Two-Point Cooperative Binding of Ketones by a Metal and by a Neighboring Pendant NH Group

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An iridium complex having a 2-aminoquinolinate ligand can bind both lone pairs of ketones such as acetone and 2-hexanone in a two-point fashion via a coordinate Ir−O bond and an N−H···O hydrogen bond. This two-point binding orients the ketone so that the fluxional exchange of the two distinct methyl groups in the acetone complex is strongly slowed relative to the situation where the pendant NH_2 group is absent. In addition, certain substrates, such as 3-hexanone, can form complexes only when the H-bonding group is absent. We propose that H-bonding orients the substrate in the mirror plane of the molecule in such a way that the Et group of the substrate causes steric repulsion with the Ir−H group. In unsymmetrical cases such as PhCHO, the orientation occurs so that the aldehyde proton is located near the Ir−H group.

Introduction

There is growing interest in the effects of hydrogen bonding in coordination and organometallic chemistry, including crystal engineering and supramolecular architecture.[1−3]

Multifunctional complexes in which the ligands have reactive groups not involved in metal−ligand binding may give rise to useful new properties not otherwise obtainable. With the ultimate aim of combining molecular recognition[4] with catalysis[5] to obtain high selectivity, we have looked at the effect of appending reactive groups to suitable organometallic ligands. This is done in such a way that these groups cannot bind directly to the metal but only bind to—or react with—an exogenous ligand that is bound to the metal. A simple example is shown as **1** below, where a pendant amino group hydrogen bonds to a water ligand. In this way two-point binding is obtained, which should in principle allow the ligands to be oriented. The pendant groups are neither inner sphere,[6] directly bound to the metal, nor outer sphere, freely diffusing, so we consider these groups as being in the intermediate sphere.

The pendant group must be rigidly held to prevent direct binding to the metal, and so a chelate system was preferred. An amino group seemed appropriate in being both a base and a hydrogen bond proton donor. 2-Aminobenzoquinoline seemed most suitable for our first efforts since it can very readily be synthesized from $NaNH_2$ and benzoquinoline and also readily cyclometalates with a number of metal centers. Related work has appeared.[7]

In prior work,[8] we have shown how such a complex (**1**), conveniently formed by cyclometalation of 2-aminobenzoquinoline (Scheme 1), allows us to observe the reversible heterolytic cleavage of H_2 and the stabilization of an HF complex by protonation of a fluoro complex.

Results and Discussion

In growing a crystal of **1** from CH_2Cl_2/hexane for structural characterization, we were surprised to find that the product was not the expected aqua complex, **1**, but proved to be the 2-hexanone complex, **2**. Subsequent investigation showed that the *n*-hexane used was autoxidized[9] and contained both 2- and 3-hexanone in

