Inorg. Chem. **2002**, *41*, 4961–4966

Inorganic Chemistry
Article

Novel Intramolecular C–H Bond Activation in an Iridium dppm Complex

Jackson S. Wiley and D. M. Heinekey*

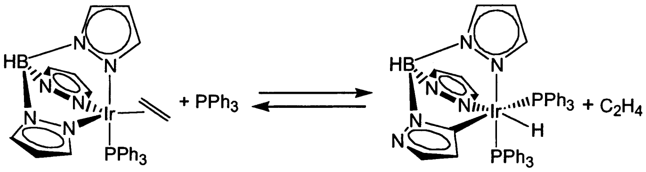
Department of Chemistry, University of Washington, Seattle, Washington 98195-1700

Received May 20, 2002

Reaction of $TpIr(C_2H_4)_2$ (Tp = tris-pyrazolylborate) with various chelating phosphine ligands has been explored. Reaction with bis-diphenylphosphinoethane leads to complete displacement of the Tp ligand. With bis-diphenylphosphinomethane, an intramolecular proton transfer from the methylene bridge to the iridium center occurs to give an iridium hydride complex formally resulting from oxidative C–H bond activation. Reaction with 2,2-bis-(diphenylphosphino)propane (dppip) affords an Ir(I) complex formulated as κ^2-TpIr(dppip). Protonation of this Ir(I) complex gives a six coordinate Ir(III) hydride species.

Introduction

Tris-pyrazolyl-borate (Tp) complexes of Ir(I) and Rh(I) have been intensively studied in recent years, due to their role in novel C−H bond activation chemistry.[1] We have previously reported an intramolecular C−H bond activation that resulted from addition of PPh_3 to $TpIr(C_2H_4)_2$ (Tp = tris-pyrazolylborate).[2] The formation of the Ir(III) complex (C-pyrazolyl Tp-H)$Ir(PPh_3)_2H$ by addition of PPh_3 to $TpIr(C_2H_4)(PPh_3)$ is reversible and requires excess PPh_3 to drive the reaction to completion.



This reaction affords a hydride complex via activation of a pyrazole ring C−H bond and is believed to involve an intermediate of the formula $TpIr(PPh_3)_2$, which is apparently unstable with respect to the Ir(III) complex.[3] In contrast to the apparent instability of $TpIr(PPh_3)_2$, Hill and co-workers have reported a facile synthesis of the rhodium complex $TpRh(PPh_3)_2$ from reaction of $RhCl(PPh_3)_3$ with KTp.[4]

Seeking a more tractable Ir(I) bis-phosphine species, we have investigated reactions of $TpIr(C_2H_4)_2$ with chelating phosphines, with the expectation that straightforward ligand substitution would lead to products of the formula $TpIrP_2$ (P_2 = chelating diphosphine ligand). Curiously, no complexes of this type have been reported in the literature to date. In related work, Carmona and co-workers reported that addition of dmpe to $Tp^{Me2}Ir(C_2H_4)_2$ results in a bridging dimer.[5] In this work, we report on the reactions of three different chelating phosphine ligands with $TpIr(C_2H_4)_2$. Surprisingly, the expected Ir(I) complex was formed in only one case.

Experimental Section

General Procedures. Unless stated otherwise, all preparations and manipulations were carried out under dry argon following conventional Schlenk techniques. Solvents were dried and degassed before use. Complexes $TpIr(C_2H_4)_2$[6] and the ligands KTp,[7] dppm-d_{20},[8] and dppip[9] were prepared according to literature procedures (dppm = bis-diphenylphosphinomethane, dppip = 2,2-bisdiphenylphosphino-propane). Microanalyses were performed by Canadian Microanalytical. Infrared spectra were recorded on a Perkin-Elmer model 1600 spectrometer. NMR spectra were recorded on Bruker AC-200, AF-300, AM-500, and DRX-499 spectrometers. The ^1H and ^{13}C spectra were referenced to the solvent resonance and are reported relative to TMS. ^{31}P chemical shifts were referenced to external 85% H_3PO_4.

---

* Author to whom correspondence should be addressed. E-mail: heinekey@chem.washington.edu.

(1) Bromberg, S. E.; Haw, Y.; Asplund, M. C.; Lian, T.; McNamara, B. K.; Kotz, K. T.; Yeston, J. S.; Wilkens, M.; Frei, H.; Bergman, R. G.; Jarris, C. B. *Science* **1997**, *278*, 260−263 and references therein.

(2) Heinekey, D. M.; Oldham, W. J., Jr.; Wiley, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 12842−12843.

(3) Wiley, J. S.; Oldham, W. J., Jr.; Heinekey, D. M. *Organometallics* **2000**, *19*, 167−1676.

