# **ORGANOMETALLICS**

# Aqueous Organometallic Chemistry of mer-Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>X Complexes

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**Supporting Information** 

**ABSTRACT:** A series of  $Ir(H)_2(PMe_3)_3X$  compounds where X = various anionic ligands has been synthesized. The most studied of this group with X = Cl has been characterized fully, including by X-ray crystallography. For X = Cl, PhCO<sub>2</sub><sup>-</sup>, dissolution in water results in the establishment of the equilibrium  $Ir(H)_2(PMe_3)_3X + H_2O \Rightarrow [Ir-(H)_2(PMe_3)_3(H_2O)]^+X^-$ , which is responsible for the reaction of these compounds with unsaturated organic compounds.



Reactions between the dihydrides and alkynes in water as well as the thermodynamics of the aqueous equilibrium are discussed.

# INTRODUCTION

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The aqueous chemistry of metal complexes for organic catalysis has received significant attention, in the main because water is more benign than many organic solvents currently in use and because it may allow for easier separation of organic products. In addition, water has been found to activate certain metal complexes for catalytic activity and accelerate reactions that proceed more slowly or not at all in organic solvents.<sup>1–5</sup> For some time, we have been investigating the oxidative addition chemistry of  $[Ir(COD)(PMe_3)_3]Cl$  (1; COD = 1,5-cycloctadiene) with a variety of E–H bonds where E has been a variety of elements, including boron, carbon, nitrogen, and oxygen as well as hydrogen.<sup>6–15</sup>

$$\begin{array}{c} & \underset{\substack{I^{+} \\ PMe_{3} \\ PMe_{3} \end{array}}{\overset{PMe_{3}}{}} CI^{+} + E-H \xrightarrow{\Delta} \begin{array}{c} & \underset{Me_{3}P}{} & \underset{CI}{\overset{H}{}} PMe_{3} \\ & \underset{Me_{3}P}{\overset{H}{}} & \underset{CI}{\overset{H}{}} \end{array}$$
(1)

The product obtained when E = hydrogen (i.e., from the oxidative addition of  $H_2$ ) is a very water-soluble iridium dihydride complex. It is soluble to the extent of 40 mg of solid/ mL of water, equivalent to 40 g/L. Previously, we published a communication on the aqueous chemistry of this dihydride  $Ir(H)_2(PMe_3)_3Cl$  (2), which reacts with unsaturated organic compounds only in aqueous solution.11 In this paper we present our detailed studies on the aqueous chemistry of  $Ir(H)_2(PMe_3)_3X$  compounds, where X = various 1- charged ligands, and on their reactions with unsaturated compounds. The work discussed in this current paper is distinct from a body of work that utilizes water-soluble phosphine ligands to impart water solubility such as sulfonated triphenylphosphine<sup>16-20</sup> or 1,3,5-triaza-7-phosphaadamantane (PTA).<sup>21-23</sup> In this work, the water solubility is derived solely by ian nteraction between water and the metal center, resulting in the dissociation of appropriate anionic ligands.

# RESULTS AND DISCUSSION

Mer-Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>Cl (2) is synthesized in high yield via the reaction between  $[Ir(COD)(PMe_3)_3]Cl$  (1; COD = 1,5-cyclooctadiene)<sup>24</sup> and H<sub>2</sub> at 80 °C (eq 2). Spectroscopy

indicates that, as we have seen in almost all of the oxidative addition reactions we have explored, the product is exclusively the meridional isomer with cis hydrides. Compound 2 is a textbook system for exploring geometries by NMR spectroscopy, given the presence of both <sup>1</sup>H and <sup>31</sup>P nuclei. The <sup>1</sup>H NMR spectrum shows a doublet for the methyl protons of the central PMe<sub>2</sub> ligand and the outer set of PMe<sub>2</sub> ligands appears as a virtual triplet.<sup>25</sup> Two different types of hydride ligands are indicated by resonances at  $\delta$  -11.2 and -24.1 ppm. The resonance at  $\delta$  –11.2 ppm is attributable to the hydride trans to one PMe<sub>3</sub> ligand, cis to two PMe<sub>3</sub> ligands, and also cis to a hydride. The net result of a strong coupling (135 Hz) to the trans phosphorus and smaller couplings to the cis phosphines and the cis hydride is a doublet of triplet of doublets pattern. The resonance at  $\delta$  –24.1 ppm arises from the hydride trans to chlorine and cis to three phosphorus atoms and one hydrogen. This hydride displays a complicated pattern best described as a closely spaced quartet of doublets. The proton-decoupled <sup>31</sup>P spectrum is also consistent with the meridional structure, showing a doublet and a triplet from the two different phosphorus environments as well as P-P coupling.

A single-crystal X-ray structure was obtained for 2, and the resulting structure is displayed as a thermal ellipsoid plot in Figure 1. The structure confirms that already deduced by various spectroscopic measurements, and crystal data for 2 are

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**Figure 1.** Solid-state structure of the dihydride **2.** Methyl hydrogens have been omitted for clarity. Select bond distances (Å): Ir1–P1, 2.2872(16); Ir1–P2, 2.3187(17); Ir1–P3, 2.2895(16); Ir1–Cl1, 2.5003(16); Ir-H1, 1.50(7); Ir-H2, 1.66(8) Select bond angles (deg): P1–Ir1–P2, 98.76(7); P1–Ir1–P3, 163.33(6); P2–Ir1–P3, 97.88(6); Cl1–Ir1–P2, 96.13(7); Cl1–Ir1–P1, 88.89(6); Cl1–Ir1–P3, 88.22(6); H2–Ir-H1, 78(4).

given in Table 1, while important bond lengths and angles are indicated in the figure caption. Forming a tris-phosphine compound with two hydrides and a chloride ligand requires a balance of the steric constraints of the phosphine ligands. Analogous compounds with PR<sub>3</sub> = PPhMe<sub>2</sub>,<sup>26–28</sup> mixture of P(i-Pr)<sub>3</sub> and PPhMe<sub>2</sub>,<sup>29</sup> PTA<sup>21</sup> have been reported. Their reactivities have not been explored in depth, and for our purposes, the presence of phenyl groups invites ortho metalation side reactions that would hamper further studies.<sup>30–32</sup> In addition, the extra organic bulk of many of the phosphine ligands previously reported would greatly reduce or eliminate water solubility.

As discussed above, 2 is very water-soluble and the aqueous chemistry is interesting in a number of ways. First, <sup>1</sup>H NMR spectroscopy shows that two different species exist in H<sub>2</sub>O or  $D_2O$  solution. The splitting patterns evident in both <sup>1</sup>H and <sup>31</sup>P spectra are consistent with both species maintaining a meridional arrangement of phosphines as well as a cis arrangement of the two hydrides. Therefore, two sets of closely spaced quartets of doublets are observed in the <sup>1</sup>H NMR spectrum at -25.3 ppm (minor) and -21.8 ppm (major) and two sets of a doublet of triplets pattern at -8.8 ppm (major) and -8.0 ppm (minor). The <sup>31</sup>P NMR spectrum appears as a set of triplets at -49.6 ppm (major) and -44.5 ppm (minor) as well as doublets at -44.7 ppm (major) and -40.2 ppm (minor). Given that five of the six coordination sites of the octahedron must be the same to explain the spectroscopic data, these two species in water can only differ in the sixth coordination site. The NMR data led us to postulate the equilibrium shown in eq 3.

$$\begin{array}{c} Me_{3}P_{2}H_{1}H_{1}\\ Me_{3}P_{1}H_{2}He_{3}\\ \mathbf{2} \end{array} + H_{2}O \longrightarrow \begin{bmatrix} Me_{3}P_{1}H_{1}\\ Me_{3}P_{1}H_{2}H_{2}\\ H_{2}O \end{bmatrix}^{+}CH \qquad (3)$$

One observation in support of this equilibrium is that addition of chloride (as NaCl) to an aqueous solution of 2/2a

