 3236 and 2214 cm^{-1}, respectively. The vibrations of the BF_4 anion are those expected for a symmetrical tetrahedral geometry, apparently unperturbed by the F···H interaction.

X-ray Structural Analysis of Complex 9. The structure of **9** (Figure 1) as determined at 173 K reveals that the iridium atom is surrounded by *cis*-PPh_3 groups, a chelating 2-pyridinethiolate ligand, and a 2-pyridiniumthiolate ligand bound *via* sulfur atom. Thus the requirement for an octahedral iridium(III) center is completed by a hydride ligand *trans* to S(1). The hydrogen on the nitrogen of the pyridiniumthiolate is well defined in Fourier difference maps, and the hydride ligand could be located. The presence of the hydride is also indicated indirectly by the presence of its *trans*-influence on S(1): 2.535(2) Å for the (*trans*)S−Ir bond length is significantly longer than 2.394(2) Å for the (*cis*)S−Ir distance. The P(2)IrS(2)C(10)N(2) units are in a plane with a maximum deviation of 0.037 Å for the iridium atom. In this plane the hydride ligand is positioned at 1.72(11) Å from iridium, at 82(4) and 98(4)° to *cis*-P(2) and S(2), respectively, and at 111(4) and 69(4)° to *cis*-P(1) and chelate nitrogen atom (N1), respectively, and 2.05(13) Å from the proton of the pyridinium ligand. The hydride is also 2.1 Å away from H1A on the η^2-SC_5H_4N ligand and also from H52A, an ortho phenyl hydrogen. The structure also shows that the H on the nitrogen has a close contact of 1.96(8) Å with one of the fluorines in the tetrafluoroborate anion. A similar type of hydrogen-bonding interaction between an anion (Cl^-) and protons on the nitrogens of two pyridine-2-thiolate rings has been reported for a rhodium(III) complex with the Cl···N distance of 3.156 Å.[21]

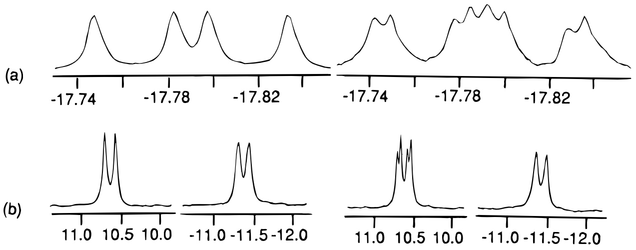
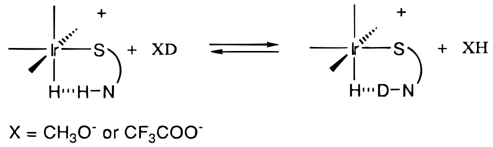


Figure 3. NMR spectra (25 °C): (a) ^{1}H (400 MHz, hydride region), and (b) $^{31}P\{^1H\}$ (300 MHz), of **9** in CD_2Cl_2 (left) and **9**-d_1 in CD_2Cl_2 with MeOD (right).

Scheme 3



H/D Exchange Studies. Complex **9** undergoes H/D exchange upon reaction with D_2 gas (1 atm), but only a very slow reaction has been observed (less than 50% deuteration of the NH group and IrH group in 24 h). However, a much faster reaction of **9** with MeOD in CD_2Cl_2 solution at 20 °C is observed (Scheme 3).

The ^{1}H NMR spectrum of the CD_2Cl_2 solution of **9** containing a small excess of MeOD or CF_3CO_2D shows after 1 h a significant decrease (37%) in the intensity of the resonance of the pyridinium proton. The hydride resonances (a doublet of doublets in CD_2Cl_2 alone) become broad and overlapping with another set of two doublets (0.009 ppm upfield from the first set). It is interesting to note that in $^{31}P\{^1H\}$ NMR spectrum of this solution, the downfield doublet at 10.65 ppm is isotopically shifted by 0.018 ppm while the upfield doublet at −11.40 ppm remains unchanged (see Figure 3). Therefore when complex **9** is deuterated at the NH group, there is an isotopic perturbation in the chemical shifts of the hydride and of one of the phosphorus groups. However, it is not clear why one phosphine group has an isotopic shift while the other does not.

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(20) The reaction of $Ir(H)_2(\eta^2\text{-}SC_5H_4N)(PCy_3)_2$ with $HSC_5H_4NH^+$ has been used as an alternative to the reported reaction of $IrH_5(PCy_3)_2$ with $HSC_5H_4NH^+$ to give the hydrogen-bonded species $[Ir\{H(\eta^1\text{-}SC_5H_4\text{-}NH)\}_2(PCy_3)_2](BF_4)$ **1**.[2a] This will be discussed elsewhere.

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Conclusion

The trihydride *fac*-$IrH_3(PPh_3)_3$ has an unusual AA′A″XX′X″ pattern which changes with temperature. A synthetic route to the novel iridium(III) complex $[IrH(\eta^1\text{-}SC_5H_4NH)(\eta^2\text{-}SC_5H_4N)(PPh_3)_2](BF_4)$, **9**, has been established from the complex $Ir(H)_2(\eta^2\text{-}Spy)(PPh_3)_2$, **8**. Complex **8** can be obtained from the *fac*- or *mer*-isomers of $IrH_3(PPh_3)_3$. $[IrH(\eta^1\text{-}SC_5H_4NH)(\eta^2\text{-}SC_5H_4N)(PPh_3)_2](BF_4)$ **9** possesses a unique hydrogen bond interaction involving Ir−H···H(N)···F−B atoms with the distances, of 2.0(1) Å for the H···H unit and of 2.0(1) Å for the F···H unit. Isotopic shifts have been observed in $^{31}P\{^1H\}$ and ^1H NMR spectra of $[IrH(\eta^1\text{-}SC_5H_4ND)(\eta^2\text{-}SC_5H_4N)(PPh_3)_2](BF_4)$, **9**-$d_1$ produced by the reaction of **9** with MeOD or CF_3CO_2D. The reaction of iridium polyhydride complexes with mercaptopyridinium seems to be a general method of generating complexes containing novel Ir−H···H−N interactions.

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Supporting Information Available: A difference electron density contour map in the plane of the P(2)IrS(2)C(10)N(2)H(2) unit and tables of X-ray structure refinement, fractional atomic coordinates, bond lengths and angles, and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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