(4) Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 3152−3154.

(5) Gutiérrez-Puebla, E.; Monge, Á.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruíz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538−4546.

(6) Tanke, R. S.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28,* 3444−3447.

(7) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.

(8) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.

(9) Pons, A.; Rossell, O.; Sexo, M.; Solans, X.; Font-Bardia, M. *J. Organomet. Chem.* **1996**, *514*, 177−182.

10.1021/ic0257367 CCC: $22.00

TpHIr(dppm-H) (1). TpIr(C_2H_4)$_2$ (100 mg, 0.22 mmol) and dppm (84 mg, 0.22 mmol) were combined in a reactor equipped with a Kontes valve. Toluene (10 mL) was added by vacuum transfer. Upon thawing, the reaction mixture was stirred for 30 min as ethylene was evolved. After cannula filtration, the solution was layered under pentane. Colorless air-stable crystals were isolated, rinsed with pentane, and dried. Yield: 150 mg (90%). ^{1}H NMR for **1**-d_{20} (500 MHz, CD_2Cl_2): 7.67 (d, 2H), 7.45 (d, 1H), 7.34 (d, 2H), 6.01 (d, 1H), 6.09 (t, 2H), 5.39 (t, 1H), 4.01 (br, 1H, PCHP), −18.56(t, 1H, $J_{H-P} = 17$ Hz). Crystals of **1** suitable for X-ray diffraction were grown by slow diffusion of pentane into a concentrated toluene solution, affording a toluene solvate of **1**. Anal. Calcd for **1**·1.5toluene: C, 57.63; H, 4.78; N, 9.07. Found: C, 57.42, H, 4.94, N, 8.98.

[TpHIr(dppm)]BF$_4$ (2). Complex **1** (40 mg, 0.05 mmol) was dissolved in a minimum of CH_2Cl_2 (approximately 0.5 mL). HBF_4 (85% in diethyl ether, 20 μL) was added and the solution was thoroughly mixed. The colorless complex **2** was precipitated by addition of Et_2O, rinsed twice with Et_2O, and dried. Yield 36 mg (82%). ^{1}H NMR for **2**-d_{20} (500 MHz, CD_2Cl_2): 7.76 (d, 2H), 7.64 (d, 1H), 7.13 (d, 2H), 6.15 (t, 2H), 6.12 (ddt $J_{HbH} = 2$ Hz, $J_{HbHa} = 17$ Hz, $J_{HbP} = 10$ Hz, 1H, PCH$_b$P), 5.63 (t, 1H), 5.59 (d, 1H), 4.36 (dt $J_{HaHb} = 17$ Hz, $J_{HaH} = 12$ Hz, 1H, PCH$_a$P), −16.27 (dt $J_{HHb} = 2$ Hz, $J_{HP} = 18$ Hz, 1H). X-ray diffraction quality crystals of **2**·0.5CH_2Cl_2 were grown by slow diffusion of pentane into a concentrated CH_2Cl_2 solution. Anal. Calcd for **2**·0.5CH_2Cl_2: C, 45.04; H, 3.73; N, 9.14. Found: C, 44.90, H, 3.81, N, 8.94.

Reaction of TpIrH(dppm-H) with MeI. Complex **1** (5 mg, 6.3 mmol) was placed in an NMR tube equipped with a Kontes valve. CD_2Cl_2 (0.5 mL) was added via vacuum transfer. Upon thawing and introduction of argon, CH_3I (1 μL, 16 mmol) was added. The tube was then frozen and flame sealed. Progress of the reaction was monitored by NMR spectroscopy. Several new hydride triplet resonances ($\delta = -15.9, -16.2, -18.9$ ppm) were observed within the first hour. After 3 days all of **1** had been consumed and a final equilibrium was reached with the signals at −15.9 and −16.2 ppm in a 10:1 ratio.

TpIr(dppip)(5). TpIr(C_2H_4)$_2$ (100 mg, 0.22 mmol) and dppip (89 mg, 0.22 mmol) were combined with 10 mL of toluene. After being stirred at room temperature for 24 h, the originally colorless solution had turned yellow. Evaporation of volatiles affords 170 mg (93%) of an orange solid. Complex **5** is extremely air sensitive and satisfactory elemental analysis could not be obtained. ^{1}H NMR (500 MHz, toluene-d_8, phenyl resonances omitted): 7.66 (d, 3H), 7.58 (d, 3H), 5.92 (t, 3H), 0.88 (t, $J_{HP} = 15$ Hz, 6H). ^{31}P NMR (toluene-d_8): −9.2 ppm. IR: 2470 cm^{-1}(ν_{B-H}).