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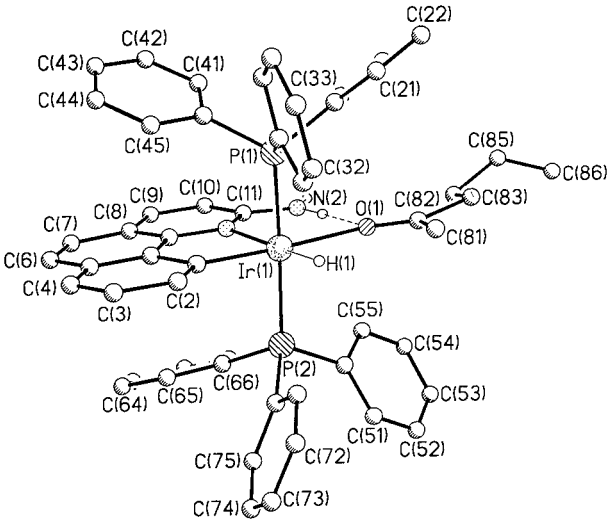
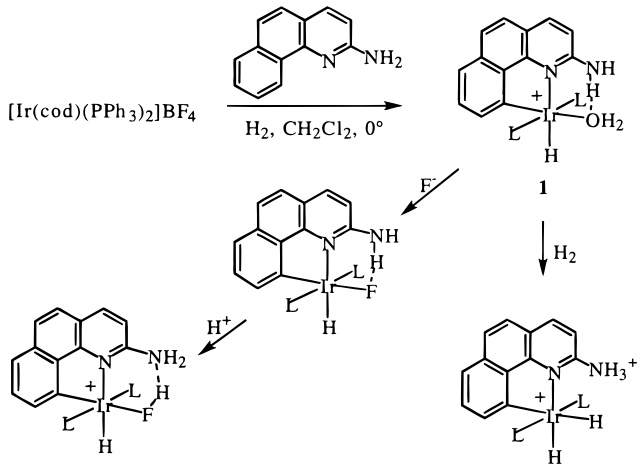
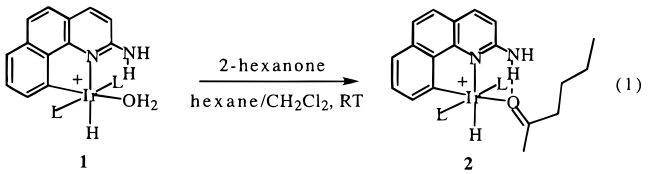


Figure 1. Overall structure of the cation of **2** with 30% probability ellipsoids and omitting the anion and all H atoms except Ir−H (calcd position) for clarity.

Scheme 1



approximately equimolar amounts, so the reaction proceeds as shown in eq 1. Confirmation was obtained by use of stoichiometric quantities of 2-hexanone, which allows **2** to be prepared on a large scale in good yield.



(1)

X-ray Crystallography of 2. The results of a single-crystal X-ray study of **2** are given in Figures 1 and 2 and Tables 1 and 2. The structure has the usual octahedral arrangement around Ir(III), with an essentially planar aminobenzoquinolate ligand. The 2-hexanone is clearly resolved. Although the NH_2 hydrogens are not observed in the crystal structure, the N···O distance of 2.897(7) Å is in the range expected for N−H···O=C hydrogen bonding.[10] Comparison with the structure of $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$, where the acetone is also η^1-bound[11] and where Ir−O is 2.235(5) Å, shows that the Ir−O(1) distance of 2.251(4) Å in **2** is consistent with a normal coordinate bond.

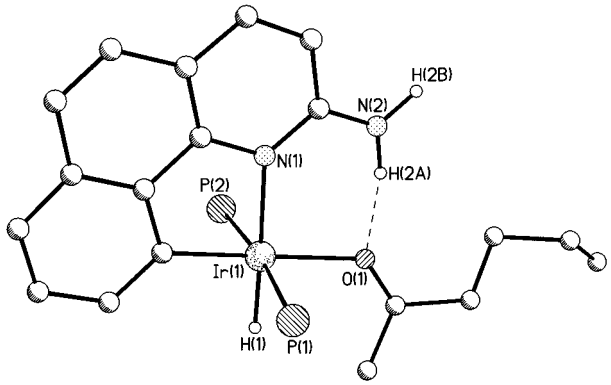


Figure 2. Details of the hydrogen-bonding interaction in **2**, omitting the PPh_3 ligands. The H atoms are normalized (d(NH) = 1.03 Å) in calculated positions assuming a planar $-NH_2$ group. Further selected bond distances (Å) and angles (deg): N(2)···O(1), 2.897(7); C(82)−O(1)−H(2A), 140.5; C(82)−O(1)···N(2), 145.6(9); C(82)−O(1)−Ir, 130.2-(9).