Table	e 1.	Experi	mental	Details	for	X-ray	Crystal	lograp	hic
Analy	ses								

param	2	4d	9	
empirical formula	C9H29ClIrP3	C15H35ClIrP3	$\mathrm{C}_{22}\mathrm{H}_{44}\mathrm{IrO}_{2}\mathrm{P}_{3}$	
formula wt	457.9	535.99	624.7	
temp (K)	293(2)	293(2)	293(2)	
wavelength (Å)	0.710 73	0.710 73	0.710 73	
cryst syst	monoclinic	orthorhombic	triclinic	
space group	$P2_1/n$	$P2_{1}2_{1}2_{1}$	$P\overline{1}$	
unit cell dimens				
a (Å)	12.507(3)	11.827(3)	8.489(7)	
b (Å)	10.265(2)	12.535(3)	11.995(5)	
c (Å)	14.000(3)	14.506(3)	14.916(7)	
$\alpha$ (deg)	90	90	84.08(4)	
$\beta$ (deg)	102.64(3)	90	76.51(5)	
γ (deg)	90	90	71.39(5)	
V (Å <sup>3</sup> ), Z	1753.8(6), 4	2150.5(9), 4	1399(1)	
calcd density (g/ cm <sup>3</sup> )	1.780	1.655	1.483	
abs coeff (mm <sup>-1</sup> )	8.015	6.58	4.936	
F(000)	960	1056	626	
cryst size (mm)	$0.4 \times 0.2 \times 0.2$	$0.4 \times 0.4 \times 0.3$	$0.3 \times 0.2 \times 0.2$	
$\theta$ range for data collection (deg)	1.98-27.5	2.15-25	1.75–25°	
limiting indices	$0 \le h \le 16$	$0 \le h \le 14$	$0 \le h \le 10$	
	$0 \le k \le 12$	$0 \le k \le 14$	$-13 \le k \le 14$	
	$-18 \le l \le 17$	$0 \le l \le 17$	$-17 \leq l \leq 17$	
no. of rflns collected	4100	2156	5289	
no. of indep rflns $(R_{int})$	3925 (0.0640)	2156	4913 (0.0246)	
completeness to $\theta$ (%)	97.6 ( $\theta$ = 27.5°)	100 ( $\theta = 25^{\circ}$ )	99.8 ( $\theta = 25^{\circ}$ )	
refinement method	full-m	natrix least squares o	on $F^2$	
no. of data/ restraints/params	3925/0/136	2156/0/182	4913/0/254	
goodness of fit on $F^2$	1.040	1.038	1.005	
final <i>R</i> indices $(I > 2\theta(I))$	R1 = 0.0387; wR2 = 0.0953	R1 = 0.0292; wR2 = 0.0648	R1 = 0.0495; wR2 = 0.0936	
R indices (all data)	R1 = 0.0473; wR2 = 0.1005	R1 = 0.0364; wR2 = 0.0674	R1 = 0.0882; wR2 = 0.0994	
absolute structure param	n/a	-0.024(14)	n/a	
extinction coeff	0.0042(3)	n/a	n/a	
largest diff peak/ hole (e Å <sup>-3</sup> )	2.904/-1.360	0.974/-0.778	1.272/-0.664	

greatly reduces the resonance from 2a and increases the intensity of the resonance from 2. In addition, calculations of equilibrium constants using either <sup>1</sup>H or <sup>31</sup>P spectroscopy and variable concentrations of 2 in solution could only be modeled satisfactorily with the simple equilibrium indicated in eq 3 (see the Supporting Information.) Attempts to isolate 2a were unsuccessful, even though we had been able to isolate and characterize a number of other noble-metal aqua species in other systems.<sup>33,34</sup>

The lability of chloride in water compared with the lability in organic solvents was probed. The addition of PMe<sub>3</sub> to a solution of **2** in dichloromethane resulted in no observable reaction. It is possible to force chloride removal with the use of  $Tl[PF_6]$  in the presence of PMe<sub>3</sub> to yield  $[IrH_2(PMe_3)_4][PF_6]$ . This is in contrast with the catecholboryliridium hydride complex we synthesized, which reacts without the need for a chloride scavenger.<sup>7</sup> In that case, the catecholboryl ligand is

trans to the chloride (as opposed to trans to H in this case), which may be responsible for the increased lability of the chloride ligand. On the other hand,  $TI^+$  is not needed in water and addition of PMe<sub>3</sub> to an aqueous solution of 2 led to the clean formation of  $IrH_2(PMe_3)_4^{+35}$  as the chloride salt 3 (eq 4).

$$\begin{array}{c} \mathsf{Me}_{3}\mathsf{P}, \mathsf{H}, \mathsf{H} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{H}, \mathsf{PHMe}_{3} + \mathsf{PMe}_{3} & \longrightarrow \\ \mathsf{CI} \\ \mathsf{2} \\ \mathsf{2} \\ \mathsf{Me}_{3} \\ \mathsf{P}, \mathsf{H}, \mathsf{PMe}_{3} \\ \mathsf{Me}_{3} \\ \mathsf{P}, \mathsf{H}, \mathsf{$$

The reactivity of **2** in aqueous solution with carbon–carbon multiple bonds, especially alkynes, was investigated. Alkynes were particularly chosen because previous work in our group<sup>6,7,10,11</sup> showed that vinyl complexes could readily be isolated, if formed, and therefore studied in greater detail. Reactions between **2** and alkynes in  $CD_2Cl_2$  at room temperature were monitored for 2 weeks with no indication of any reaction. On the other hand, reaction between **2** and various alkynes in water led to complete reaction from insertion of the alkyne into an Ir–H bond. <sup>1</sup>H NMR tube-scale experiments indicated that most alkyne reactions were complete within a few minutes.

In preparative studies, reactions took place upon addition of the alkyne to aqueous solutions of 2 with immediate precipitation of product (eq 5). The <sup>1</sup>H and <sup>31</sup>P NMR spectra



for the *tert*-butylvinyl product **4a** are illustrative of all complexes. Both spectra indicated that the meridional arrangement of phosphines persists. The remaining hydride signal is observed at  $\delta$  –23.9 ppm, a chemical shift indicative of a placement trans to chloride (see the discussion on Chemical Shift Relationships), and is a quartet with  $J_{P-H} = 16.9$  Hz from splitting by three cis PMe<sub>3</sub> ligands. The vinyl protons both display H–H coupling to each other as well as long-range P–H coupling to all three PMe<sub>3</sub> groups.

Observation of the <sup>1</sup>H NMR spectrum of the hydride region of **2** in  $D_2O$  showed that H/D exchange occurs between the hydride ligands and solvent over time, albeit at very different rates. The hydride ligand cis to the chloride (or aqua group) exchanges quickly, the reaction being complete in approximately 30 min. The hydride ligand trans to chloride (or water) shows appreciable exchange only after 24 h (eq 6).

$$\begin{array}{c} \mathsf{Me}_{3}\mathsf{P}, \mathsf{I}, \mathsf{H} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I}, \mathsf{F} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I}, \mathsf{F} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I}, \mathsf{F} \\ \mathsf{CI} \\ \mathsf{I} \\ \mathbf{2} \end{array} \xrightarrow{\mathsf{D}_{2}} \begin{array}{c} \mathsf{Me}_{3}\mathsf{P}, \mathsf{I}, \mathsf{P} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I}, \mathsf{F} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I}, \mathsf{I} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I} \\ \mathsf{I} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I} \\ \mathsf{I} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I} \\ \mathsf{Me}_{3} \\ \mathsf{I} \\ \mathsf{I} \\ \mathsf{I} \\ \mathsf{Me}_{3}\mathsf{P}, \mathsf{I} \\ \mathsf{I} \\$$

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We took advantage of this H/D exchange to probe the insertion reaction in more depth. Complex 2 was dissolved in  $D_2O$ , and the H/D exchange was allowed to proceed for 60 min to ensure complete exchange of the hydride cis to chlorine with minimal exchange of the trans hydride. *tert*-Butylacetylene was added to the solution to form the *tert*-butylvinyl complex and the <sup>1</sup>H NMR spectrum recorded. In comparison with the

fully protio vinyl compound, the resonance at  $\delta$  5.2 disappears and the resonance at  $\delta$  6.6 loses H–H coupling, all indicating that the deuteride ligand is the migrating group, consistent with the alkyne initially replacing the aqua ligand and being cis to the deuteride (eq 7).

The exact driving force for the final product geometry of having hydride trans to chloride is not known, but the reaction proceeding through a five-coordinate intermediate gives a low-energy pathway to rearrangement to the more thermodynamically favored product. Having the vinyl group cis to two PMe<sub>3</sub> groups rather than all three lowers unfavorable nonbonded interactions and is the most likely driving force for the geometry of the isolated product. The only exception observed was found for **4b**, where an 80/20 mixture of products with the vinyl group cis to chloride/trans to chloride was observed. Of all of the vinyl compounds, suitable crystals were obtained for **4d** and Table 1 contains a condensed listing of experimental parameters. The thermal ellipsoid plot for **4d** can be found in Figure 2, and select bond lengths and angles may be found in the figure caption.