[TpIrH(dppip)]BF$_4$(6). **5** (20 mg) was dissolved in 2 mL of CH_2Cl_2 to give a deep yellow solution. The solution immediately became colorless upon addition of HBF_4·Et_2O (5μL, excess). The solution was layered with 10 mL of Et_2O. After 24 h at 5 °C, a colorless precipitate of **6** was collected by filtration. ^{1}H NMR (500 MHz, CD_2Cl_2, phenyl resonances omitted): 7.92 (d, 1H), 7.86 (d, 2H), 7.20 (d, 2H), 6.82 (d, 1H), 6.16 (t, 2H), 6.01 (t, 1H), 1.73 (t, $J_{HP} = 17$ Hz, 6H), −16.80 (t, $J_{HP} = 18$ Hz, 1H). ^{31}P NMR {sel ^{1}H}: 18.2 ppm (d, $J = 18$ Hz). IR: 2510 (ν_{B-H}), 2142 cm^{-1} (ν_{Ir-H}). Anal. Calcd for **6**: C, 47.75; H, 4.12; N, 9.28. Found: C, 47.50; H, 4.24; N, 9.12.

Crystal Structure Analyses. Crystal data were collected with a Nonius KappaCCD diffractometer. Crystals were grown as described above and mounted on glass capillaries with epoxy. Empirical absorption corrections were applied before structure solutions. Hydrogen atoms were refined with a riding model and U_{iso} values were fixed such that they were 1.1U_{eq} of their parent atom. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods.

Table 1. Summary of Crystallographic Details for **1** and **2**

	1	**2**
empirical formula	$C_{44.50}H_{43.50}IrN_6P_2$	$C_{34.50}H_{34}B_2ClF_4IrN_6P_2$
fw	927.30	919.89
temp (K)	161(2)	161(2)
wavelength (Å)	0.71070	0.71070
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
unit cell dimens:		
a (Å)	10.1678(2)	9.90760(10)
b (Å)	10.5260(2)	32.2120(5)
c (Å)	18.9275(3)	11.4773(2)
α (deg)	87.126(1)	90
β (deg)	87.871(1)	102.5670(10)
γ (deg)	80.643(1)	90
V (Å^3)	1995.41(6)	3575.15(9)
Z, calcd density (Mg/m^3)	2, 1.543	4, 1.709
abs coeff (mm^{-1})	3.466	3.955
F(000)	929	1812
θ range for data collection (deg)	2.59 to 28.71	2.63 to 28.48
reflns collected/unique	58313/9872 [R(int) = 0.055]	87803/8736 [R(int) = 0.055]
max. and min. transmission	0.430 and 0.339	0.534 and 0.484
data/restraints/parameters	9872/0/486	8736/0/460
goodness-of-fit on F^2	1.033	1.074
final R indices [$I > 4\sigma(I)$]	*R1 = 0.0405, wR2 = 0.1017	*R1 = 0.0307, wR2 = 0.0830
R indices (all data)	R1 = 0.0505, *wR2 = 0.1157	R1 = 0.0391, *wR2 = 0.0903

Table 2. Selected Bond Lengths and Angles for **1**

bond distances (Å)			
Ir−N1	2.126(4)	Ir−P2	2.2692(13)
Ir−N3	2.154(4)	P1−C10	1.728(5)
Ir−N5	2.120(4)	P2−C10	1.726(5)
Ir−P1	2.2757(12)		
bond angles (deg)			
P1−Ir−P2	69.70(4)	N3−Ir−P2	98.39(11)
N1−Ir−P1	103.32(11)	N5−Ir−P2	102.31(11)
N3−Ir−P1	96.90(11)	N1−Ir−N3	85.17(16)
N5−Ir−P1	171.88(11)	N1−Ir−N5	84.58(15)
N1−Ir−P2	172.43(11)	N3−Ir−N5	85.51(15)

Structural Study of 1. A set of 58 313 reflections was collected, of which 9 872 were symmetry independent. Indexing and unit cell refinement, based on 881 reflections, indicated a triclinic lattice. The structure was solved and refined in $P\bar{1}$ (No. 2). Two toluene molecules were located during refinement; one was found disordered on the inversion center. The C42 atom was given 0.5 occupancy and C44 and C45 were refined isotropically since their anisotropic displacement parameters were nonpositive definite. Shift-limiting restraints did not solve this problem. All hydrogen atoms were placed with idealized geometry except for H10 and H1Ir which were located by difference Fourier synthesis. The maximum residual electron density was located near the disordered toluene.

