An η^1-Aldehyde Complex and the Role of Hydrogen Bonding in Its Conversion to an η^1-Imine Complex

Wenbin Yao and Robert H. Crabtree*

Yale Chemistry Laboratory, 225 Prospect Street, New Haven, Connecticut 06520-8107

Received June 28, 1995[⊗]

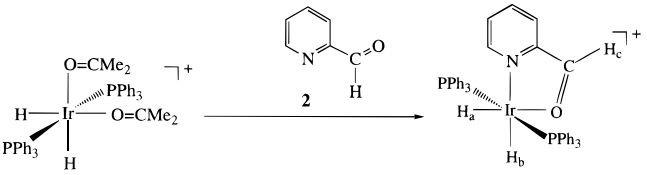
2-Pyridinecarboxaldehyde displaces Me_2CO from $[IrH_2(Me_2CO)_2(PPh_3)_2]^+$ to give a chelating N,O-bound product containing an η^1-O-bound aldehyde group. This is converted to the η^1-N-bound imine complex with a variety of substituted amines. When the amine contains a suitably positioned −OH group, intramolecular O−H···H−Ir dihydrogen bonds are detected in the products. This hydrogen bonding influences the relative rates of product formation from 2- and 4-aminophenol (rate ratio 6:1), where only the 2-isomer is capable of forming an intramolecular H-bond.

Introduction

A new type of hydrogen bond involving an H···H interaction has been observed for a number of complexes containing the M−H···H−X group (M = transition metal; X = O or N).[1,2] An intermolecular case has been verified by neutron diffraction: $[ReH_5(PPh_3)_3(indole)]$.[1e] The M−H···H−X H-bond energy, typically 4−6 kcal·mol^{-1},[1] should be sufficient to have significant effects on equilibrium constants if an H-bond is present in one isomer but not the other. There could also be a strong effect on rate constants if an H-bond is present in only one of two related transition states. In trying to develop this aspect of the chemistry, we have looked at the imination of a coordinated aldehyde and find a small effect of H-bonding on the product distribution. We have also observed examples of η^1-aldehyde and η^1-imine complexes and an unexpected long-range coupling between the aldehyde proton and one of the metal hydride protons.

Results and Discussion

$[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ (**1**)[3] reacts at room temperature with 2-pyridinecarboxaldehyde (**2**) to give the fully characterized orange microcrystalline derivative (**3**) in 95% yield (eq 1).



(1)

Assigning the Aldehyde-Binding Mode. A variety of complexes containing coordinated aldehyde or ketone ligands have been reported. Both σ (η^1) and π (η^2) binding modes have been reported in the literature,[4] and the mode of binding can be assessed by IR and NMR.[5] In IR spectra, coordination shifts $\Delta\nu$(CO) for η^1-aldehydes are in the range 50−100 cm^{-1}, while $\Delta\nu$(CO) values for η^2-aldehydes are 500−750 cm^{-1}. In ^{13}C NMR spectra, aldehyde carbons in η^1-bound complexes typically exhibit coordination shifts of <20−30 ppm from their uncoordinated values, while the η^2-bound complexes exhibit upfield shifts of ∼50 ppm and more.

Our complex **3** shows $\nu_{C=O}$ at 1616 cm^{-1}, versus the uncoordinated ligand $\nu_{C=O}$ at 1734 cm^{-1} ($\Delta\nu$(CO) = 118 cm^{-1}). The ^{13}C NMR for **3**, which can be completely assigned by the DEPT technique, shows a carbonyl chemical shift of 201.1 ppm, versus 193.5 ppm for the uncoordinated ligand ($\Delta\delta$ = +7.6 ppm). Both IR and ^{13}C NMR data are therefore consistent with the presence of an η^1-aldehyde. This is unsurprising because the closely related complex **1** is known (X-ray structure) to have η^1-ketone binding and the chelation implicit in **3** only permits η^1-aldehyde binding.

Long-Range Coupling. A surprise in the ^{1}H NMR spectrum of **3** is the presence of an unusual long-range coupling between H_a and H_c. In order to clearly assign the peaks due to the non-phosphine ligands, we studied the ^{1}H NMR of the PPh_3-d_{15} substituted complex, **3-*d*$_{30}$**. H_b is assigned as trans to N rather than O because of the chemical shift; in this Ir(III) system, the

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) (a) Lee, J. C., Jr.; Rheingold, A. L.; Muller, B.; Pregosin, P. S.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1021. (b) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. (c) Peris, E.; Lee, J. C., Jr.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2573. (d) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485. (e) Wessel, J.; Lee J. C., Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507. (f) Patel, B. P.; Yao, W.; Yap, G. P. A.; Rheingold, A. L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.*, submitted.

(2) (a) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201. (b) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356.

(3) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 6994.

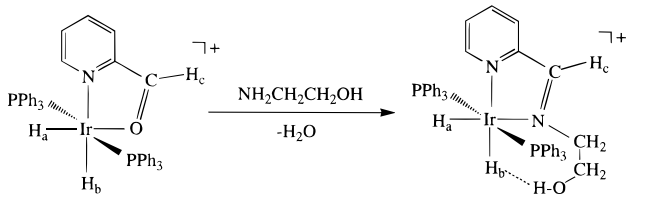
(4) (a) Bullock, R. M.; Rappoli, B. J.; Samsel, E. G.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261. (b) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256. (c) Huang, Y.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298. (d) Bullock, R. M.; Ricci, J. S.; Szalda, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 2741. (e) Mendez, N. Q.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1473. (f) Klein, D. P.; Dalton, D. M.; Mendez, N. Q.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1991**, *412*, C7. (g) Saura-Llamas, I.; Dalton, D. M.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 683. (h) Dalton, D. M.; Fernandez, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198. (i) Agbossou, F.; Ramsden, J. A.; Huang, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 693. (j) Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579.