**Figure 2.** Solid-state structure of vinyl hydride complex **4d**. Hydrogen atoms ae omitted for clarity. Select bond distances (Å): Ir–H1, 1.499(8); Ir1–P1, 2.314(3); Ir1–P2, 2.540(3); Ir1–P3, 2.320(3); Ir1–C3, 2.143(9); C3–C2, 1.334(15); C2–C1, 1.505(15); C3–C4, 1.424(15); C4–C5, 1.204(15); C5–C6, 1.447(15). Select bond angles (deg): P1–Ir1–P2, 94.1(1); P1–Ir1–P3, 168.4(1); P2–Ir1–P3, 93.2(1); C11–Ir1–P1, 9.4(1); C11–Ir1–P2, 86.8(1); C11–Ir1–P3, 94.04(9); C11–Ir1–C3, 93.2(3); C1–C2–C3, 127.0(1); C2–C3–Ir1, 123.5(8); C2–C3–C4, 118.2(9); Ir1–C3–C4, 118.3(7); C3–C4–C5, 179.2(1).

An unusual reaction with ethynylpyridine led to the formation of a product where a metallacycle composed of three alkynes formed; we have already reported on this reaction.<sup>36</sup>

**Equilibrium Studies.** Further studies on the nature of the aqueous equilibrium between **2** and **2a** through a variable-temperature <sup>31</sup>P NMR study was undertaken to examine the thermodynamics of this system. <sup>31</sup>P NMR spectroscopy was chosen because the H/D exchange discussed above precluded using the hydrides as the probe with <sup>1</sup>H NMR spectroscopy. By measurement of the <sup>31</sup>P integrals, the equilibrium constants at

the various temperatures were calculated and the resulting van't Hoff plot is shown in Figure 3. The data is a reasonable linear



Figure 3. van't Hoff plot for the equilibrium between 2 and 2a in aqueous solution as depicted in eq 3. Details are provided in the Supporting Information.

fit ( $R^2 = 0.996$ ) allowing for calculation of enthalpic and entropic parameters, yielding  $\Delta H$  and  $\Delta S$  values of  $34 \pm 3$  kJ/ mol and  $68 \pm 10$  J/(K mol), respectively. While little can be concluded from the exact values of these numbers, the signs and relative magnitudes make sense. All other factors being more or less equal, the  $\Delta H$  value represents the difference between the Ir–Cl bond energy and the Ir–O bond energy, a value that would be expected to favor the Ir–Cl bond. The positive value of  $\Delta S$  is also to be expected in a dissociative equilibrium such as this.

**Other Anionic Groups.** We investigated other anionic leaving groups in the  $Ir(H)_2(PMe_3)_3X$  system. While we were interested in studying a broad range of X groups, the actual number we were able to make was limited by synthetic methodologies. Simple replacement of X in 2 with other anionic ligands was successful for some, but not for all variations of X. Addition of NaI or NaBr to an aqueous solution of 2 resulted in the immediate precipitation of  $Ir(H)_2(PMe_3)_3I$  or  $Ir(H)_2(PMe_3)_3Br$  (eq 8). This is not an unexpected



outcome, given that I<sup>-</sup> and Br<sup>-</sup> are not as strongly solvated by water as Cl<sup>-</sup> and a simple hard/soft acid/base view would argue that I<sup>-</sup> and Br<sup>-</sup> would bind more strongly to the iridium to yield insoluble complexes. <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra are all consistent with the meridional phosphine, cisdihydride structure shown in eq 8. Attempted replacement of chloride with fluoride led to decomposition with no isolable products. Syntheses of the heavier transition-metal fluoride complexes in general and iridium fluoride compounds specifically have proven to be a challenge.<sup>37</sup>

For carboxylate ligands, a synthetic scheme introducing the carboxylate at the COD dimer stage proved to be the most successful. The method shown in eq 9 was used to prepare



 $[Ir(COD)X]_2$  compounds with the bridging groups X = PhCO<sub>2</sub><sup>-</sup>, MeCO<sub>2</sub><sup>-</sup>, F<sub>3</sub>CCO<sub>2</sub><sup>-</sup>. The carboxylates are drawn as  $\eta^2$  bridging on the basis of previous work on rhodium chemistry that supported this bonding mode.<sup>38</sup> In addition, Finke<sup>39</sup> recently reported the crystal structure of an iridium COD dimer bridged by 2-ethylhexanoate which clearly shows the  $\eta^2$  bonding. It is interesting to note that one of the earliest reports on bridging carboxylates indicated that the Ir COD acetate dimer was unstable in solution and could not be made with silver acetate,<sup>38</sup> but that is not our experience at all.

Addition of PMe<sub>3</sub> to 6a-c yielded tris-PMe<sub>3</sub> COD iridium complexes with the appropriate carboxylate counterion (eq 10).



The final step in this sequence, the synthesis of the dihydrido iridium complex 8, was only completely successful for R = Ph(eq 11). For acetate and trifluoroacetate, NMR spectroscopy indicated that some of the desired product was formed among a complicated mixture of products. We are not able to explain these results at this time, but it is clear that the counterion plays a critical role at some stage in the H<sub>2</sub> addition reaction. We will be investigating the role the counterion plays in the mechanism of the oxidative addition reactions of the  $[Ir(COD)(PMe_3)_3]^+$ cation as part of our continuing studies on this system.

Given the excellent yield of the benzoate compound, further studies were carried out on it.  $Ir(H)_2(PMe_3)_3(O_2CPh)$  (8) is as water-soluble as 2 and, in some respects, more reactive. One indication of the increased reactivity is that both hydrides exchange with  $D_2O$  within the time required for mixing and acquiring a <sup>1</sup>H NMR spectrum (eq 12).



Given the difference in H/D exchange rates between compounds 2 and 8, some discussion on the nature of the H/D exchange reaction seems warranted. While no specific studies were aimed at probing the mechanism of the exchange reaction directly, it would seem reasonable that the exchange occurs via a mechanism similar to one already described in the

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literature.<sup>22</sup> Since the first H to exchange with D is the one cis to the putative aqua group, an intramolecular mechanism seems appropriate to postulate wherein D from the coordinated  $D_2O$ "protonates" the Ir–H bond, forming a transient iridium dihydrogen complex. The reverse of that reaction regenerates the hydride with a 50% probability of the formation of Ir-D. Continued steps as well as aqua exchange result in complete deuteration. Ultimate deuteration of both hydrides likely stems from a five-coordinate intermediate that has a low barrier to rearrangement, allowing for the interchange between the two hydride positions. Figure 4 sketches this hypothetical exchange mechanism.



**Figure 4.** Hypothetical mechanism for H/D exchange between iridium hydrides and D<sub>2</sub>O.

<sup>31</sup>P NMR spectroscopy revealed a single set of resonances, indicating that only one species was present in solution, with spectral properties identical with those observed for the aqua complex **2a**. Addition of varying amounts of NaCl establishes the same two species in equilibrium observed upon dissolution of **2** in water. This indicates that the benzoate ligand is completely dissociated in water, a result in keeping with our findings from the equilibrium involving **2** and **2a**, where the positive  $\Delta H$  value is in the main responsible for the unfavorable  $K_{eq}$  value. For the benzoate complex the exchange of one oxygen ligand (benzoate) for another (aqua) has ostensibly a  $\Delta H$  value close to zero and the favorable entropic changes drives the equilibrium completely to the aqua complex.

The reaction of 8 with alkynes is complete within a few minutes in aqueous solution (monitoring by <sup>1</sup>H NMR spectroscopy), leading to the formation of a vinyl iridium hydride compound 9, analogous in all respects to the chloride compounds reported above except for benzoate in place of chloride in the sixth coordination site (eq 13). Suitable crystals



of **9** were obtained, and a single-crystal X-ray structure analysis was performed. Table 1 contains a concise tabulation of experimental data for the structure of **9**. The overall structure is presented as a thermal ellipsoid plot in Figure 5 with selected bond lengths and angles given in the figure caption.

**Chemical Shift Relationships.** While we were reviewing <sup>1</sup>H NMR data, a trend was observed in the chemical shifts of the hydrides. The doublet of triplet of doublets due to the hydride trans to the phosphine group shifted upfield as the ligand in the sixth coordination site was changed from I to Br to Cl. Examination of the data found a significant relationship



Figure 5. Solid-state structure of the vinyl hydride benzoate complex 9. Phosphorus methyl groups and hydrogen atoms other than the hydride and vinyl hydrogens are omitted for clarity. Select bond distances (Å): Ir1-C1, 2.094(9); Ir1-O1, 2.193(6); Ir1-P1, 2.321(3); Ir1-P2, 2,317(3); Ir1-P3, 2.304(3). Select bond angles (deg): Ir1-C1-C2, 131.1(8); P1-Ir1-P2, 99.6(1); P2-Ir1-P3, 94.5(1); P1-Ir1-P3, 165.8(1); O1-Ir1-C1, 89.2(3); O2-C7-O1, 125.8(8).

between the chemical shift of the trans hydride versus the electronegativity of the trans ligand atom bonded to the iridium center. The <sup>1</sup>H NMR chemical shift data and the electronegativity data are given in Table 2, and a plot of chemical shift

Table 2. <sup>1</sup>H Chemical Shifts of Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>X in CD<sub>2</sub>Cl<sub>2</sub>

Х	electronegativity <sup>40</sup>	H(trans) (ppm)
0	2.82	-26.4
Cl	2.76	-24.0
Br	2.6	-23.0
Ι	2.45	-20.8
N <sup>15</sup>	2.28	-19.4
Р	1.84	-13.6

vs electronegativity is shown in Figure 6. Specifically, the plot of Mulliken–Jaffee "p" electronegativity values<sup>40</sup> vs chemical shifts of the trans hydrides yielded a very good linear relationship. The use of the "p" values is justified in that the highest occupied molecular orbital on each atom involved in the bonding to iridium has nearly 100% p character. (See the



Figure 6. Plot of hydride chemical shifts vs Mulliken–Jaffee p electronegativity of  $Ir(H)_2(PMe_3)_3 X$  in  $CD_2Cl_2$ . Data are given in Table 2.