Table 1. Crystal Data and Structure Refinement for $2\cdot CH_2Cl_2$

empirical formula	$C_{56}H_{54}Cl_2F_6IrN_2OP_3$
fw	1241.02
temp (K)	173(2)
wavelength (Å)	0.71073
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimensions	
a (Å)	13.5162(2)
b (Å)	17.9411(2)
c (Å)	21.8105(3)
α (deg)	90
β (deg)	100.1738(5)
γ (deg)	90
volume (Å^3), Z	5205.80(14), 4
density (calcd) (g/cm^3)	1.583
abs coeff (mm^{-1})	2.823
F(000)	2488
cryst dimens (mm)	0.50 × 0.40 × 0.40
θ range for data collection (deg)	1.48−28.23
limitig indices	$-17 \le h \le 17$, $0 \le k \le 20$, $0 \le l \le 28$
no. of reflns collected	20 479
no. of ind reflns	10899 (R_{int} = 0.0597)
transmission factors	0.3980 and 0.3326
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	10899/9/680
goodness-of-fit on F^2	0.939
final R indices [$I > 2\sigma(I)$]	R1 = 0.0459, wR2 = 0.0922
R indices (all data)	R1 = 0.0794, wR2 = 0.1033
largest diff peak and hole (e Å^{-3})	1.051 and −1.265

Spectroscopy of 2. Spectroscopic data are also consistent with hydrogen bonding.[10] The thin-film IR spectroscopic study shows two distinctive ν(NH) stretching bands at 3427 and 3364 cm^{-1}, both shifted from the single band observed at 3411 cm^{-1} for the free ligand. In the ^{1}H NMR spectrum, at room temperature, the signal at 4.84 ppm of the free ligand is shifted toward the aromatic region (6−8 ppm) once bonded to the metal, and at low temperature the hydrogen-bonded NH is observed at 7.70 ppm, whereas the non-hydrogen-bonded NH is observed at 5.89 ppm.

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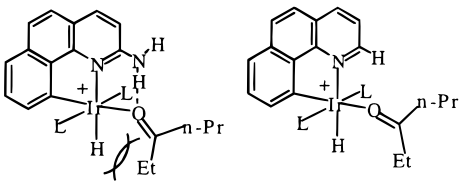
(11) Crabtree, R. H.; Hlatky, G. G.; Parnell, C. A.; Segmuller, B. E.; Uriarte, R. J. *Inorg. Chem*. **1984**, *23*, 354

Table 2. Selected Bond Lengths and Angles for Complex 2·CH_2Cl_2

bond distances (Å)		bond angles (deg)	
Ir(1)−P(1)	2.3395(14)	C(14)−Ir(1)−N(1)	79.8(2)
Ir(1)−P(2)	2.3516(14)	C(14)−Ir(1)−H(1)	97.6(14)
Ir(1)−O(1)	2.251(4)	C(14)−Ir(1)−O(1)	117.38(17)
Ir(1)−N(1)	2.196(5)	H(1)−Ir(1)−P(1)	84.1(13)
Ir(1)−C(14)	2.024(5)	N(1)−Ir(1)−P(1)	93.04(12)
C(82)−O(1)	1.283(10)	H(1)−Ir(1)−P(2)	91.0(13)
		N(1)−Ir(1)−P(2)	91.59(12)
		N(1)−Ir(1)−P(2)	91.59(12)
		P(1)−Ir(1)−P(2)	172.85(5)
		H(1)−Ir(1)−N(1)	176.3(14)
		H(1)−Ir(1)−O(1)	83.8(14)
		N(1)− Ir(1)−O(1)	98.63(17)
		O(1)−Ir(1)−P(1)	90.64(11)
		O(1)−Ir(1)−P(2)	88.13(14)