(5) (a) Garner, C. M.; Mendez, N. Q.; Kowalczyk, J. J.; Fernandez, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146. (b) Faller, J. W.; Ma, Y.; Smart, C. J.; DiVerdi, M. J. *J. Organomet. Chem.* **1991**, *420*, 237. (c) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Perkin Trans.* **1982**, *2*, 711. (d) Courtot, P.; Pichon, R.; Salaun, J. Y. *J. Organomet. Chem.* **1985**, *286*, C17. (e) Auffret, J.; Courtot, P.; Pichon, R.; Salaun, J. Y. *J. Chem. Soc., Dalton Trans.* **1987**, 1687.

S0020-1669(95)00807-X CCC: $12.00

hydride resonance positions are known[3] to depend on the nature of the trans ligand, and H_b at −18.93 ppm is in the typical range for H trans to pyridine nitrogen (−15 to −20 ppm), while H_a at −27.60 ppm is in the typical range for H trans to oxygen (−25 to −30 ppm). H_c resonates at 9.78 ppm as a single broad peak with $w_{1/2} = 7.5$ Hz, while H_a resonates at −27.60 ppm as a doublet of doublets of triplets. Decoupling experiments revealed the presence of a 2.5 Hz coupling between H_a and H_c: when the peak due to H_c was irradiated, the doublet of doublets of triplets due to H_a collapsed to a doublet of triplets. To our knowledge, this type of four-bond coupling has not previously been observed.

Reactions of 3 with Amines. In the hope of synthesizing a series of examples of hydrogen-bonded species, we synthesized a variety of substituted imine complexes. For example, complex **3** rapidly reacts with ethanolamine to give the η^1-N═CH- Schiff base complex **4** (eq 2).

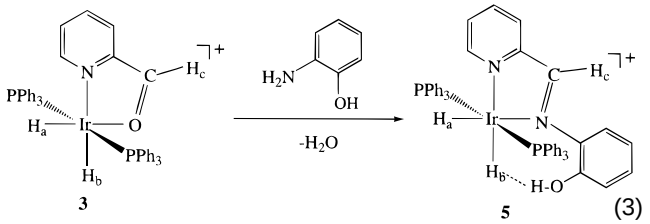


3 **4** (2)

Spectroscopy of 4. Complex **4** has been characterized by IR, ^{1}H NMR, ^{31}P NMR, and elemental analysis. In particular, the imine proton is observed at 8.78 ppm as a broad singlet peak ($w_{1/2} = 5.6$ Hz) and shows a similar long-range 1.2 Hz coupling with one of the hydrides in the ^{1}H NMR.

H-Bonding in 4. A weak Ir−H···H−O interaction is present in complex **4**, because the IR spectrum (thin film) shows ν_{O-H} at 3540 cm^{-1}; in CH_2Cl_2, the hydrogen-bonded and non-hydrogen-bonded forms coexist, as shown by the presence of bands at 3541 and 3601 cm^{-1}, respectively. The $\Delta\nu_{O-H}$ of 60 cm^{-1} corresponds to an H-bond strength of about 2.4 kcal·mol^{-1}, according to the Iogansen equation for the enthalpy of hydrogen-bonding ($\Delta H = -1.28(\Delta\nu)^{1/2}$).[6]

Synthesis of 5. In the hope of moving to a more acidic OH and therefore a stronger hydrogen-bonding interaction, we looked at the reaction of complex **3** with 2-aminophenol (eq 3), which gave complex **5**, characterized by IR, ^{1}H NMR, ^{31}P NMR, and elemental analysis.



3 **5** (3)

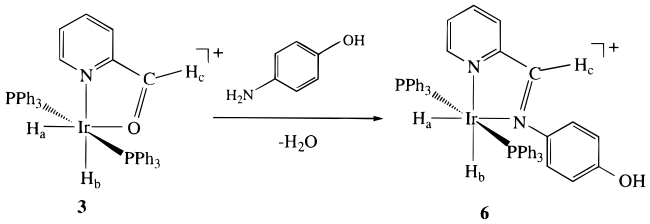
Spectroscopy of 5. The ^{1}H NMR spectrum in CD_2Cl_2 solution shows that the imine proton H_c is observed at 8.83 ppm as a broad singlet peak ($w_{1/2} = 5.0$ Hz) and also shows a similar long-range 1.7 Hz coupling with one of the hydrides, H_a, which resonates as a doublet of doublets of triplets (ddt).

Hydrogen Bonding in 5. The hydrogen bonding is somewhat stronger in this case. The IR spectrum of **5** in a thin film or as a KBr pellet shows a broad peak around 3384 cm^{-1} due to ν_{O-H}; in CH_2Cl_2, the H-bonded and non-H-bonded forms coexist, as shown by the presence of bands at 3379 and 3600 cm^{-1}, respectively. The $\Delta\nu_{O-H}$ of 221 cm^{-1} corresponds to an H-bond strength of about 4.5 kcal·mol^{-1}. However, the H···H coupling constant was too small to be observed by NMR.