Supporting Information for the results of Gaussian calculations of molecular orbitals using the WebMO interface.) As the ligand  $\mathbf{X}$  becomes more electronegative, the chemical shifts of the hydride cis to the ligand  $\mathbf{X}$  and the phosphines all shift downfield, corresponding to a greater withdrawal of electron density from the metal center onto the more electronegative ligand, thus deshielding these ligands. However, the chemical shift of the hydride trans to  $\mathbf{X}$  displays an opposite effect. This cannot be explained in terms of electronegativity; otherwise, a downfield shift similar to the cis hydride and the phosphines would be expected. The chemical shift behavior of the trans hydride can be rationalized as a "trans effect", with the H being pulled closer to the metal, thus embedding it further in the metal electron density.

In 1971 Birnbaum described similar results in a study of the hydride shifts of monohydrido halo transition-metal complexes. He observed that the chemical shift of a hydride trans to the halide decreased in the order Cl<sup>-</sup> > Br<sup>-</sup> > I<sup>-</sup>, while the chemical shifts of the hydride cis to the halide increased in the order Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>. These experimental results were exactly the opposite of the trends theoretically predicted by Buckingham and Stevens in 1964. Birnbaum attributed this to an increase in the covalent character of the complexes in the order Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>.

Specific chemical shift data on a different iridium complex were found in the research of Eisenberg et al. on iridium dihydrides formed by hydrogenation of Ir(CO)(dppe)X (X = Cl, Br, I).<sup>41</sup>

It is obvious from the plot of chemical shifts versus electronegativity of ligand X in Eisenberg's complexes and from Birnbaum's studies that this is not an isolated phenomenon.

# CONCLUSIONS

*mer*-Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>Cl and *mer*-Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>O<sub>2</sub>CPh are both very water-soluble hydride complexes and have proven to have very interesting aqueous chemistry. The loss of an anionic ligand provides a facile route in water to open a coordination site to allow for reaction chemistry, and the migratory insertion of hydride into carbon–carbon multiple bonds shows the potential for these complexes to catalyze organic reactions in aqueous solutions. Future work will elaborate on the expansion of the anionic leaving groups as well as investigate the reactivity of monohydrido systems in water, including their catalytic activity for hydrogenation and terminal alkyne dimerization.

# EXPERIMENTAL SECTION

General Methods. All reactions were performed under an inert atmosphere of purified nitrogen. Standard glassware and Schlenk line techniques were used.  $[Ir(COD)(PMe_3)_3]Cl(1)$  was synthesized by a previously reported procedure.<sup>24</sup> All other chemicals were reagent grade and were used without further purification. Unless otherwise noted, solvents used were of reagent grade and were dried by the appropriate technique before use. Water was deionized with a reverse osmosis system. The proton and carbon NMR spectra were obtained on a Bruker WP270SY or WP200SY instrument. The <sup>31</sup>P NMR spectra were obtained on a Bruker WP200SY instrument operating at 81 MHz and referenced using an internal standard of 85% H<sub>3</sub>PO<sub>4</sub>. All elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. X-ray crystal structures were obtained using a Siemens/Bruker R3m/v diffractometer and Mo K $\alpha$  ( $\lambda$  = 0.71071 Å) radiation at 303 K, and solution and refinement was carried out with the SHELX<sup>42</sup> suite of programs. ORTEP plots were generated using the program Olex2.<sup>43</sup> Hydrides were located using the program XHydex and were placed in indicated positions without further refinement.<sup>44</sup> The program JMP was used for statistical analyses.<sup>45</sup>

**Synthesis of Ir(H)**<sub>2</sub>(**PMe**<sub>3</sub>)<sub>3</sub>**CI** (2). A 50.0 mL three-necked flask equipped with a magnetic stir bar and a septum was charged with 2.78 g of [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>]Cl (1) under nitrogen in a drybox. The flask was then connected to a double-manifold (vacuum/nitrogen) Schlenk line, and 20.0 mL of mesitylene was added by syringe. The flask was then fitted with a reflux column equipped with a nitrogen inlet and connected to the Schlenk line. H<sub>2</sub> was bubbled through the mixture at a very slow rate, and the suspension was stirred by magnetic stirrer and heated to about 100 °C. Upon heating, the white solids dissolved, and after 3 h of heating, a light yellow solution was observed. The solvent was removed under reduced pressure, and the resulting solids were washed three times with copious amounts of pentane to give whitish yellow solids. The white solids were dried in vacuo to give 2.13 g of 2 (4.65 mmol, 94.3% yield).

Anal. Calcd (found) for  $C_{9}H_{29}IrClP_{3}$ : *C*, 23.60 (23.38); H, 6.40 (6.12). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –24.1 (m,  $J_{HP}$  = 11 Hz,  $J_{HH}$  = 5.56 Hz, 1H), -11.2 (dtd,  $J_{HP}$ trans = 135 Hz,  $J_{HPcis}$  = 22.2 Hz,  $J_{HH}$  = 5.56 Hz, 1H), 1.63 (t,  $J_{HP}$  = 4.8 Hz, 18H of trans PMe<sub>3</sub>), 1.55 (d,  $J_{HP}$  = 11.1 Hz, 9 Hz of cis PMe<sub>3</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –48.44 (t,  $J_{PP}$  = 54.57 Hz, 1P of cis PMe<sub>3</sub>), -42.6 (d,  $J_{PP}$  = 54.2 Hz, 2P of trans PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  22.48 (t,  $J_{CP}$  = 66.31 Hz, 6C of trans PMe<sub>3</sub>), 20.09 (d,  $J_{CP}$  = 104.22 Hz, 3C of cis PMe<sub>3</sub>).

Crystals suitable for X-ray diffraction were grown by slow evaporation of a diethyl ether solution of 1 under nitrogen.

Synthesis of  $[Ir(H)_2(PMe_3)_4][PF_6]$  (3a). A 25.0 mL one-necked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.10 g (0.22 mmol) of  $Ir(H)_2(PMe_3)_3Cl$  and 0.08 g (0.22 mmol) of  $Tl[PF_6]$  under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 5.00 mL of methylene chloride was added by syringe followed by 0.023 mL (4.36 mmol) of trimethylphosphine. The reaction mixture was stirred magnetically. A white precipitate formed in a clear solution. The precipitate was removed by filtration, and the methylene chloride solution was stripped under reduced pressure to give white solids, which were dried in vacuo to give 0.060 g of 3a (0.110 mol, 51.5% yield).

Anal. Calcd (found) for  $C_{12}H_{37}P_5IrF_6$ : *C*, 22.40 (22.47); H, 5.95 (5.92). <sup>1</sup>H NMR (acetone-*d*):  $\delta$  –13.7 (dt,  $J_{HPtrans}$  = 115.0 Hz,  $J_{HPcis}$  = 23.2 Hz, 2H), 1.0 (t,  $J_{HP}$  = 7.7 Hz, 18H of trans PMe<sub>3</sub>), 1.4 (d,  $J_{HP}$  = 13.8 Hz, 18 H of cis PMe<sub>3</sub>).

Synthesis of  $[Ir(H)_2(PMe_3)_4][CI]$  (3b). A 10.0 mL one-necked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.030 g (0.066 mmol) of  $Ir(H)_2(PMe_3)_3CI$  under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 2.00 mL of distilled water was added by syringe followed by 7.20  $\mu$ L of trimethylphosphine. The solution was stirred magnetically at room temperature for 2 h. At completion, a clear solution was observed. The water solution was stripped under reduced pressure to give white solids, which were dried in vacuo at room temperature to give 0.025 g of 3b (0.045 mol, 70.0% yield) (C, H analysis obtained only for the PF<sub>6</sub><sup>-</sup> complex).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -12.95 (dt,  $J_{\rm HPtrans}$  = 115.0 Hz,  $J_{\rm HPcis}$  = 22.0 Hz, 2H), 1.65 (d,  $J_{\rm HP}$  = 8.1 Hz, 18 H of cis PMe<sub>3</sub>), 1.73 (t,  $J_{\rm HP}$  = 3.2 Hz, 18 H of trans PMe<sub>3</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -59.82 (t,  $J_{\rm PP}$  = 20.2 Hz, 2P of cis PMe<sub>3</sub>), -53.6 (t,  $J_{\rm PP}$  = 19.4 Hz, 2P of trans PMe<sub>3</sub>).