Structural Study of 2. A set of 87 803 reflections was collected, of which 8 736 were symmetry independent. The structure was solved and refined in $P2_1/c$ (No. 14). One methylene chloride molecule was found disordered about an inversion center. The C35 atom was given 0.5 occupancy during refinement. All hydrogen atoms were located by difference Fourier synthesis except for H35A and H35B of the methylene chloride which were placed with idealized geometry.

Results

Addition of 1 equiv of dppe to TpIr(C_2H_4)$_2$ resulted in the extrusion of the Tp anion and the formation of the very

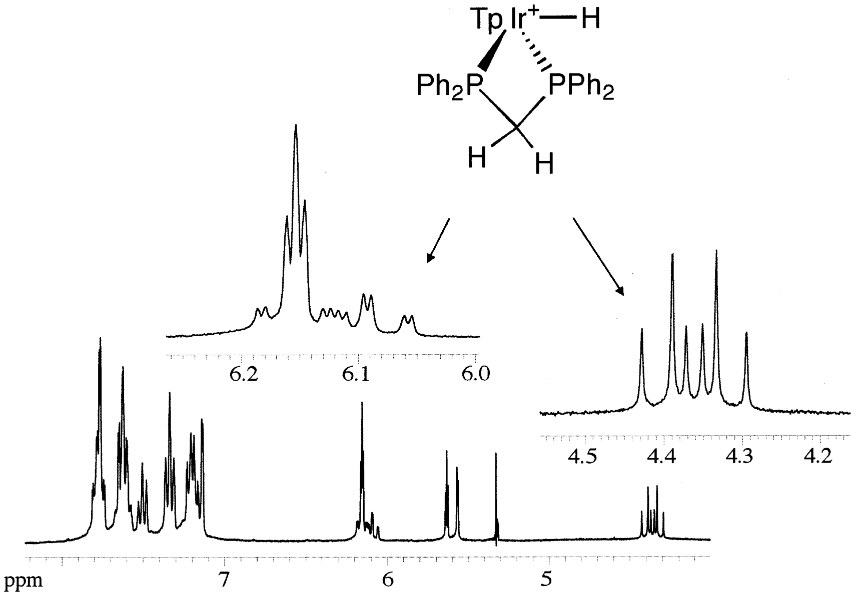
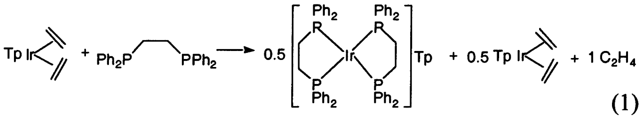


Figure 1. Partial ^{1}H NMR spectrum of complex **2**.

Table 3. Selected Bond Lengths and Angles for **2**

	bond distances (Å)		
Ir−N1	2.122(3)	Ir−P2	2.2557(10)
Ir−N3	2.120(3)	P1−C10	1.840(4)
Ir−N5	2.165(3)	P2−C10	1.842(4)
Ir−P1	2.2637(10)		
	bond angles (deg)		
P1−Ir−P2	72.80(4)	N3−Ir−P2	98.39(9)
N1−Ir−P1	101.27(9)	N5−Ir−P2	100.83(9)
N3−Ir−P1	171.10(9)	N1−Ir−N3	86.33(12)
N5−Ir−P1	100.64(9)	N1−Ir−N5	84.42(12)
N1−Ir−P2	171.95(9)	N3−Ir−N5	85.48(12)

stable square-planar Ir(dppe)$_2^+$ cation.[10] The same product was obtained with half an equivalent of dppe. No intermediates were detected when the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy (eq 1.)



(1)

In contrast, addition of dppm to TpIr(C$_2$H$_4$)$_2$ results in formation of a new iridium hydride complex (**1**). The ^{1}H and ^{31}P NMR spectra of complex **1** were consistent with a C_s symmetric molecule. To simplify the aromatic region of the ^{1}H NMR spectrum, the complex was also prepared with dppm-d_{20}. The pyrazole resonances in the ^{1}H NMR spectrum of **1** are in 2:1 ratios and the hydride resonance is a triplet, consistent with equal coupling to two ^{31}P nuclei. In the methylene region, only one broad resonance with an integration of ca. 1H was observed.

Protonation of **1** with HBF$_4$·Et$_2$O led to a new cationic complex formulated as [TpIrH(dppm)]BF$_4$ (**2**) that did show the expected dppm methylene resonances in the ^{1}H NMR spectrum (Figure 1). The two distinct methylene protons each exhibit an ABX$_2$ spin system (X = ^{31}P) with $J_{\mathrm{HaHb}} = 17$ Hz, $J_{\mathrm{HbP}} = 10$ Hz, and $J_{\mathrm{HaP}} = 12$ Hz. One of the methylene proton resonances also has an additional small (2 Hz) coupling to the hydride.