Further NMR Studies of 5. To obtain further information about the hydrogen bond found in complex **5**, the T_1(min), measured for the hydrides at 300 MHz, was found at −40 °C (CD_2Cl_2). The H_a and H_b hydrides had T_1(min) values of 200 and 167 ms, respectively, implying an excess relaxation rate of 1.0 s^{-1} for the H-bonded hydride, H_b. Applying the standard equation[7] allows this excess relaxation to be interpreted in terms of an H_b···H(O) distance of 2.4 Å. This is a longer distance than the 1.7−1.8 Å range found for the strong X−H···H−M hydrogen bonds (X = O, N) previously studied;[1,2] this lengthening is in line with the weak bonding found for **5** by IR spectroscopy. Milstein *et al.* found the same long H···H distance of 2.4 Å for a weak O−H···H−Ir interaction in *cis*-[IrH(OH)(PMe_3)$_4$][PF_6] by neutron diffraction, however.[8]

This study also allows us to assign the peak at −19.81 ppm (ddt) to H_a. This in turn shows that it is the hydride trans to the imine N which shows long-range coupling to H_c. Addition of D_2O to the sample causes no significant change in the hydride region of the NMR spectrum of **5**, unlike the cases having strong hydrogen bonding.[1,2] There is therefore no significant exchange between the OH and IrH sites.

Synthesis of 6. In order to compare with **5**, we looked at the reaction of complex **3** with 4-aminophenol (eq 4), which

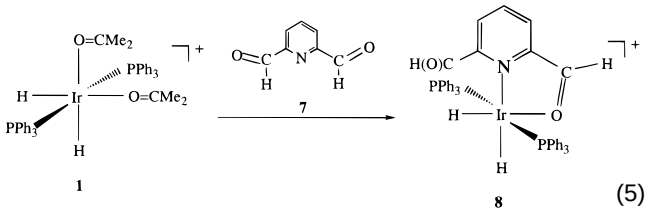


3 **6** (4)

gave complex **6**, fully characterized by analytical and spectral data. The solution IR (in CH_2Cl_2) shows only free ν_{O-H} at 3601 cm^{-1}, very close to free ν_{O-H} at 3600 cm^{-1} for complex **5**, indicating the very similar electronic effects of 2-amino and 4-amino groups.

Other Derivatives. In an attempt to obtain a more flexible system, we looked at the reaction of complex **3** with 2-aminobenzyl alcohol, but no reaction took place.

With 2,6-pyridinedicarboxaldehyde (**7**), **1** reacts at room temperature to give the orange microcrystalline species **8** in 81% yield (eq 5), in which only one of the two carbonyl groups are



1 **8** (5)

coordinated, as expected by analogy with **3**. The IR spectrum of **8** shows a strong peak at 1708 cm^{-1} due to the uncoordinated

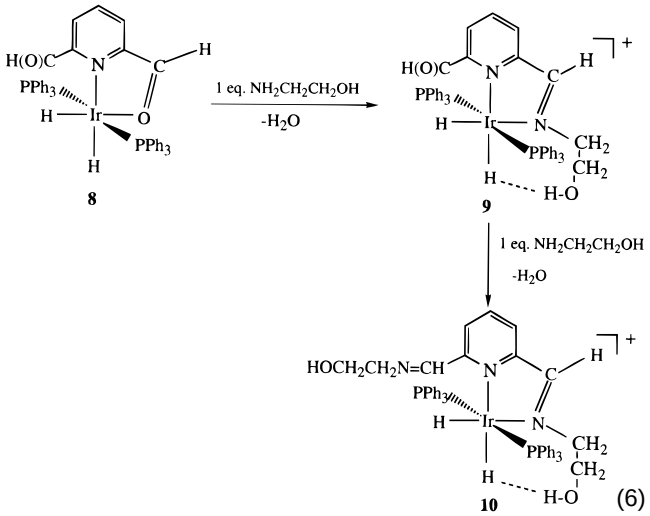
(6) (a) Iogansen, A. V.; Kurkchi, G. A.; Furman, V. M.; Glazunov, V. P.; Odinokov, S. E. *Zh. Prikl. Spektrosk.* **1980**, *33*, 460. (b) Kazarian, S. G.; Hamley, P. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 9069.

(7) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Luo, X. L.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 2788. (c) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

(8) (a) Milstein, D.; Calabrese, C.; Williams, I. D. *J. Am. Chem. Soc.* **1986**, *108*, 6387. (b) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429.

carbonyl and a weak peak at 1620 cm^{-1} due to the coordinated carbonyl. The ^1H NMR spectrum shows a broad peak at 9.88 ppm ($w_{1/2}$ = 2.2 Hz) due to the uncoordinated aldehyde hydrogen and a broader peak at 10.11 ppm ($w_{1/2}$ = 4.2 Hz) due to the coordinated aldehyde hydrogen. Decoupling experiments confirmed the presence of a 2.4 Hz long-range coupling between the coordinated aldehyde hydrogen and the hydride at −26.25 ppm, which allowed the coordinated and free aldehyde signals to be assigned.

Selective Reaction of 8 with Amines. Addition of 1 equiv of ethanolamine to complex **8** results in complete reaction only with the coordinated carbonyl group, leading to the formation of complex **9**. Addition of another equivalent of ethanolamine results in reaction with the uncoordinated carbonyl group and the formation of complex **10** (eq 6). This clearly shows that



8 9 10 (6)

coordination of the carbonyl group to the metal enhances its reactivity with amine. Indeed, the second step takes several hours and is obviously much slower than the first step, which takes place on mixing.

Complexes **9** and **10** have been characterized by IR, ^1H NMR, ^{31}P NMR, and elemental analyses. The hydrogen bonds in these complexes are weak like that found in complex **4**. The $\Delta\nu_{O-H}$ of ∼70 cm^{-1} corresponds to an H-bond strength of about 2.5 kcal/mol in complex **9** and **10**.

Kinetic Study of the Reaction of 3 with Amines. The Ir−H···H−O interaction in complex **5** suggested that the product ratios might be affected if one product could form such a hydrogen bond and the other could not. So that the electronic effects would be comparable (although the pK_a's have not been measured), we chose to study a competition between 4-aminophenol and 2-aminophenol. Since 2-aminophenol has larger steric hindrance than 4-aminophenol, any increase in reactivity could be ascribed to intramolecular H-bond formation, possible only for the 2-isomer.