Synthesis of  $Ir(H)(C(H)=C(H)CMe_3)(PMe_3)_3CI (4a)$ . A 250.0 mL one-necked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.400 g (0.090 mmol) of  $Ir(H)_2(PMe_3)_3CI$  under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 14.0 mL of distilled water was added by syringe followed by 244 mL (1.98 mmol) of *tert*-butylacetylene. A milky solution formed, and white solids were observed immediately. The solution was stirred magnetically at room temperature for 3 h. The water was stripped under reduced pressure to give white solids, which were dried in vacuo to give 0.380 g of 4 (7.02 mmol, 78.0% yield).

Anal. Calcd (found) for  $C_{15}H_{39}P_3$ ClIr: C, 33.36 (32.82); H, 7.28 (7.35). <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta$  –23.9 (q,  $J_{HP}$  = 16.9 Hz, 1H), 0.95 (s,

9H, CMe<sub>3</sub>), 1.45 (t,  $J_{\rm HP}$  = 4.3 Hz, 18H of trans PMe<sub>3</sub>), 1.52 (d,  $J_{\rm HP}$  = 7.6 Hz, 9H of cis PMe<sub>3</sub>), 6.7(ddt,  $J_{\rm HH}$  = 17.5 Hz,  $J_{\rm HPtrans}$  = 3.5 Hz,  $J_{\rm HP,cis}$  = 3.5 Hz, <sup>1</sup>H, vinyl IrCH), 5.33 (ddt,  $J_{\rm HH}$  = 17.5 Hz,  $J_{\rm HPtrans}$  = 7.0 Hz,  $J_{\rm HPcis}$  = 2.7 Hz, <sup>1</sup>H, vinyl Me<sub>3</sub>CCH). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -42.34 (d,  $J_{\rm PP}$  = 65.1 Hz, 1P of cis PMe<sub>3</sub>), -51.38 (t,  $J_{\rm PP}$  = 65.1 Hz, 2P of trans PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  16.62 (t,  $J_{\rm CP}$  = 74.9 Hz, 6C of trans PMe<sub>3</sub>), 21.5 (d,  $J_{\rm CP}$  = 108.22 Hz, 3C of cis PMe<sub>3</sub>), 29.86 (s, 3 C of CMe<sub>3</sub>), 37.3(s, 1C of CMe<sub>3</sub>), 128.27 (t,  $J_{\rm CP}$  = 15.0 Hz, 1C of vinyl C(H)CMe<sub>3</sub>), 148.95 (s, 1C of vinyl CH).

Synthesis of Ir(H)(C(H)==C(H)(SiMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>3</sub>Cl (4b). A 250.0 mL one-necked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.200 g (0.440 mol) of Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>Cl under N<sub>2</sub> in a drybox. The flask was then connected to a double-manifold Schlenk line, and 5.00 mL of distilled water was added by syringe. Next, 67.9  $\mu$ L (0.480 mol) of trimethylsilylacetylene was added by syringe. Light yellow solids were formed. The reaction mixture was stirred overnight. The light yellow solids were collected by filtration, and the solids were dried in vacuo to yield a product mixture of 6 with two different isomers, which were identified by <sup>1</sup>H NMR spectroscopy. C,H analysis was not obtained for this mixture; other compounds in this family have been characterized.

Major isomer: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ −23.45 (q, *J*<sub>HP</sub> = 16.9 Hz, 1H), 1.44 (t, *J*<sub>HP</sub> = 3.4 Hz, 18H of trans PMe<sub>3</sub>), 1.49 (d, *J*<sub>HP</sub> = 7.6 Hz, 9H of cis PMe<sub>3</sub>), −0.03 (s, 9H of SiMe<sub>3</sub>), 6.15 (ddt, *J*<sub>HH</sub> = 20.2 Hz, *J*<sub>HPtrans</sub> = 11.2 Hz, *J*<sub>HPcis</sub> ≤ 3 Hz, <sup>1</sup>H of vinyl C(H)(SiMe<sub>3</sub>)), 8.3 (ddt, *J*<sub>HH</sub> = 20.2 Hz, *J*<sub>HPtrans</sub> = 5.9 Hz, *J*<sub>HPcis</sub> = 3.7 Hz, <sup>1</sup>H of vinyl IrC(H)).

Minor isomer: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ −10.75 (dt, J<sub>HPtrans</sub> = 135.0 Hz,  $J_{HPcis}$  = 16.9 Hz, 1H), 1.49 (d,  $J_{HP}$  = 7.6 Hz, 18H of trans PMe<sub>3</sub>), 1.6 (t,  $J_{HP}$  = 3.4 Hz, 9H of cis PMe<sub>3</sub>), −0.003 (s, 9H of SiMe<sub>3</sub>), 7.9 (dtd,  $J_{HH}$  = 20.2 Hz,  $J_{HPtrans}$  = 11.2 Hz,  $J_{HPcis}$  ≤ 3 Hz, <sup>1</sup>H of vinyl C(H)(SiMe<sub>3</sub>)), signal for vinyl IrC(H) was not seen.

Attempts to separate the two isomers led to decomposition of the material, and complete spectral characterization was not obtained. However, the <sup>1</sup>H NMR spectra of the hydride region (both the chemical shift and the splitting patterns) clearly indicate the presence of the two indicated isomers.

Synthesis of Ir(H)(C(H)=C(H)(Ph))(PMe<sub>3</sub>)<sub>3</sub>Cl (4c). A 250.0 mL one-necked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.500 g (1.09 mmol) of Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>Cl under nitrogen in a drybox. The flask was then connected to a double-manifold (Schlenk line, and 14 mL of distilled water was added by syringe. Next, 132  $\mu$ L (1.20 mmol) of phenylacetylene was added by syringe. A milky white solution formed, and white solids precipitated immediately. The water was stripped off under reduced pressure to give white solids, which were dried in vacuo to give 0.400 g of 5 (0.714 mmol, 66.0% yield).

Anal. Calcd (found) for  $C_{17}H_{35}ClP_3Ir$ : C, 36.46 (36.55); H, 6.30 (6.25). <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta$  –23.2 (q,  $J_{HP}$  = 17.0 Hz, 1H), 1.45 (t,  $J_{HP}$  = 5.4 Hz, 18H of trans PMe<sub>3</sub>), 1.57 (d,  $J_{HP}$  = 10.5 Hz, 9H of cis PMe<sub>3</sub>), 6.55 (ddt,  $J_{HH}$  = 22.0 Hz,  $J_{HPtrans}$  = 9.2 Hz,  $J_{HPcis}$  = 3.7 Hz, <sup>1</sup>H, vinyl PhCCH), 8.25 (ddt,  $J_{HH}$  = 19.24 Hz,  $J_{HPtrans}$  = 4.2 Hz,  $J_{HPcis} \leq$  3.0 Hz, <sup>1</sup>H, vinyl IrCH), 7.0–7.4 (m, 5H of phenyl). <sup>31</sup>P NMR ( $CD_2Cl_2$ ): d-40.85 ppm (d,  $J_{PP}$  = 53.38 Hz, 2P of trans PMe<sub>3</sub>), -51.77 (t,  $J_{PP}$  = 52.52 Hz, 1P of cis PMe<sub>3</sub>), <sup>13</sup>C NMR ( $CD_2Cl_2$ ):  $\delta$  16.96 ppm (t,  $J_{CP}$  = 15 Hz, 6C of trans PMe<sub>3</sub>), 21.34 (d,  $J_{CP}$  = 18.5 Hz, 3C of cis PMe<sub>3</sub>), 146.1 (t,  $J_{CP}$  = 15.0 Hz, 1C of vinyl C(H)(Ph), 138.51 (s, 1C of vinyl IrC(H)), 124.38 (s, 1C, para carbons of phenyl), 124.74 (s, 2C, ortho carbons of phenyl), 128.63 (s, 2C, meta carbons of phenyl).