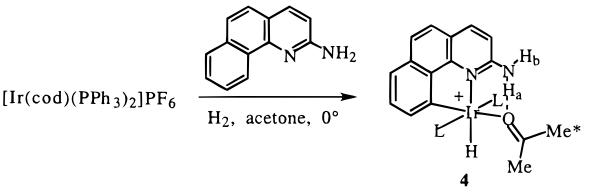
Consequences of Ligand Orientation by Two-Point Binding. The ketone in **2** is held in a two-point binding mode. Because both keto lone pairs lie in the Me(C═O)R plane, this plane is forced to be coincident with the plane of the bq ligand. The ketone is therefore oriented by the hydrogen bonding so that the methyl group is close to the adjacent Ir−H group. If the methyl group of 2-hexanone is replaced by the ethyl group of 3-hexanone, as in **3**, steric interference might be expected to disfavor binding. The fact that the 2-hexanone complex was formed from an equimolar mixture of 2- and 3-hexanone suggests that there is indeed selectivity for binding the 2-isomer. Unsuccessful attempts were made to prepare the 3-hexanone derivative, **3**, under several different conditions, including ones that gave the 2-hexanone complex.

Control studies are possible with the unsubstituted derivatives lacking the 2-NH_2 group and therefore being incapable of significant hydrogen bonding and ligand orientation. We refer to these compounds using the same numbering scheme as before but with a postscript **H**, as in **3H**. These controls are not perfect because the $-NH_2$ and −H groups are expected to have different electronic effects, but they are expected to be satisfactory for the purposes for which they have been used. We found that with the unsubstituted benzoquinoline, 3-hexanone complex, **3H**, could readily be made. Because of the absence of hydrogen bonding, the ketone may be able to rotate in such a way as to avoid prohibitive steric repulsions.



3 not formed **3H** stable

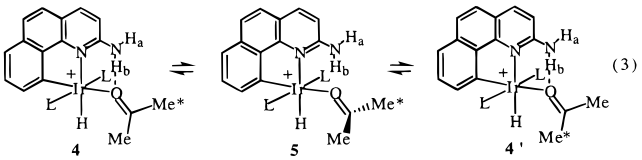
If binding to **1** really does orient the ketone, this ought to have consequences on the dynamic NMR spectrum. We therefore prepared the acetone complex **4** via the route of eq 2. Although **4** has two distinct Me groups, labeled Me and Me* in the diagram, at room temperature the NMR spectrum shows only one methyl group at 1.57 ppm. On cooling, the signal decoalesces to give two peaks at 1.36 and 1.45 ppm in a 1:1 ratio as the acetone rotation is frozen. Addition of free acetone to the solution leads to observation of a distinct peak for free acetone at 2.08 ppm, showing that free and bound acetone do not exchange at a significant rate at the decoalescence temperature.



(2)

In contrast, in **4H** when the pendant $-NH_2$ group is replaced by an −H, above −80 °C the acetone shows one Me resonance, indicating that the rotation is faster than for **4** and the pendant group is responsible for the slow rotation in **4**, and shows incipient decoalescence at −90 °C. In other words the two-point binding does indeed favor the oriented mode of acetone binding.

This can best be interpreted in terms of a model[12] in which the N−H···O hydrogen bond is broken on C−N bond rotation by 90° to give the proposed transition state, **5**, where the lone pair that was H-bonded to the NH_2 group in **4** is now pointing away from the pendant NH bond. Fast exchange with free acetone is prevented by maintenance of the relatively strong Ir−O bond in **4**, and the observed barrier can therefore be interpreted as the sum of the intrinsic barrier for rotation about the Ir−O bond and the N−H···O H-bond.



(3)

As we have previously discussed,[12] we can learn about the N−H···O H-bond strength by looking at the exchange between H_a and H_b in the amino group. The two hydrogens decoalesce on cooling and give separate resonances at −90 °C. Once again, at the transition state for $-NH_2$ rotation, the N−H···O H-bond is broken and the observed barrier can be interpreted as the sum of the intrinsic C−NH_2 rotation barrier and the N−H···O H-bond. We have previously estimated[12] the intrinsic barrier at 5.8 kcal/mol, and so the observed barrier of 8.9 kcal/mol, obtained by conventional line shape analysis,[13] implies that the N−H···O H-bond strength is ca. 3.1 kcal/mol. Since the observed barrier for acetone rotation in **4** (Me/Me* exchange) is 9.9 kcal/mol, we can estimate an intrinsic barrier for rotation about the Ir−O bond of 6.8 kcal/mol. This is too low for decoalescence in **4H**, the corresponding complex lacking the pendant NH_2 group, as indeed is found experimentally: an incipient decoalescence is seen for **4H** down to −90 °C, the limit set by the solvent.