The limited solubility of the aminophenols in common solvents such as methylene chloride prevents us from using pseudo-first-order conditions. Instead, an equimolar mixture of 2-aminophenol, 4-aminophenol, and complex **3** was placed in 1 mL of CD_2Cl_2 in a 5 mm NMR tube, at room temperature (298 K), and monitored by ^1H NMR spectroscopy for 5 h (eq 7). The ^1H NMR spectrum showed that both **5** and **6** were formed to give a final ratio of 4.2:1. Free 2-aminophenol did not react with the 4-aminophenol complex, **6**, so we conclude that the observed product ratio reflects the kinetic and not thermodynamic product ratio.

We simulated the kinetic processes using the program shown in the Supporting Information, in which a second-order reaction

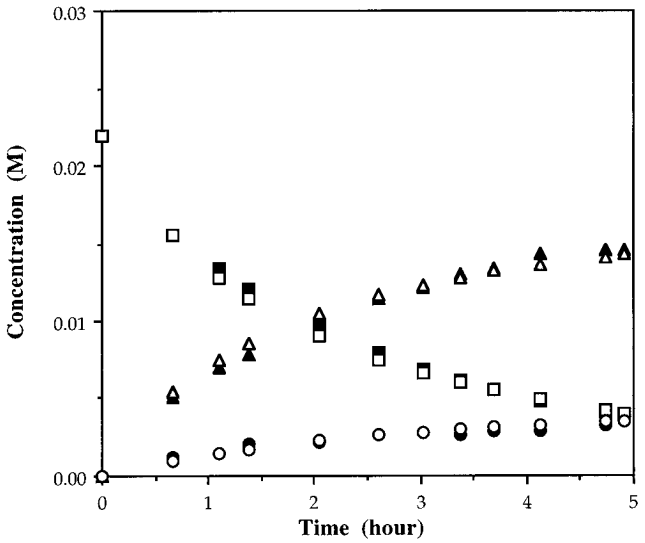
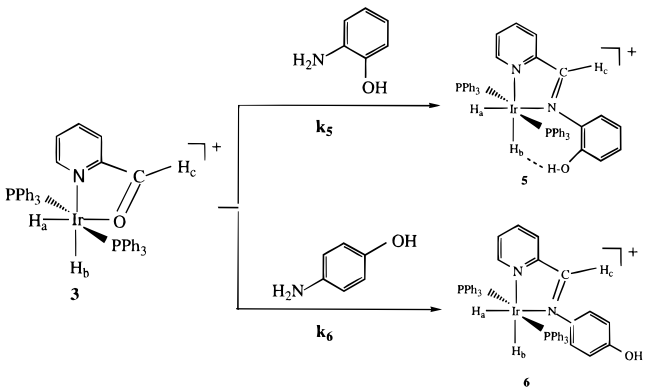


Figure 1. Experimental and simulated concentrations of **3**, **5**, and **6** versus time: ■, experimental [**3**]; ▲, experimental [**5**]; ●, experimental [**6**]; □, simulated [**3**]; △, simulated [**5**]; ○, simulated [**6**].



3 5 6 (7)

(rate = k[amine][complex]) was assumed and the rate constants were varied until agreement with experiment was achieved. The values k_5/k_6 = 6.0 (±0.2) and k_6 = 0.0014 (±0.0002) M^{-1} s^{-1} gave the best fit with the observations (Figure 1). No other assumption fitted the data so well.

Since the ratio of rate constants for the formation of **5** and **6** is 6.0, we can deduce the difference in free energy of activation $\Delta\Delta G^{\ddagger}$ is 1.1 kcal·mol^{-1}. The H-bond strength we found in **5** (4.5 kcal·mol^{-1}) is much larger than this value, and the difference, 3.4 kcal·mol^{-1}, presumably results from an unfavorable chelate ring conformation being required for efficient H-bonding in the transition state for the reaction of eq 7 in the case of **5**.

Conclusion

We have synthesized and clearly characterized an η^1-coordinated aldehyde complex, **3**, which shows an unusual long-range coupling and reacts with amine to give η^1 Schiff-base complexes.

Complex **3** reacts with 2-aminophenol to give complex **5**, which possesses an Ir−H···H−O interaction. Reaction of complex **3** with 2-aminophenol and 4-aminophenol gave a mixture that favored the complex containing the intramolecular H-bond.

Experimental Section

General Procedures and Materials. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk

techniques. Solvents were dried by standard procedures. Ligands, such as PPh_3-d_{15}, 2-pyridinecarboxaldehyde, ethanolamine, 2-aminophenol, 4-aminophenol, 2,6-pyridinedicarboxaldehyde, 2-aminobenzyl alcohol (Aldrich), were used as received. $[IrH_2(acetone)_2(PPh_3)_2][BF_4]$ was obtained according to the literature methods.[3] $[IrH_2(acetone)_2(PPh_3$-$d_{15})_2][BF_4]$ was obtained by a similar method, using the PPh_3-d_{15} ligand instead of the regular PPh_3.

^1H, ^{13}C, and ^{31}P NMR measurements were recorded on a GE Omega-300 or QE 300-plus spectrometer; chemical shifts were measured relative to residual solvent (^1H, ^{13}C NMR) or to external 85% H_3PO_4 (^{31}P NMR). IR spectra were recorded on a MIDAC M1200 FT-IR spectrometer. Elemental microanalyses were carried out by Atlantic Microlabs. Melting points were not determined because the complexes decomposed.