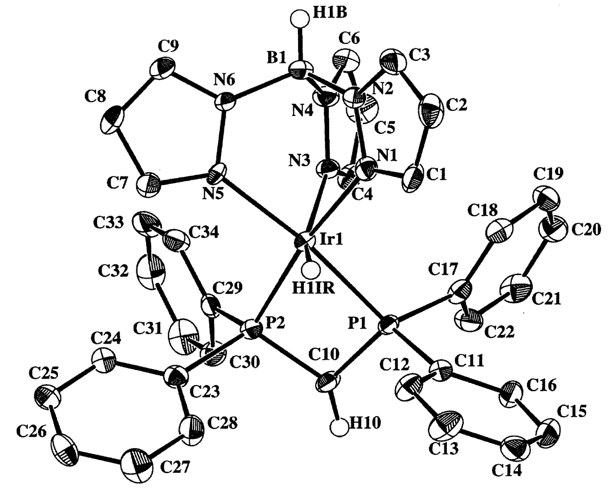


Figure 2. ORTEP diagram of complex **1**.

The crystal structures of both complexes **1** and **2** were determined. Both complexes are best described as distorted octahedral structures. The main difference between the two structures is in the P−C bond length between the coordinated P atoms and the central carbon of the phosphine ligand. In complex **1** the P−C distance is 1.73 Å and in complex **2** the corresponding bond length is 1.84 Å.

Addition of electrophiles other than H$^+$ to **1** also results in formation of a new bond to the backbone carbon. The reaction of **1** with excess MeI is much slower than protonation, and over the course of several hours affords primarily a species tentatively identified as a mono-methyl derivative. The progress of the reaction was conveniently monitored by ^{1}H NMR spectroscopy. The hydride region of the spectrum for various reaction times is shown in Figure 4. Possible products of this reaction are shown in Scheme 1. As the reaction proceeded, a methyl group was added to the dppm backbone of **1** to form complex **3**. An intermediate species,

---

(10) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324−5325.

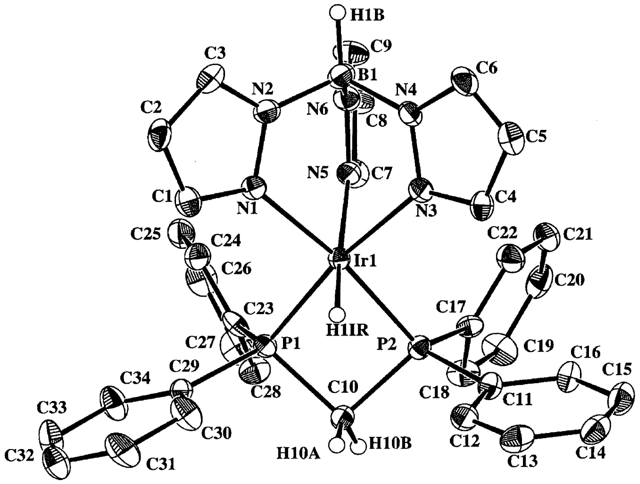


Figure 3. ORTEP diagram for the cation of complex **2**.

tentatively attributed to complex **4**, is rapidly formed as indicated by the hydride signal at −18.9 ppm but then quickly converts to the final product complex **3**. After 4 h all of **1** was consumed and the main product was **3** along with 10% of the protonated product **2**. Subsequently, the hydride region of the ^{1}H NMR spectrum remained unchanged for several days. MeI does not appear to react with **4** since the dimethylated complex **6** was not observed, although this complex has been prepared independently (see below).

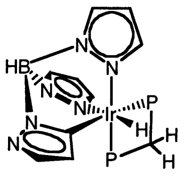
Reaction of 2,2-bis(diphenylphosphino)propane (dppip) with TpIr(C_2H_4)$_2$ affords a yellow Ir(I) complex, which is formulated as κ^2-TpIr(dppip) (**5**). The infrared spectrum of **5** exhibits a B−H stretch at 2475 cm^{-1}. A single ^{31}P resonance is observed for **5** at −9.2 ppm. In addition to phenyl resonances, the ^{1}H NMR spectrum exhibits a triplet (3H) at 5.92 ppm due to H_4 of the pyrazole rings and two doublet resonances at 7.58 and 7.66 ppm due to H_3 and H_5. Heating of **5** in benzene (55 °C, 24 H) gave no reaction.