Synthesis of  $Ir(H)(Me_3CC(H)=CMe)(PMe_3)_3Cl (4d)$ . A 250.0 mL one-necked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.300 g (0.655 mmol) of  $Ir(H)_2(PMe_3)_3Cl$  under N<sub>2</sub> in a drybox. The flask was then connected to a double-manifold Schlenk line, and 14.0 mL of distilled water was added by syringe. Next, 0.050 g (0.655 mmol) of 2,4-hexadiyne was charged quickly. A milky white solution was formed, and white solids were observed immediately. The reaction mixture was stirred magnetically at room temperature. After 4 h, the water was stripped under reduced pressure to give light whitish brown solids. The solids were dissolved in 0.500 mL of methylene chloride, and 5.00 mL of diethyl ether was used to recrystallize the compound. The methylene chloride/diethyl

ether solution was filtered off, and the solids were dried in vacuo to yield 0.300 g of 7 (0.560 mmol, 85.5% yield).

Anal. Calcd (found) for  $C_{14}H_{41}IrP_3Cl: C, 31.72$  (32.17); H, 7.79 (8.09). <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta$  –23.7 (q,  $J_{HP}$  = 12.0 Hz, 1H), 1.45 (t,  $J_{HP}$  = 4.9 Hz, 18H of trans PMe<sub>3</sub>), 1.52 (d,  $J_{HP}$  = 8.2 Hz, 9H of cis PMe<sub>3</sub>), 1.6–1.8 (m, 3H of =CMe), 2.0 (s, 3H of CCC*Me*), 6.25 (m, <sup>1</sup>H of vinyl CH). <sup>31</sup>P NMR ( $CD_2Cl_2$ ):  $\delta$  –51.30 (t,  $J_{PP}$  = 49.8 Hz, 2P of trans PMe<sub>3</sub>), -40.72 (d,  $J_{PP}$  = 29.8 Hz, 1P of cis PMe<sub>3</sub>).

Crystals suitable for X-ray diffraction were grown by slow vapor diffusion of diethyl ether into a dichloromethane solution of **4d**.

Synthesis of  $Ir(H)_2(PMe_3)_3Br$  (5a). A side-arm flask equipped with septa and stirrer was charged with 1 (0.25 g, 0.55 mmol) under nitrogen. A 10.0 mL portion of H<sub>2</sub>O was added by syringe and the solution stirred until homogeneous. Excess KBr (0.65 g, 5.5 mmol) was added, and a white precipitate immediately formed, while the solution was stirred for 1 h. The solvent was removed under reduced pressure and the residue extracted with 2 × 5 mL of CH<sub>2</sub>Cl<sub>2</sub> to give pure 6 (0.23 g, 85%) as a white powder.

Anal. Calcd (found) for C<sub>9</sub>H<sub>29</sub>IrP<sub>3</sub>Br: C, 21.80 (21.5); H, 5.81 (5.87). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –23.0 (m, 1 H), –11.3 (dtd, *J*<sub>HPtrans</sub> = 134 Hz, *J*<sub>HPcis</sub> = 22.3 Hz, *J*<sub>HHcis</sub> =5.1 Hz, 1 H), 1.50 (d, *J*<sub>HP</sub> = 7.3 Hz, 9 H of cis PMe<sub>3</sub>), 1.65 (t, *J*<sub>HP</sub> = 5.7 Hz, 18 H of trans PMe<sub>3</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –53.7 ppm (t, *J*<sub>PP</sub> = 62.1 Hz, cis PMe<sub>3</sub>), -46.7 (d, *J*<sub>PP</sub> = 54.1 Hz, trans PMe<sub>3</sub>). <sup>31</sup>P NMR (H<sub>2</sub>O): major species  $\delta$  –53.4 (t, *J*<sub>PP</sub> = 48.1 Hz, cis PMe<sub>3</sub>), -47.3 (d, *J*<sub>PP</sub> = 55.0 Hz, trans PMe<sub>3</sub>); minor species  $\delta$  –44.0 (t, cis PMe<sub>3</sub>), -39.5 (d, *J*<sub>PP</sub> = 54.4 Hz, trans PMe<sub>3</sub>).

**Synthesis of Ir(H)**<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>I (5b). A 100.0 mL one-necked sidearmed flask equipped with a magnetic stir bar and a septum was charged with 0.300 g (0.660 mmol) of 2 under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 14.0 mL of distilled water was added by syringe. The mixture was stirred magnetically at room temperature. Next, 0.130 g (0.790 mmol) of potassium iodide was added quickly. White solids precipitated out immediately. After 24 h, the precipitate was filtered. The white solids were washed three times with excess distilled water and dried in vacuo to give 0.250 g of  $Ir(H)_2(PMe_3)_3I$  (0.230 mmol, 70.0% yield).

Anal. Calcd (found): I, 25.2 (25.12). <sup>1</sup>H NMR (methylene-*d* chloride):  $\delta$  -20.7 (m,  $J_{\rm HP}$  = 11.2 Hz,  $J_{\rm HH}$  = 5.2 Hz), -12.0 (dtd,  $J_{\rm HPtrans}$  = 132.2 Hz,  $J_{\rm HPcis}$  = 22.0 Hz,  $J_{\rm HH}$  = 5.9 Hz, 1H), 1.58 (d,  $J_{\rm HP}$  = 7.79 Hz, 9H of cis PMe<sub>3</sub>), 1.72 (t,  $J_{\rm HP}$  = 3.28 Hz, 18H of trans PMe<sub>3</sub>). <sup>31</sup>P NMR (methylene-*d* chloride):  $\delta$  -61.0 (t,  $J_{\rm PP}$  = 54.46 Hz, 1P of cis PMe<sub>3</sub>), -51.6 (d,  $J_{\rm PP}$  = 52.3 Hz, 2P of trans PMe<sub>3</sub>). <sup>13</sup>C NMR (methylene-*d* chloride):  $\delta$  22.0 ( $J_{\rm CP}$  = 110.0 Hz, 3C of cis PMe<sub>3</sub>), 24.4 (t,  $J_{\rm CP}$  = 67.1 Hz, 6C of trans PMe<sub>3</sub>).

**Synthesis of**  $[Ir(COD)(O_2CCH_3)]_2$  (6a). A 250 mL one-necked side-armed flask equipped with a magnetic stir bar and a septum was charged with 1.00 g (1.49 mmol) of  $[Ir(COD)Cl]_2$  under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 25.0 mL of toluene was added by syringe. A 0.550 g portion (3.27 mmol) of Ag[O\_2CCH\_3] was added quickly and the flask covered to protect it from light. The reaction mixture was stirred magnetically at room temperature for 2 days. The reddish purple solution was filtered away from the white AgCl salt. A 100 mL portion of toluene was used to wash the white solid AgCl salt. The solutions were all combined, and the solvent was removed under reduced pressure to give reddish purple solids. The reddish purple solids were dried in vacuo to give 0.890 g of  $[Ir(COD)(O_2CCH_3)]_2$  (1.24 mol, 83.0% yield).

Anal. Calcd (found) for  $C_{20}H_{30}IrO_4$ : C, 45.6 (45.9); H, 5.74 (6.13). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.06 (br s, 2H of COD olefinic), 3.86 (br s, 2H of COD olefinic), 2.52 (br s, 2H of COD aliphatic), 2.30 (br m, 2H of COD aliphatic), 1.45 (br m, 4 H of COD aliphatic), 1.89 (s, 3H of CH<sub>3</sub>).

Synthesis of  $[Ir(COD)(O_2CPh)]_2$  (6b). A 500 mL one-necked sidearmed flask equipped with a stir bar and a septum was charged with 3.50 g (5.21 mmol) of  $[Ir(COD)Cl]_2$  under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 100 mL of toluene was added by syringe. Next, 2.63 g (11.5 mmol) of Ag[O\_2CPh] was added quickly and the flask covered to protect it from light. The suspension was stirred magnetically at room temperature for 3 days. The reddish purple solution was filtered away from the white AgCl salt. A 300 mL portion of toluene was used to wash the white AgCl salt. All of the reddish purple solution was concentrated by evaporating at reduced pressure to give reddish purple solids. The reddish purple solids were dried in vacuo to give 3.30 g of  $[Ir(COD)(OCOPh)]_2$  (3.93 mmol, 75.4% yield).

Anal. Calcd (found) for  $C_{30}H_{34}O_4Ir: C, 42.74$  (42.52): H, 4.07 (4.03). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.25 (br s, 2H of COD olefinic), 3.96 (br s, 2H of COD olefinic), 2.57 (br m, 2H of COD aliphatic), 2.43 (br m, 2H of COD aliphatic), 1.50 (br m, 4H of COD), 7.94 (m, 2H of C<sub>6</sub>H<sub>5</sub>), 7.4–7.2 (m, 3 H of C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  32.07 (s, 4C of COD), 56.5 (s, 4C of COD), 127.75 (s, 2C, meta carbons, phenyl ring), 129.92 (s, 2C, ortho carbons, phenyl ring), 131.84 (s, 1C, para carbon, phenyl ring).