Dihydrido(η^2-2-pyridinecarboxaldehyde-*N,O*-)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (3). A suspension of $[IrH_2(acetone)_2(PPh_3)_2][BF_4]$ (310 mg, 0.34 mmol) in benzene (15 mL) was treated with 2-pyridinecarboxaldehyde (73 μL, 0.77 mmol) at room temperature. The off-white suspension immediately turned to an orange suspension, and the mixture was stirred under N_2 atmosphere for 2 h. The resulting orange precipitate was collected by filtration, washed with hexanes (15 mL), and dried *in vacuo*. Yield: 292 mg (0.32 mmol, 95%). Recrystallization from CH_2Cl_2/hexane afforded brilliant orange prisms. Anal. Calcd for $C_{42}H_{37}BF_4IrNOP_2$: C, 55.27; H, 4.09; N, 1.53. Found: C, 55.11; H, 4.10; N, 1.46. IR (film) in cm^{-1}: 2250, 2166 (br, Ir−H), 1616 (s, C═O). ^1H NMR (CD_2Cl_2, 298 K): δ 9.78 (s, br, $w_{1/2}$ = 7.5 Hz, 1H, HC(O)-), 5.3−7.9 (m, 34H, PPh_3, C_5H_4N), −18.93 (dt, 1H, $^2J_{HP}$ = 15.6 Hz, $^2J_{HH}$ = 9.0 Hz, Ir−H), −27.60 (ddt, 1H, $^2J_{HP}$ = 15.6 Hz, $^2J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.5 Hz, Ir−H). $^{31}P\{$partially ^1H decoupled$\}$ NMR (CD_2Cl_2, 298 K): δ 23.2 (t, $^2J_{PH}$ = 13.6 Hz). $^{13}C\{H\}$ NMR (CD_2Cl_2, 298 K): δ 201.1 (s, -C(O)H), 154.4 (s, C_5H_4N), 151.6 (s, C_5H_4N), 137.9 (s, C_5H_4N), 133.8 (virtual t, J_{CP} = 6.3 Hz, PPh_3), 133.4 (s, C_5H_4N), 132.2 (s, C_5H_4N), 131.8 (virtual t, J_{CP} = 27.5 Hz, PPh_3), 131.0 (s, PPh_3), 128.9 (virtual t, J_{CP} = 5.0 Hz, PPh_3).

3-d_{30}. A suspension of $[IrH_2(acetone)_2(PPh_3)_2][BF_4]$ (30 mg, 0.027 mmol) in benzene (2 mL) was treated with 2-pyridinecarboxaldehyde (6 μL, 0.063 mmol) at room temperature. The off-white suspension immediately turned to an orange suspension, which was stirred under N_2 atmosphere for 2 h. The resulting orange precipitate was collected by filtration, washed with hexanes (5 mL), and dried *in vacuo*. Yield: 28 mg (0.025 mmol, 93%). ^1H NMR (CD_2Cl_2, 298 K): δ 9.66 (s, br, $w_{1/2}$ = 5.3 Hz, 1H, HC(O)-), 7.94 (d, 1H, $^3J_{HH}$ = 4.3 Hz, aromatic hydrogen ortho to N), 7.83 (t, 1H, $^3J_{HH}$ = 7.4 Hz, aromatic hydrogen para to -C(O)H), 7.74 (d, 1H, $^3J_{HH}$ = 7.8 Hz, aromatic hydrogen ortho to -C(O)H), 6.96 (dt, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz aromatic hydrogen para to N), −18.93 (dt, 1H, $^2J_{HP}$ = 15.6 Hz, $^2J_{HH}$ = 8.7 Hz, Ir−H), −27.61 (ddt, 1H, $^2J_{HP}$ = 15.6 Hz, $^2J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.6 Hz, Ir−H).

Dihydrido(η^2-2-pyridinecarboxaldehyde 2-hydroxyethylimine-*N,N′*)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (4). A suspension of **3** (51 mg, 0.056 mmol) in benzene (5 mL) was treated with ethanolamine (5 μL, 0.083 mmol) at room temperature. The orange suspension turned immediately to a clear yellow solution and after 20 min to a yellow suspension, which was stirred under N_2 atmosphere for 3 h. The resulting yellow precipitate was collected by filtration, washed with hexanes (10 mL), and dried *in vacuo*. Yield: 41 mg (0.043 mmol, 77%). Recrystallization from CH_2Cl_2/hexane afforded a bright yellow product. Anal. Calcd for $C_{44}H_{42}BF_4IrN_2OP_2$: C, 55.29; H, 4.43; N, 2.93. Found: C, 55.04; H, 4.50; N, 2.91. IR (film) in cm^{-1}: 3540 (br, O−H), 2223, 2144 (br, Ir−H), 1586 (w, C═N). IR (CH_2Cl_2) in cm^{-1}: 3601 (s, O−H), 3541 (br, O−H), 2185 (br, Ir−H), 1574 (w, C═N). ^1H NMR (CD_2Cl_2, 298 K): δ 8.78 (s, br, $w_{1/2}$ = 5.6 Hz, 1H, -HC═N-), 6.7−8.0 (m, 34H, PPh_3, C_5H_4N), 3.35 (t, 2H, $^3J_{HH}$ = 4.5 Hz, -C*H*$_2$CH$_2$OH), 3.13 (q, 2H, $^3J_{HH}$ = 4.9 Hz, -CH$_2$C*H*$_2$OH), 1.95 (t, 1H, $^3J_{HH}$ = 5.2 Hz, -CH$_2$CH$_2$O*H*), −19.04 (ddt, 1H, $^2J_{HP}$ = 17.0 Hz, $^2J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.2 Hz, Ir−H), −19.62 (dt, 1H, $^2J_{HP}$ = 16.4 Hz, $^2J_{HH}$ = 6.9 Hz, Ir−H). $^{31}P\{$partially ^1H decoupled$\}$ NMR (CD_2Cl_2, 298 K): δ 19.4 (t, $^2J_{PH}$ = 15.0 Hz).