Protonation of complex **5** affords a cationic species **6** that exhibits a hydride resonance at −16.8 ppm (t, $J_{H-P} = 18$ Hz). Appropriate pyrazole resonances (in a 2:1 ratio) were observed in the ^{1}H NMR spectrum, consistent with formulation of this species as a six-coordinate Ir(III) complex.

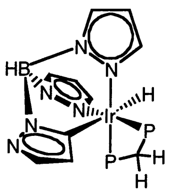
Discussion

Reaction of TpIr(C_2H_4)$_2$ with dppe leads to loss of the Tp ligand and formation of the previously reported[11] Ir(I) cation [Ir(dppe)$_2$]$^+$, which was identified by ^{1}H and ^{31}P NMR spectroscopy. The counterion is the tris-pyrazolylborate anion, confirmed by ^{1}H NMR spectroscopy. The anticipated product of this reaction, TpIr(dppe), was not observed as an intermediate, even in the presence of a deficiency of dppe. This suggests that if TpIr(dppe) is formed, it reacts with additional dppe faster than does the starting material TpIr(C_2H_4)$_2$.

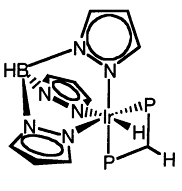
In contrast, reaction of TpIr(C_2H_4)$_2$ with dppm gives a neutral complex **1** containing a hydride ligand that exhibits a triplet resonance in the ^{1}H NMR spectrum, consistent with *equal* coupling to two phosphorus ligands. In our previous study of the reaction of TpIr(C_2H_4)$_2$ with PPh$_3$, we had found that activation of a pyrazole C−H bond occurred, leading to an Ir(III) hydride complex. If a similar reaction occurs in this case, a structure such as that depicted below as **A** would be expected. Since structure **A** contains two inequivalent phosphorus ligands, it is not consistent with the observation of equal coupling to two phosporus ligands. Structure **B** would be consistent with the observation of a triplet hydride resonance, but it is not clear how such an isomerization could take place. Also inconsistent with structure **B** for this complex is the failure to observe the expected signals for the two methylene protons. The NMR data suggest formulation of complex **1** as TpIrH(dppm-H), depicted as structure **C**. Particularly important in this respect is the broad signal of intensity 1H observed for the methanide hydrogen atom, which is consistent with reports in the literature. Several other dppm-H complexes have been reported to have a broad signal for the planar methanide hydrogen while the hydrogen atoms in dppm complexes showed resolvable coupling to the phosphorus atoms.[12]



A



B



C

In contrast to chelating phosphine ligands with two carbon bridges between the phosphorus atoms, dppm is susceptible to deprotonation in both the free and coordinated forms.[13] In several cases, deprotonation of coordinated dppm has been reported with bases such as BuLi or KOH. In other cases such as with M(dppm)$_2$ (M = Rh, Ir) a departing anionic ligand is a sufficiently strong base. Sharp and co-workers have also reported several examples of a coordinated imido group that can deprotonate coordinated dppm.[14]

It is reasonable to postulate that formation of **1** proceeds via the intermediacy of an Ir(I) complex TpIr(dppm). Formation of complex **1** would then require a proton transfer from the methylene group of bound dppm to the Ir center. This outcome suggests that the Ir center in the intermediate must be strongly basic. The formation of complex **1** by transfer of a proton from carbon to the metal center is a type of C−H bond activation of coordinated dppm that has not been previously reported.

Confirmation of structure **C** for complex **1** is provided by the observed chemical reactivity of **1**. Protonation occurs at the methanide carbon, affording complex **2**, which exhibits the expected pattern of signals in the ^{1}H NMR spectrum for a methylene group with inequivalent hydrogen atoms (see Figure 1). In the ^{1}H NMR spectrum of complex **2** both of the dppm hydrogen atoms show coupling to each other and to the two phosphorus atoms. Of these two signals (6.12 and 4.36 ppm) the resonance at 6.12 ppm shows a 2 Hz coupling

---

(11) Vaska, L.; Catone, D. L. *J. Am. Chem. Soc.* **1966**, *88*, 5324−5325

(12) Li, J. J.; Sharp, P. R. *Inorg. Chem.* **1994**, *33*, 183−184.

(13) Puddephatt, R. *J. Chem. Soc. Rev.* **1983**, 99−127.

(14) Ye, C.; Sharp, P. R. *Inorg. Chem.* **1995**, *34*, 55−59 and references therein.