**Synthesis of [Ir(COD)(O<sub>2</sub>CCF<sub>3</sub>)]<sub>2</sub> (6c).** A 250 mL one-necked side-armed flask equipped with a stir bar and a septum was charged with 1.00 g (1.49 mmol) of  $[Ir(COD)Cl]_2$  under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 25.0 mL of toluene was added by syringe. A 0.720 g portion (3.27 mmol) of Ag[O<sub>2</sub>CCF<sub>3</sub>] was added quickly, and the flask was covered to protect the solution from light. The reaction mixture was stirred magnetically at room temperature for 2 days. The reddish orange solution was concentrated by removing toluene under reduced pressure to give reddish orange solids. The reddish orange solids were dried in vacuo to give 1.11 g of  $[Ir(COD)(OCOCF_3)]_2$  (1.35 mmol, 90.3% yield).

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  4.5 (br s, 2H of COD olefinic), 4.15 (br s, 2H of COD olefinic), 2.6 (br s, 2H of COD aliphatic), 2.3 (br s, 2H of COD aliphatic), 1.7 (br s, 4H of COD aliphatic).

Synthesis of  $[Ir(COD)(PMe_3)_3][O_2CCH_3]$  (7a). A 250 mL onenecked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.630 g (8.76 mmol) of  $[Ir(COD)-(O_2CCH_3)]_2$  (6a) under nitrogen in a drybox. The flask was connected to a double-manifold Schlenk line, and 40.0 mL of toluene was added by syringe. Next, 0.550 mL (5.34 mmol) of trimethylphosphine was added slowly by syringe. White solids precipitated immediately. The suspension was stirred magnetically at room temperature for 1 day, and the solids were collected by filtration. The solids were washed three times each with an excess of pentane and tetrahydrofuran and dried in vacuo to give 0.700 g of  $[Ir(COD)(PMe_3)_3][O_2CCH_3]$  (1.20 mmol, 68.0% yield).

Anal. Calcd (found) for  $C_{19}H_{42}IrP_3O_2$ : C, 40.1 (39.76); H, 4.25 (4.01). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.1 (broad s, 4H of COD olefinic), 2.3 (broad s, 4H of COD aliphatic), 2.1 (br s, 4H of COD aliphatic), 1.8 (s, 3H of CH<sub>3</sub>), 1.62 (virtual t, 27H of 3 PMe<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  -53.15 (s, 3P of 3 PMe<sub>3</sub>).

Synthesis of  $[Ir(COD)(PMe_3)_3][O_2CPh]$  (7b). A 250 mL onenecked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.500 g (0.593 mmol) of  $[Ir(COD)-(OOCPh)]_2$  (6b) under nitrogen in a drybox. The flask was then connected to a double-manifold (vacuum, nitrogen) Schlenk line, and 30.0 mL of toluene was added by syringe. Next, 0.400 mL (3.80 mmol) of trimethylphosphine was added slowly also by syringe. White solids precipitated immediately. The suspension was stirred at room temperature overnight. The light pink liquid solution was filtered off from the white solid product. Three 15.0 mL portions of pentane were used to wash the white solids. Three 15.0 mL portions of tetrahydrofuran were also used to wash the white solids. The white solids were then dried in vacuo to give 0.580 g of  $[Ir(COD)-(PMe_3)_3][O_2CPh]$  (0.883 mmol, 74.5% yield).

Anal. Calcd (found) for  $C_{24}H_{44}O_2P_3Ir$ : C, 44.32 (44.23); H, 6.92 (6.95). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.15 (m, 2H of phenyl ring), 7.2 (m, 3H of phenyl ring), 3.1 (br s, 4H of COD olefinic), 2.35 (br s, 4H of COD aliphatic), 2.19 (br s, 4H of COD aliphatic), 1.52 (t, *J* = 2.77 Hz, 27H of 3 PMe<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  –53.27 (s, 3P of 3 PMe<sub>3</sub>), <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  128.92 (s, 2C, meta carbons, phenyl ring), 130.21 (s, 2C, ortho carbons, phenyl ring), 133.99 (s, 1C, para carbons,

phenyl ring), 69.20 (s, 4C of COD), 34.37 (s, 4C of COD), 20.02-20.54 (m, 9C of PMe<sub>3</sub>).

Synthesis of ]Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>][O<sub>2</sub>CCF<sub>3</sub>] (7c). A 250 mL onenecked side-armed flask equipped with a magnetic stir bar and a septum was charged with 0.600 g (0.726 mmol) of [Ir(COD)-(O<sub>2</sub>CCF<sub>3</sub>)]<sub>2</sub> (6c) under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 50.0 mL of toluene was added by syringe. Next, 47.0  $\mu$ L (4.57 mmol) of trimethylphosphine was added slowly by syringe. White solids precipitated immediately. The suspension was stirred at room temperature for 1 day. The solid was then collected by filtration. The white solids were washed three times with pentane and tetrahydrofuran and dried in vacuo to give 0.760 g of [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>][O<sub>2</sub>CCF<sub>3</sub>] (1.20 mmol, 82.1% yield).

Anal. Calcd (found) for  $C_{19}H_{39}O_2F_3Ir$ : C, 35.57 (35.82); H, 6.13 (6.01). <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta$  3.3 (br s, 4H of COD olefinic), 2.5 (br s, 4H of COD aliphatic), 2.2 (br s, 4H of COD aliphatic), 1.5 (virtual t, 27H of 3 PMe<sub>3</sub>).

Synthesis of  $Ir(H)_2(PMe_3)_3(O_2CPh)$  (8). A 50.0 mL three-necked flask equipped with a magnetic stir bar and septa was charged with 1.37 g (2.08 mmol) of  $[Ir(COD)(PMe_3)_3][O_2CPh]$  (7b) under nitrogen in a drybox. The flask was then connected to a doublemanifold (vacuum, nitrogen) Schlenk line, and 20.0 mL of dried mesitylene was added by syringe. The flask was then fitted with a reflux column equipped with a nitrogen inlet and connected to the Schlenk line. H<sub>2</sub> was bubbled through the solution at a very slow rate. The suspension was stirred magnetically and heated to about 100 °C. Upon heating, the white solids dissolved to give a light yellow solution. After 3 h of heating, all of the solids had dissolved to yield a light yellow solution. The solution was concentrated under reduced pressure, yielding white solids which were washed three times with copious amounts of pentane. The solids were dried in vacuo to give 1.08 g of  $Ir(H)_2(PMe_1)_3(O_2CPh)$  (1.98 mmol, 95.2% yield).

Anal. Calcd (found) for  $C_{16}H_{34}O_2P_3Ir$ : C, 35.36 (35.61); H, 6.30 (6.24). <sup>1</sup>H NMR ( $CD_2CI_2$ ):  $\delta$  –26.3 (m,  $J_{HP}$  = 12.5 Hz,  $J_{HH}$  = 5.4 Hz, 1H), -10.52 (dtd,  $J_{HPtrans}$  = 134.1 hz,  $J_{HPcis}$  = 23.9 Hz,  $J_{HH}$  = 6.06 Hz, 1H), 1.55 (d,  $J_{HP}$  = 8.3 Hz, 9H of cis PMe<sub>3</sub>), 1.6 (t,  $J_{HP}$  = 4.2 Hz, 18 H of trans PMe<sub>3</sub>), 7.1–7.3 (m, 3H of phenyl ring), 7.85–7.9 (m, 2H of phenyl ring). <sup>31</sup>P NMR ( $CD_2CI_2$ ):  $\delta$  –42.45 (t,  $J_{PP}$  = 52.94 Hz, 1P of cis PMe<sub>3</sub>), -38.31 (d,  $J_{PP}$  = 52.76 Hz, 2P of trans PMe<sub>3</sub>). <sup>13</sup>C NMR ( $CD_2CI_2$ ):  $\delta$  21.34 (d,  $J_{CP}$  = 105.3 Hz, 3C of cis PMe<sub>3</sub>), 23.02 (t,  $J_{CP}$  = 66.34 Hz, 6C of cis PMe<sub>3</sub>), 127.72 (s, 2C, meta carbons of phenyl ring), 129.45 (s, 1C, para carbons of phenyl ring), 129.95 (s, 2C, ortho carbons of phenyl ring).

Oxidative Addition of H<sub>2</sub> to [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>][O<sub>2</sub>CCF<sub>3</sub>]. A 250 mL three-necked flask equipped with a magnetic stir bar and septa was charged with 1.95 g (3.04 mmol) of  $[Ir(COD)(PMe_3)_3][O_2CCF_3]$ under nitrogen in a drybox. The flask was then connected to a doublemanifold Schlenk line, and 20.0 mL of dried mesitylene was added by syringe. The flask was then fitted with a reflux column equipped with a nitrogen inlet and connected to the Schlenk line. H<sub>2</sub> was bubbled through the solution at a very slow rate. The suspension was stirred magnetically and heated slowly to about 100 °C. Upon heating, the white solids dissolved to give a light yellow solution. After 3 h of heating, a light yellow solution was observed. The solution was concentrated under reduced pressure to give a light yellow oily crude product. Methylene chloride/ether was used to recrystallize the oily crude product. Yellow solids were obtained upon recrystallization and dried in vacuo to give a very low yield of  $[Ir(H)_2(PMe_3)_4][OC(O) CF_3$ ].