Dihydrido(η^2-2-pyridinecarboxaldehyde 2-hydroxybenzylimine-*N,N′*)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (5). A solution of **3** (100 mg, 0.11 mmol) in CH_2Cl_2 (20 mL) was treated with 2-aminophenol (12 mg, 0.11 mmol), and the solution was stirred at room temperature under N_2 atmosphere for 36 h, during which time the color changed from orange to brown. The solution was filtered through Celite, the volume of the filtrate was concentrated under reduced pressure to *ca.* 3 mL, and addition of Et_2O (5 mL) caused the precipitation of a mustard yellow solid, which was collected by filtration, washed with hexanes, and dried *in vacuo*. Yield: 72 mg (0.07 mmol, 64%). Recrystallization from CH_2Cl_2/Et_2O afforded a yellow orange product. Anal. Calcd for $C_{48}H_{42}BF_4IrN_2OP_2$·0.2$CH_2Cl_2$: C, 56.71; H, 4.19; N, 2.74. Found: C, 56.62; H, 4.30; N, 2.72. IR (film) in cm^{-1}: 3375 (br, O−H), 2178 (br, Ir−H), 1588 (w, C═N). IR (KBr) in cm^{-1}: 3376 (br, O−H), 2184 (br, Ir−H), 1587 (w, C═N). IR (CH_2Cl_2) in cm^{-1}: 3600 (s, O−H), 3379 (br, O−H), 2186 (br, Ir−H), 1575 (w, C═N). ^1H NMR (CD_2Cl_2, 298 K): δ 8.83 (s, br, $w_{1/2}$ = 5.0 Hz, 1H, -HC═N-), 7.0−7.9 (m, 34H, PPh_3, C_5H_4N), 6.95 (d, 1H, $^3J_{HH}$ = 8.0 Hz, aromatic hydrogen ortho to -OH), 6.73 (d, 1H, $^3J_{HH}$ = 5.9 Hz, aromatic hydrogen ortho to -N═CH-), 6.69 (s, 1H, HO-), 6.65 (t, 1H, $^3J_{HH}$ = 6.2 Hz, aromatic hydrogen para to -N═CH-), 6.51 (t, $^3J_{HH}$ = 7.7 Hz, aromatic hydrogen para to -OH), −19.20 (dt, 1H, $^2J_{HP}$ = 16.1 Hz, $^2J_{HH}$ = 7.3 Hz, Ir−H), −19.81 (ddt, 1H, $^2J_{HP}$ = 6.8 Hz, $^2J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.7 Hz Ir−H). $^{31}P\{$partially ^1H decoupled$\}$ NMR (CD_2Cl_2, 298 K): δ 19.9 (t, $^2J_{PH}$ = 12.9 Hz).

5-d_{30}. In a 5 mm NMR tube, a solution of **3-d_{30}** (12 mg, 0.013 mmol) in CD_2Cl_2 was treated with 2-aminophenol (1 mg, 0.009 mmol), and the solution was monitored by ^1H NMR spectroscopy. After 2 days, the ^1H NMR showed the absence of **3-d_{30}** and the presence of **5-d_{30}**. ^1H NMR (CD_2Cl_2, 298 K): δ 8.64 (d, $^4J_{HH}$ = 2.0 Hz, 1H, -HC═N-), 7.90 (d, 1H, $^3J_{HH}$ = 5.1 Hz, aromatic hydrogen ortho to N), 7.68 (t, 1H, $^3J_{HH}$ = 7.2 Hz, aromatic hydrogen para to -C(N)H), 7.57 (d, 1H, $^3J_{HH}$ = 8.0 Hz, aromatic hydrogen ortho to -CH═N-), 7.06 (dt, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, aromatic hydrogen para to N), 6.73 (s, 1H, -OH), 6.72 (dt, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.2 Hz, aromatic hydrogen para to -N═CH-), 6.68 (dd, 1H, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.5 Hz, aromatic hydrogen ortho to -OH), 6.62 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.4 Hz, aromatic hydrogen ortho to -N═CH-), 6.56 (dt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.4 Hz, aromatic hydrogen para to -OH), −19.13 (dt, 1H, $^2J_{HP}$ = 15.9 Hz, $^2J_{HH}$ = 7.2 Hz, Ir−H), −19.67 (ddt, 1H, $^2J_{HP}$ = 16.6 Hz, $^2J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.2 Hz, Ir−H).