Other Substrates. Other organic molecules can also be bound in a two-point manner by the system. Of most interest is the urea present in complex **6H**, where the steric effect of the NMe group is close to that of the Et

(12) Peris, E.; Lee., J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3845

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group in 3-hexanone. While **6H** is readily formed, attempts to prepare **6** led to failure; this is reminiscent of the situation for **3** versus **3H**.

Conclusion

Complex **1** allows ketone ligands to be oriented so that the complex is selective for binding 2-hexanone over 3-hexanone. The fluxional exchange of Me and Me* in the acetone complex is also significantly slowed. Comparisons with the complex lacking the pendant NH_2 were made. This two-point binding approach offers possibilities for future development.

Experimental Section

All operations were carried out under argon atmosphere using standard Schenk techniques. Solvents were dried over calcium hydride (CH_2Cl_2) or sodium/benzophenone (Et_2O). Hexane was degassed prior use. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on either GE Omega 300 or GE Omega 500 spectrometers. Chemical shifts were measured with reference to the residual solvent resonance. IR spectra were recorded on a Midac M1200 FT-IR spectrometer. Microanalyses were carried out by Robertson Microlit Laboratories.

Crystal Data for 2·CH_2Cl_2: $C_{56}H_{54}Cl_2F_6IrN_2OP_3$, fw = 1241.02, monoclinic, space $P2_1/c$, a = 13.5162(2) Å, b = 17.9411(2) Å, c = 21.8105(3) Å, α = 90°, β = 100.1738(5)°, γ = 90°, V = 5205.80(14) Å^3, Z = 4, D_c =1.583 g cm^{-3}, $F(000)$ = 2488, μ = 2.823 mm^{-1}, T =173 K, R(int) = 0.0597, Mo Kα(λ = 0.71073 Å), ω and φ scans, 20 479 reflections collected, 10 899 independent reflections, $R(F)$ = 4.59% for 7255 observed independent reflections ($4° \le 2\theta \le 57°$). Data were collected on a Siemens P4 diffractometer with a SMART/CCD detector. An empirical absorption correction was applied, based on a Fourier series in the polar angles of the incident and diffracted rays, and was used to model an absorption surface for the difference between the observed and calculated structure factors.[14] Four equatorial F atoms on the PF_6^- counterion are equally disordered over two positions, and the distances were constrained to an average P−F distance of 1.54 Å. A molecule of CH_2Cl_2 is cocrystallized in the asymmetric unit. The hydride H was located from the difference map, and its distance was constrained to Ir−H = 1.60 Å. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all other hydrogen atoms were treated as idealized contributions. Final R indices are R1 = 0.0459, wR2 = 0.0922. Further details may be obtained from the Cambridge Crystallographic Data Centre.