Anal. Calcd (found): C, 27.5 (27.28); H, 6.26 (6.13). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –12.9 (dt, J<sub>HPtrans</sub> = 113.16 Hz, J<sub>HPcis</sub> = 24.79 Hz, 1H), 1.63 (d, J<sub>HP</sub> = 7.63 Hz, 18H of cis PMe<sub>3</sub>), 1.71 (t, J<sub>HP</sub> = 3.5 Hz, 18H of trans PMe<sub>3</sub>). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –59.95 (t, J<sub>PP</sub> = 51.4 Hz, 2P of cis PMe<sub>3</sub>), -53.69 (t, J<sub>PP</sub> = 52.04 Hz, 2P of trans PMe<sub>3</sub>).

**Oxidative Addition of H**<sub>2</sub> to [lr(COD)(PMe<sub>3</sub>)<sub>3</sub>][O<sub>2</sub>CCH<sub>3</sub>]. A 250 mL three-necked flask equipped with a magnetic stir bar and septa was charged with 0.500 g (0.779 mmol) of [Ir(COD)(PMe<sub>3</sub>)<sub>3</sub>][O<sub>2</sub>CCH<sub>3</sub>] under nitrogen in a drybox. The flask was then connected to a double-manifold Schlenk line, and 20.0 mL of mesitylene was connected to

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the Schlenk line. H<sub>2</sub> was bubbled through the solution at a very slow rate. The suspension was magnetically stirred and heated slowly up to about 100 °C. Upon heating, the white solids dissolved to give a light yellow solution. After 3 h of heating, a light yellow solution was observed. The solution was concentrated under reduced pressure and washed three times with copious amounts of pentane to give a light yellow oily crude product. <sup>1</sup>H NMR spectroscopy indicated that the crude product was a mixture of at least two products: Ir-(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>) and [Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>][O<sub>2</sub>CCH<sub>3</sub>]. Recrystallization and separation by methylene chloride/ether was not successful. No further work was carried out.

**Reaction of PMe<sub>3</sub> with 20 in Water.** A 25.0 mL one-necked sidearmed flask equipped with a magnetic stir bar and a septum was charged with 0.050 g (0.092 mmol) of Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>(O<sub>2</sub>CPh) (**20**) under nitrogen in a drybox. The flask was then connected to a doublemanifold Schlenk line, and 5.00 mL of distilled water was added. Next, 19.1  $\mu$ L (0.184 mmol) of trimethylphosphine was added by syringe. The solution was magnetically stirred for 1 day. Water was stripped off under reduced pressure to yield white solids. The white solids were dried in vacuo to yield Ir(H)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub>][O<sub>2</sub>CPh]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –12.98 (dt, J<sub>HPtrans</sub> = 100.52, J<sub>HPcis</sub> = 21.74 Hz, 1H), 1.62 (d, J<sub>HP</sub> = 7.52 Hz, 18H of cis PMe<sub>3</sub>), 1.70 (t, J<sub>HP</sub> = 3.24 Hz, 18H of trans PMe<sub>3</sub>), 7.23 (t, 3H of phenyl ring), 8.0 (q, 2H of phenyl ring). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ -59.84 (t, J<sub>PP</sub> = 50.48 Hz, 2P of cis PMe<sub>3</sub>), -53.62 (t, J<sub>PP</sub> = 50.34 Hz, 2P of trans PMe<sub>3</sub>).

Synthesis of Ir(H)(C(H)=C(H)(CMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>3</sub>(O<sub>2</sub>CPh) (9). A 250 mL one-necked side-armed flask equipped with a magnetic stirrer and a septum was charged with 0.215 g (0.400 mmol) of 8 under nitrogen in a drybox. The flask was connected to a double-manifold Schlenk line, and 10.0 mL of distilled water was added by syringe. Next, 53.6  $\mu$ L (0.435 mmol) of *tert*-butylacetylene was added also by syringe. A milky solution and white solids were observed immediately. The solution was magnetically stirred at room temperature for 4 h. The water was then stripped under reduced pressure to give white solids, which were dried in vacuo to give 0.226 g of Ir(H)(C(H)=C(H)(CMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>3</sub>(O<sub>2</sub>CPh) (0.361 mmol, 91.2% yield).

Anal. Calcd (found): C, 42.23 (41.33); H, 7.09 (6.98). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –26.1 (q,  $J_{\rm HP}$  = 15.14 Hz, 1H), 0.96 (s, 9H of CMe<sub>3</sub>), 1.45 (t,  $J_{\rm HP}$  = 3.46 Hz, 18H of trans PMe<sub>3</sub>), 1.5 (d,  $J_{\rm HP}$  = 8.03 Hz, 9H of cis PMe<sub>3</sub>), 5.45 (dtd,  $J_{\rm HH}$  = 17.2 Hz,  $J_{\rm HPtrans}$ = 7.68 Hz,  $J_{\rm HPcis}$  < 3.0 Hz, <sup>1</sup>H of vinyl C(H)(CMe<sub>3</sub>)), 6.66 (dtd,  $J_{\rm HH}$  = 17.2 Hz,  $J_{\rm HPcins}$  < 3.0 Hz, <sup>1</sup>H of vinyl C(H)), 7.24–7.33 (m, 3H of phenyl ring), 7.98–8.03 (m, 2H of phenyl ring). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  –47.08 (t,  $J_{\rm PP}$  = 49.4 Hz, 1P of cis PMe<sub>3</sub>), -40.1 (d,  $J_{\rm PP}$  = 50.8 Hz, 2P of trans PMe<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  17.14 (t,  $J_{\rm CP}$ = 74.8 Hz, 6C of trans PMe<sub>3</sub>), 137.0 (s, 1C of vinyl C(H)(CMe<sub>3</sub>)), 148.0 (s, 1C of vinyl C(H)), 127.4 (s, 2C, meta carbons of phenyl ring), 129.2 (s, 1C, para carbon of phenyl ring), 129.4 (s, 2C, ortho carbon of phenyl ring).

Crystals suitable for X-ray diffraction were grown by slow evaporation of a diethyl ether solution of **9** under nitrogen.

Variable-Temperature <sup>31</sup>P NMR of  $IrH_2(PMe_3)_3CI$  (2) in  $H_2O$ . <sup>31</sup>P NMR spectra were acquired over the temperature range 280–310 K and integration values determined; 310 K was not exceeded to avoid decomposition. The first spectrum was acquired at 300 K and used as a reference spectrum. The temperature was incrementally lowered by 5 K, the temperature of the sample was allowed to equilibrate, and then data were acquired; and the whole process was repeated down 280 K. The probe was then slowly warmed to 300 K, the sample was allowed to equilibrate, and then data were acquired. This spectrum was checked against the reference spectrum to ensure that no decomposition had occurred. The temperature was then incrementally increased by 5 K, the temperature of the sample was allowed to equilibrate, and then data were acquired; the whole process was repeated until 310 K. The probe was slowly cooled to 300 K, the sample was allowed to equilibrate, and then data were acquired. This spectrum was again checked against the reference spectrum, which indicated no decomposition had occurred.

Variable-Concentration <sup>31</sup>P NMR of  $IrH_2(PMe_3)_3(O_2CPh)$  (8) and Chloride Ion in  $H_2O$ . A 0.054 M solution of 8 was prepared by

charging a septum bottle equipped with a magnetic stir bar with 0.088 g (0.162 mmol) of  $IrH_2(PMe_3)_3(O_2CPh)$ , sealing under nitrogen in a glovebox, and adding 3.0 mL of  $H_2O$  by syringe. The mixture was stirred until the solution became homogeneous to give a pale yellow solution. Sample NMR tubes were flushed and sealed under argon with a septum. A 0.486 M aqueous NaCl solution was prepared by dissolving 0.0852 g of NaCl in 3.0 mL of  $H_2O$ . The samples were prepared by adding appropriate aliquots of the standard solution of **8** followed by NaCl. <sup>31</sup>P NMR spectra were acquired and integration values determined.

#### ASSOCIATED CONTENT

#### Supporting Information

CIF files giving full crystallographic information for compounds 2, 4d, and 9, text, tables, and figures describing the detailed analysis used to determine and compute the aqueous equilibrium involving 2 and 2a, and figures and tables showing the Gaussian calculations used in support of the use of Mulliken "p" electronegativities in Table 2 and in constructing Figure 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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