Dihydrido(η^2-2-pyridinecarboxaldehyde 4-hydroxybenzylimine-*N,N′*)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (6). A solution of **3** (100 mg, 0.11 mmol) in CH_2Cl_2 (20 mL) was treated with 4-aminophenol (12 mg, 0.11 mmol), and the solution was stirred at room temperature under N_2 atmosphere for 60 h, during which time the color changed from orange to yellow-orange. The solution was filtered through Celite, the volume of filtrate was concentrated under reduced pressure to *ca.* 3 mL, and addition of Et_2O (5 mL) caused the precipitation of a yellow orange solid, which was collected by filtration, washed with hexanes, and dried *in vacuo*. Yield: 82 mg (0.08 mmol, 73%). Recrystallization from CH_2Cl_2/Et_2O afforded a yellow-orange product. Anal. Calcd for $C_{48}H_{42}BF_4IrN_2OP_2$·0.2$CH_2Cl_2$: C, 56.71; H, 4.19; N, 2.74. Found: C, 56.64; H, 4.30; N, 2.72. IR (CH_2Cl_2) in cm^{-1}: 3601 (s, O−H), 2185 (br, Ir−H), 1576 (w, C═N). ^1H NMR (CD_2Cl_2, 298 K): δ 8.40 (s, br, $w_{1/2}$ = 4.8 Hz, 1H, -HC═N-), 7.99 (d, 1H, $^3J_{HH}$ = 5.4 Hz, aromatic hydrogen ortho to N), 7.67 (t, 1H, $^3J_{HH}$ = 7.7 Hz, aromatic hydrogen para to -C(N)H), 7.57 (d, 1H, $^3J_{HH}$ = 7.7 Hz, aromatic hydrogen ortho to -C(N)H), 7.2−7.5 (m, 30H, PPh_3), 6.89 (s, 1H, -OH), 6.87 (d, 2H, $^3J_{HH}$ = 8.5 Hz, aromatic hydrogen ortho to -OH), 6.73 (t, 1H, $^3J_{HH}$ = 6.3 Hz, aromatic hydrogen para to N), 6.55 (d, 2H, $^3J_{HH}$ = 8.5 Hz, aromatic hydrogen meta to -OH), −19.28 (dt, 1H, $^2J_{HP}$ = 16.1 Hz, $^2J_{HH}$ = 6.9 Hz, Ir−H), −19.49 (ddt, 1H, $^2J_{HP}$ = 16.9 Hz, $^2J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.3 Hz, Ir−H). $^{31}P\{$partially ^1H decoupled$\}$ NMR (CD_2Cl_2, 298 K): δ 19.7 (t, $^2J_{PH}$ = 11.7 Hz).

6-d_{30}. In a 5 mm NMR tube, a solution of **3-d_{30}** (12 mg, 0.013 mmol) in CD_2Cl_2 was treated with 4-aminophenol (1 mg, 0.009 mmol), and the solution was monitored by ^1H NMR spectroscopy. After 1 week, the ^1H NMR showed the absence of **3-d_{30}** and the presence of **6-d_{30}**. ^1H NMR (CD_2Cl_2, 298 K): δ 8.36 (s, br, $w_{1/2}$ = 6.4 Hz, 1H, -HC═N-), 7.95 (d, 1H, $^3J_{HH}$ = 5.1 Hz, aromatic hydrogen ortho to N), 7.67 (t, 1H, $^3J_{HH}$ = 8.1 Hz, aromatic hydrogen para to -C(N)H), 7.54 (d, 1H, $^3J_{HH}$ = 7.2 Hz, aromatic hydrogen ortho to -CH═N-), 6.92 (s, 1H, -OH), 6.84 (d, 2H, $^3J_{HH}$ = 8.4 Hz, aromatic hydrogen ortho to -OH), 6.73 (t, 1H, $^3J_{HH}$ = 6.0 Hz, aromatic hydrogen para to N), 6.49 (d, 2H, $^3J_{HH}$ = 8.4 Hz, aromatic hydrogen meta to -OH), −19.26 (dt,

1H, $^2J_{HP}$ = 16.4 Hz, $^2J_{HH}$ = 7.2 Hz, Ir−H), −19.46 (ddt, 1H, $^2J_{HP}$ = 16.4 Hz, $^2J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.1 Hz Ir−H).

Dihydrido(η^2-2,6-pyridinedicarboxaldehyde)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (8). A suspension of $[IrH_2(acetone)_2(PPh_3)_2][BF_4]$ (115 mg, 0.12 mmol) in benzene (5 mL) was treated with 2,6-pyridinedicarboxaldehyde (37 mg, 0.27 mmol) at room temperature. The off-white suspension immediately turned to an orange suspension, which was stirred under N_2 atmosphere for 2 h. The resulting orange precipitate was collected by filtration, washed with pentane (15 mL), and dried *in vacuo*. Yield: 95 mg (0.10 mmol, 81%). Recrystallization from CH_2Cl_2/pentane afforded a pure orange product. Anal. Calcd for $C_{43}H_{37}BF_4IrNO_2P_2$: C, 54.90; H, 3.96; N, 1.49. Found: C, 54.63; H, 4.21; N, 1.34. IR (film) in cm^{-1}: 2263, 2185 (br, Ir−H), 1708 (s, uncoordinated C═O), 1620 (w, coordinated C═O). ^{1}H NMR (CD_2Cl_2, 298 K): δ 10.11 (s, br, $w_{1/2}$ = 4.2 Hz, 1H, coordinated HC(O)-), 9.88 (s, br, $w_{1/2}$ = 2.2 Hz, 1H, uncoordinated HC(O)-), 7.2−8.5 (m, 33H, PPh_3, C_5H_3N), −19.04 (dt, 1H, $^2J_{HP}$ = 15.4 Hz, $^2J_{HH}$ = 8.1 Hz, Ir−H), −26.25 (ddt, 1H, $^2J_{HP}$ = 15.4 Hz, $^2J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.4 Hz, Ir−H). ^{31}P{partially ^{1}H decoupled} NMR (CD_2Cl_2, 298 K): δ 22.7 (t, $^2J_{PH}$ = 13.4 Hz).