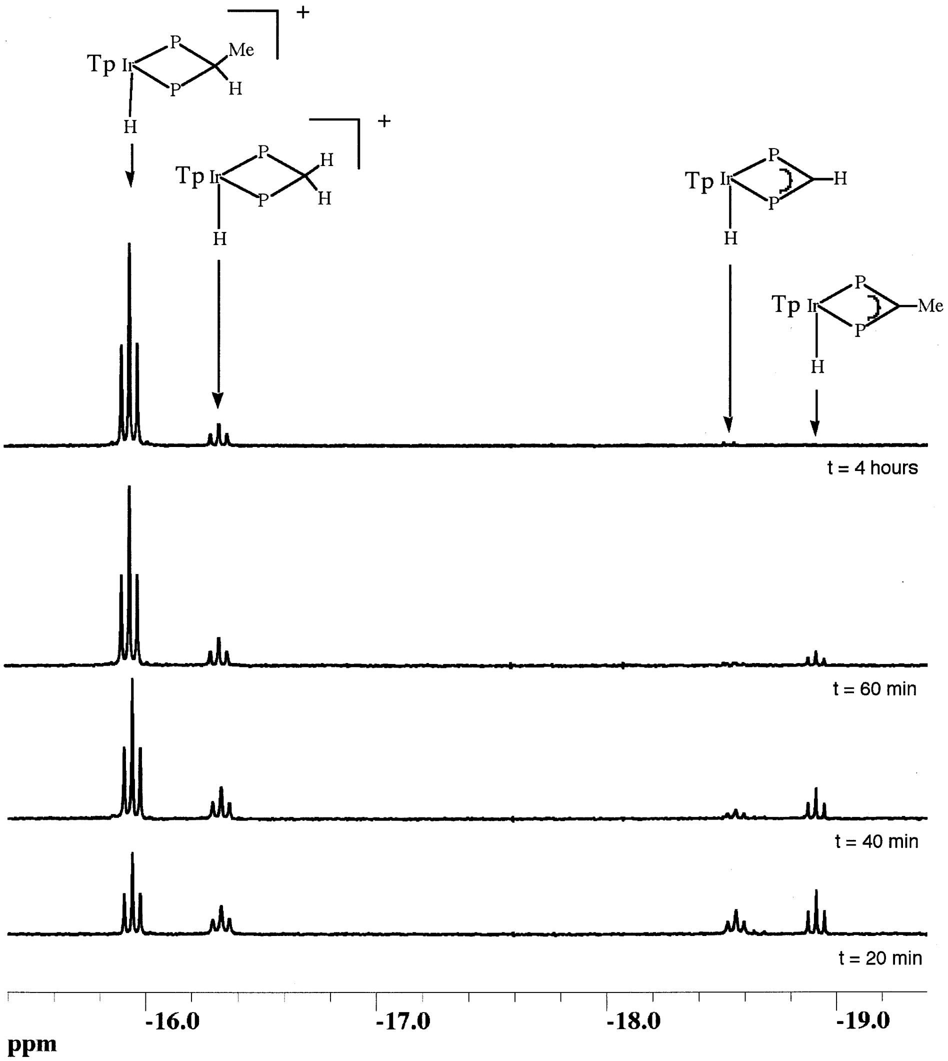
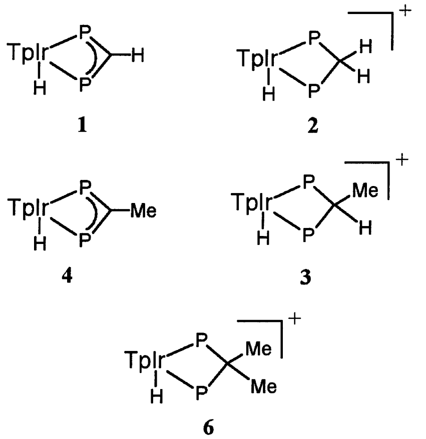


Figure 4. Partial ^{1}H NMR spectra (hydride region) during the reaction of TpIrH(dppm-H) with excess MeI.

Scheme 1



1 2 4 3 6

to the hydride. NOE experiments were attempted to locate which of the two methylene protons were nearest to the hydride; however, no useful information was obtained. The assignments for Ha and Hb remain speculative.

Reaction of **1** with MeI occurs more slowly than protonation and affords primarily a cationic species **3** resulting from methylation at the methanide carbon atom. Also observed was a neutral complex **4** that results from intermolecular proton transfer to afford **2**. Addition of a second methyl group to complex **4** was not observed, although the expected product of this reaction (complex **6**) has been prepared independently (see below).

The structures of complexes **1** and **2** were confirmed by X-ray crystallography (see Figures 2 and 3). The key metrical parameters in these two structures are the dppm backbone phosphorus−carbon bond lengths. In X-ray structures of dppm complexes the P−C bond length in the dppm backbone is diagnostic of the protonation state of the ligand. When compared to literature values obtained via a search of the Cambride Structural Database,[15] complex **1** (P−C distanceof 1.73 Å) fits within the range of P−C distances reported for complexes (11 examples) containing the dppm-H moiety (1.71−1.74 Å). Complex **2** (P−C distance = 1.84 Å) was within the reported range (260 examples) for dppm complexes (1.75−1.95 Å).