(2-Amino-7,8-benzoquinolinato)hydrido(2-hexanone)-bis(triphenylphosphine)iridium(III) Hexafluorophosphate (2). The PF_6 salt of **1** (200 g, 0.20 mmol)[5c] was dissolved in degassed CH_2Cl_2 (10 mL), and distilled 2-hexanone (100 mg, 1 mmol) was added. The resulting solution was stirred for 30 min. To the yellow solution was added hexane (ca. 20 mL) until the solution became cloudy. The solution was then filtered through a medium-porosity frit, and addition of more hexane (50 mL) gave a light yellow precipitate, which was washed with ether (30 mL) and dried in vacuo to directly yield 160 mg (70%) of pure powder. ^1H NMR (CD_2Cl_2, 500 MHz, 293 K, ppm): δ −16.60 (t, 1H, $^2J_{H-P}$ = 14.80 Hz, Ir−H), 1.28−2.00 (m, 12H), 6.70−8.10 (m, 39H). ^1H NMR (CD_2Cl_2, 500 MHz, 183 K, ppm): δ −16.35 (t, 1H, $^2J_{H-P}$ = 14.80 Hz, Ir−H), 1.34−2.41 (m, 12H), 5.89 (s, 1H, NH_a) 6.62−7.80 (m, 37H), 7.70 (s, 1H, NH_b). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, 293 K, ppm): δ 19.41 (s). IR (thin film, cm^{-1}): ν 1564 (C═O), 2176 (IrH), 3364 (NH), 3427 (NH). Anal. Calcd for $C_{55}H_{52}F_6IrN_2OP_3$: C, 57.13, H, 4.53, N, 2.42. Found: C, 56.89, H, 4.45, N, 2.22.

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(2-Amino-7,8-benzoquinolinato)hydrido(2-hexanone)-bis(triphenylphosphine)iridium(III) Hexafluorophosphate (2H). [Ir(cod)(PPh_3)$_2$]PF_6 (263 mg, 0.27 mmol) and 7,8-benzoquinoline (48 mg, 0.27 mmol) were dissolved in freshly distilled dichloromethane (10 mL). The resulting red solution was allowed to cool to 0 °C. 2-Hexanone was added (335 μL, 2.7 mmol). Dihydrogen gas was bubbled for 15 min with constant stirring to give a yellow solution. The ice bath was removed, and dihydrogen gas was allowed to bubble for an additional 15 min. Then, heptane (100 mL) was added dropwise. The solution was filtered in vacuo to give a pale yellow precipitate, which was dried in vacuo to yield 238 mg of **2H** as a powder (80%). ^1H NMR (CD_2Cl_2, 500 MHz, 293 K, ppm): δ −16.18 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 1.27−1.89 (m, 12H), 6.70−9.33 (m, 38H). ^1H NMR (CD_2Cl_2, 500 MHz, 183 K, ppm): δ −16.01 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 1.34−2.00 (m, 12H), 6.60−9.07 (m, 38H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, 293 K, ppm): δ 18.11 (s). IR (thin-film, cm^{-1}): η, 1640.6 (C═O), 2232.9 (Ir−H). Anal. Calcd for $C_{55}H_{51}F_6IrNOP_3$·0.5(CH_2Cl_2): C, 56.32, H, 4.43, N, 1.18. Found: C, 56.34, H, 4.35, N, 0.95.

(7,8-Benzoquinolinato)hydrido(3-hexanone)bis(triphenylphosphine)iridium(III) Hexafluorophosphate (3H). [Ir(cod)(PPh_3)$_2$]PF_6 (192 mg, 0.20 mmol) and 7,8-benzoquinoline (35 mg, 0.20 mmol) were dissolved in freshly distilled dichloromethane (10 mL). The resulting red solution was allowed to cool to 0 °C. 3-Hexanone was added (25 mL, 0.20 mmol). Dihydrogen gas was bubbled for 5 min with constant stirring. The yellow solution was allowed to warm to room temperature. Then, dry diethyl ether (100 mL) was added dropwise. The solution was filtered in vacuo to give a yellow precipitate, which was dried in vacuo to yield 67 mg of **3H** as a powder (29%). ^1H NMR (CD_2Cl_2, 500 MHz, 293 K, ppm): δ −16.07 (m, 1H, Ir−H), 0.80−2.20 (m, 12H), 6.70−9.40 (m, 38H). ^1H NMR (CD_2Cl_2, 500 MHz, 183 K, ppm): δ −16.71 (t, 1H, $^2J_{H-P}$ = 14.99 Hz, Ir−H), 0.40−2.00 (m, 12H), 6.50−9.00 (m, 38H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, 293 K, ppm): δ 18.46 (s). IR (thin-film, cm^{-1}): ν, 1630.3 (C═O), 2222.6 (Ir−H). Anal. Calcd for $C_{55}H_{51}NOP_3F_6Ir$·1.4(CH_2Cl_2): C, 53.76, H, 4.30, N, 1.11. Found: C, 54.11, H, 3.80, N, 1.36.