Dihydrido(η^2-2,6-pyridinedicarboxaldehyde 2-hydroxyethylimine-*N,N′*)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (9). A suspension of **8** (29 mg, 0.031 mmol) in benzene (5 mL) was treated with ethanolamine (1.8 μL, 0.030 mmol) at room temperature. The orange suspension turned immediately to a clear yellow solution and after 20 min to a yellow suspension, which was stirred under N_2 atmosphere for 3 h. The resulting yellow precipitate was collected by filtration, washed with pentane (5 mL), and dried *in vacuo*. Yield: 28 mg (0.029 mmol, 93%). Anal. Calcd for $C_{45}H_{42}BF_4IrN_2O_2P_2\cdot0.5CH_2Cl_2$: C, 53.25; H, 4.22; N, 2.73. Found: C, 52.99; H, 4.26; N, 3.00. IR (film) in cm^{-1}: 3533 (br, O−H), 2177 (br, Ir−H), 1707 (s, uncoordinated C═O), 1592 (w, coordinated C═N). ^{1}H NMR (CD_2Cl_2, 298 K): δ 9.98 (s, br, $w_{1/2}$ = 2.4 Hz, 1H, uncoordinated HC(O)-), 9.08 (s, br, $w_{1/2}$ = 4.9 Hz, 1H, coordinated HC(N)-), 7.3−8.0 (m, 33H, PPh_3, C_5H_3N), 3.52 (m, 2H, -CH_2CH_2OH), 3.11 (t, 2H, $^3J_{HH}$ = 4.3 Hz, -CH_2CH_2OH), 2.52 (br, 1H, -CH_2CH_2O*H*), −18.84 (dt, br, 1H, $^2J_{HP}$ = 16.4 Hz, $^2J_{HH}$ = 7.1 Hz, Ir−H), −19.68 (dt, 1H, $^2J_{HP}$ = 15.7 Hz, $^2J_{HH}$ = 7.1 Hz, Ir−H). ^{31}P{partially ^{1}H decoupled} NMR (CD_2Cl_2, 298 K): δ 18.5 (t, $^2J_{PH}$ = 14.7 Hz).

Dihydrido(η^2-2,6-pyridinedicarboxaldehyde 2-hydroxyethylimine-*N,N′*)bis(triphenylphosphine)iridium(III) Tetrafluoroborate (10). A solution of **9** (60 mg, 0.062 mmol) in CH_2Cl_2 (10 mL) was treated with ethanolamine (10 μL, 0.166 mmol), and the solution was stirred at room temperature under N_2 atmosphere for 36 h. The solution was concentrated under reduced pressure to *ca.* 3 mL, and addition of Et_2O (10 mL) caused the precipitation of a yellow solid, which was collected by filtration, washed with hexanes, and dried *in vacuo*. Yield: 42 mg (0.042 mmol, 68%). Anal. Calcd for $C_{47}H_{47}BF_4IrN_3O_2P_2\cdot0.7CH_2Cl_2$: C, 52.74; H, 4.43; N, 3.87. Found: C, 52.63; H, 4.66; N, 3.87. IR (CH_2Cl_2) in cm^{-1}: 3601 (s, free O−H), 3531 (br, O−H), 2188 (br, Ir−H), 1643 (s, uncoordinated C═N), 1574 (w, coordinated C═N). ^{1}H NMR (CD_2Cl_2, 298 K): δ 8.77 (s, br, $w_{1/2}$ = 2.3 Hz, 1H, uncoordinated HC(N)-), 8.56 (s, br, $w_{1/2}$ = 5.1 Hz, 1H, coordinated HC(N)-), 7.2−7.8 (m, 33H, PPh_3, C_5H_3N), 3.59 (q, 2H, -CH_2CH_2OH), 3.48 (br, 2H, -CH_2CH_2OH), 3.40 (q, 2H, $^3J_{HH}$ = 5.7 Hz, -CH_2CH_2-OH), 3.12 (t, 2H, $^3J_{HH}$ = 5.7 Hz, -CH_2CH_2OH), 2.57 (br, 1H, -CH_2-CH_2O*H*), 1.68 (t, 1H, $^3J_{HH}$ = 5.7 Hz, -CH_2CH_2O*H*), −18.82 (dt, br, 1H, $^2J_{HP}$ = 16.9 Hz, $^2J_{HH}$ = 7.2 Hz, Ir−H), −19.92 (dt, 1H, $^2J_{HP}$ = 15.3 Hz, $^2J_{HH}$ = 7.2 Hz, Ir−H). ^{31}P{partially ^{1}H decoupled} NMR (CD_2Cl_2, 298 K): δ 19.4 (t, $^2J_{PH}$ = 13.0 Hz).

***T*$_1$ Study.** Determination of T_1(min) was performed on **5** using a conventional inversion-recovery pulse sequence (CD_2Cl_2,193−293 K, 300 MHz).[7]

Kinetic Study of Complex 3 with 2-Aminophenol and 4-Aminophenol. A 12 mg sample of 2-aminophenol and 12 mg of 4-aminophenol were dissolved in 5 mL of CH_2Cl_2 in a 5 mL volumetric flask. A 1 mL portion of the solution was removed to a vial, and the solvent was removed by a N_2 stream. After this, 2.4 mg (2.2×10^{-2} mmol) of 2-aminophenol and 2.4 mg (2.2×10^{-2} mmol) of 4-aminophenol were obtained. Then 20 mg (2.2×10^{-2} mmol) of **3** was placed in a 5 mm NMR tube with 2.4 mg of 2-aminophenol and 2.4 mg of 4-aminophenol. By monitoring of the solution by ^{1}H NMR spectroscopy for a 5-h period, the concentrations of complex **3** and two competing products, **5** and **6**, were determined from the integration of the peaks due to -O═CH- and -N═CH-.

Simulation of the Kinetics. The kinetic processes were simulated using the program shown in the Supporting Information, in which a second-order reaction (rate = k[amine][complex]) was assumed and the rate constants were varied until agreement with experiment was achieved. The values k_5/k_6 = 6.0 (±0.2) and k_6 = 0.0014 (±0.0002) M^{-1} s^{-1} gave the best fit with the observations (Figure 1). No other assumption fitted the data so well.

Acknowledgment. We thank the NSF for support of this work.

Supporting Information Available: The program used to simulate the kinetic process and listings of experimental and simulated kinetic data for **3**−**6** (2 pages). Ordering information is given on any current masthead page.

IC9508076