In complex **1**, The Ir(III) center has 3 nominally anionic ligands. Protonation to complex **2** forms an Ir(III) cation with only two anionic ligands. It is expected that the iridium−

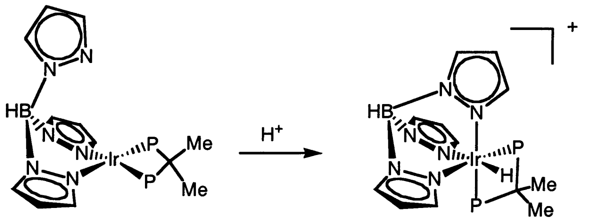
---

[15] Allen, F. H.; Kennard, O. *Chem. Design Automation News* **1993**, *8*, 1, 31−37.

phosphorus bonds would be somewhat shorter in **1** than **2**. This is not the case, however, as the Ir−P bond lengths are approximately 0.01 Å longer in **1** than in **2**.

A small change in the iridium−nitrogen bond lengths would be expected when comparing the neutral complex **1** to the cationic complex **2**. The structural data show that the Ir−N bond distances are essentially equal in **1** and **2**. These observations suggest that the electron density at the metal center is largely unchanged after protonation at the methanide carbon atom and that **1** is best described as a zwitterion, with a positive charge on the metal and a negative charge localized on the methanide carbon.

An authentic Ir(I) complex was ultimately prepared by replacing the methylene hydrogen atoms of dppm with methyl groups. Reaction of TpIr(C_2H_4)$_2$ with dppip affords complex **5**, which exhibits appropriate signals in the ^{1}H NMR spectrum for a Tp ligand (2:1 ratio of pyrazole resonances) and bound dppip. There are two structural possibilities for complex **5**, in that the Tp ligand could be tridentate or bidentate. A distinction between these two structures cannot be made based on NMR spectroscopy due to rapid fluxional processes which interconvert the pyrazole rings. The NMR spectrum is invariant with temperature down to 200 K. As demonstrated by Akita and co-workers, the B−H stretching frequency of bound Tp ligands is a useful diagnostic of bidentate versus tridentate coordination.[16] For several Tp complexes, it was reported that κ^2-Tp complexes have B−H stretching modes below 2500 cm^{-1}, while κ^3-Tp complexes have B−H stretches above 2500 cm^{-1}. In the case of complex **5**, the observation of a B−H stretching vibration at 2475 cm^{-1} suggests formulation of this complex as κ^2-TpIr(dppip).



5 **6**

Protonation of complex **5** occurs to afford an Ir(III) hydride derivative (**6**). The ^{1}H NMR spectrum of complex **6** exhibits pyrazole resonances in a 2:1 ratio and a triplet hydride resonance, consistent with a six-coordinate Ir(III) hydride complex. The infrared spectrum shows a B−H stretching mode at 2510 cm^{-1}, confirming κ^3-Tp coordination. This outcome is in contrast to the protonation at nitrogen observed for κ^2-TpIr(CO)$_2$, although initial protonation of **5** at the free pyrazole nitrogen cannot be ruled out.[17] This difference in reactivity is consistent with the higher basicity at Ir in complex **5** with the strongly donating bidentate phosphine ligand.

In our previous study of intramolecular C−H bond activation to form Ir(III) hydride complexes, we reported kinetic evidence for the involvement of a three-coordinate intermediate with ligation of Ir(I) by two pyrazole nitrogen donors and a phosphine ligand.[3] These observations provided confirmation of Goldberg's studies of similar processes in Pt complexes.[18] In the case of complex **5**, since the Tp ligand is bidentate and the complex is overall four coordinate, we anticipated that *intermolecular* C−H activation reactions might be feasible, since only one additional coordination site needs to be opened up. Complex **5** is in fact quite unreactive thermally. Prolonged heating of **5** in benzene did not lead to any reaction with the solvent.

Acknowledgment. This work was supported by the National Science Foundation. We acknowledge NSF support (CHE-9710008) of a 500-MHz spectrometer upgrade. We thank Dr. Scott Lovell for assistance with X-ray crystallography.

Supporting Information Available: Crystallographic data for TpIrH(dppm-H) (**1**) and [TpIr(dppm)H]BF_4 (**2**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0257367

---

(16) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121−4128.
(17) Ball, R. G.; Gosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 341−342.
(18) Wick, D. H.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235−10236.