(2-Amino-7,8-benzoquinolinato)hydrido(acetone)bis-(triphenylphosphine)iridium(III) Hexafluorophosphate (4). [Ir(cod)(PPh_3)$_2$]PF_6 (417 mg, 0.43 mmol) and 2-amino-7,8-benzoquinoline (83 mg, 0.43 mmol) were dissolved in acetone (10 mL). The resulting red solution was allowed to cool to 0 °C. Dihydrogen gas was bubbled for 30 min with constant stirring. The beige solution was allowed to warm to room temperature. Then, heptane (100 mL) was added dropwise. The solution was filtered in vacuo to give a beige precipitate, which was dried in vacuo to yield 404 mg of **3** as a powder (84%). ^1H NMR (CD_2Cl_2, 300 MHz, 293 K, ppm): δ −16.70 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 1.57 (br s, 12H, coord + free $CH_3-CO-CH_3$), 6.65−7.58 (m, 39H, NH_2 + bq + Ph). ^1H NMR (CD_2Cl_2, 300 MHz, 183 K, ppm): δ −16.57 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 1.36 (s, 3H, $CO-CH_3$), 1.45 (s, 3H, $CO-CH_3$), 2.08 (s, 6H, $CH_3-CO-CH_3$), 6.19 (s, 1H, NH_a), 6.55−7.48 (m, 37H, bq + Ph), 7.86 (s, 1H, NH_b). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121 MHz, 293 K, ppm): δ 20.54 (s). IR (thin-film, cm^{-1}): ν, 1650.9 (C═O), 2207.3 (Ir−H), 3366.4 (NH), 3479.6 (NH). Anal. Calcd for $C_{52}H_{46}F_6IrN_2OP_3$: C, 56.02, H, 4.16, N, 2.51. Found: C, 56.23, H, 4.41, N, 2.46.

(7,8-Benzoquinolinato)hydrido(acetone)bis(triphenylphosphine)iridium(III) Hexafluorophosphate (4H). [Ir(cod)(PPh_3)$_2$]PF_6 (334 mg, 0.34 mmol) and 7,8-benzoquinoline (61 mg, 0.34 mmol) were dissolved in acetone (10 mL). The resulting red solution was allowed to cool to 0 °C. Dihydrogen gas was bubbled for 15 min with constant stirring to lead to a milky yellow solution. The ice bath was removed, and dihydrogen gas was allowed to bubble for an additional 15 min. Then, heptane (100 mL) was added dropwise. The solution was filtered in vacuo to give a pale yellow precipitate, which was

dried in vacuo to yield 273 mg of **4H** as a powder (74%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 293 K, ppm): δ −16.20 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 1.57 (br s, 12H, coord + free CH_3−CO−CH_3), 6.80−9.15 (m, 38H, bq + Ph). ^{1}H NMR (CD_2Cl_2, 300 MHz, 183 K, ppm): δ −16.09 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 1.26 (v br s, 3H, CO−CH_3), 1.64 (v br s, 3H, CO−CH_3), 2.09 (s, 6H, CH_3−CO−CH_3), 6.78−9.36 (m, 38H, bq + Ph). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121 MHz, 293 K, ppm): δ 17.97 (s). IR (thin-film, cm^{-1}): ν, 1655.9 (C═O), 2176.2 (Ir−H). Anal. Calcd for $C_{52}H_{45}F_6IrNOP_3$: C, 56.78, H, 4.12, N, 1.27. Found: C, 56.46, H, 4.06, N, 1.08.

(7,8-Benzoquinolinato)hydrido(1,3-dimethyl-2-imidazolidinone)bis(triphenylphosphine)iridium(III) Hexafluorophosphate (6H). [Ir(cod)(PPh_3)$_2$]PF_6 (258 mg, 0.27 mmol) and 7,8-benzoquinoline (47 mg, 0.27 mmol) were dissolved in freshly distilled dichloromethane (10 mL). The resulting red solution was allowed to cool to 0 °C. 1,3-Dimethyl-2-imidazolidinone was added (291 μL, 2.7 mmol). Dihydrogen gas was bubbled for 15 min with constant stirring to give a yellow solution. The ice bath was removed, and dihydrogen gas was allowed to bubble for an additional 15 min. Then, degassed heptane (100 mL) was added dropwise. The solution was filtered in vacuo to give a pale yellow precipitate, which was dried in vacuo to yield 130 mg of **6H** as a powder (42%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K, ppm): δ −15.97 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 2.62−3.29 (m, 10H), 6.75−9.19 (m, 38H). ^{1}H NMR (CD_2Cl_2, 500 MHz, 183 K, ppm): δ −15.71 (t, 1H, $^2J_{H-P}$ = 14.99 Hz, Ir−H), 2.13−3.21 (m, 10H), 6.58−8.90 (m, 38H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 125 MHz, 293 K, ppm): δ 18.19 (s). IR (thin-film, cm^{-1}): ν, 1649 (C═O), 2136 (Ir−H). Anal. Calcd for $C_{54}H_{49}N_3OP_3F_6Ir\cdot0.5(CH_2Cl_2)$: C, 53.27, H, 4.14, N, 3.39. Found: C, 53.48, H, 4.32, N, 3.07.

(2-Amino-7,8-benzoquinolinato)hydrido(trimethylacetaldehyde)bis(triphenylphosphine)iridium(III) Hexafluorophosphate (7). [Ir(cod)(PPh_3)$_2$]PF_6 (304 mg, 0.31 mmol) and 2-amino-7,8-benzoquinoline (60 mg, 0.31 mmol) were dissolved in freshly distilled dichloromethane (10 mL). The resulting red solution was allowed to cool to 0 °C. Trimethylacetaldehyde was added (34 μL, 0.31 mmol). Dihydrogen gas was bubbled for 5 min with constant stirring to give a yellow solution. The solution was allowed to warm to room temperature and gave an orange solution. Then, dry diethyl ether (100 mL) was added dropwise. The solution was filtered in vacuo to give a pink precipitate, which was dried in vacuo to yield 72 mg of **7** as a powder (20%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K, ppm): δ −16.23 (m 1H, Ir−H), 0.60 (br s, 18H, coord + free CH_3), 6.40−8.00 (m, 39H), 9.18 (s, 2H, coord + free CH). ^{1}H NMR (CD_2Cl_2, 500 MHz, 183 K, ppm): δ −15.89 (m, 1H, Ir−H), 0.10 (s, 9H, coord CH_3), 0.97 (s, 9H, free CH_3), 6.08−8.50 (m, 39H), 8.81 (s, 1H, coord CH), 9.36 (s, 1H, free CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 125 MHz, 293 K, ppm): δ 20.94 (s). IR (thin-film, cm^{-1}): ν, 1635.3 (C═O), 2197.0 (Ir−H), 3376.7 (NH), 3479.6 (NH). Anal. Calcd for $C_{54}H_{50}N_2OP_3F_6Ir\cdot0.75(CH_2Cl_2)$: C, 54.50, H, 4.30, N, 2.32. Found: C, 54.49, H, 3.89, N, 2.44.

(7,8-Benzoquinolinato)hydrido(trimethylacetaldehyde)bis(triphenylphosphine)iridium(III) Hexafluorophosphate (7H). [Ir(cod)(PPh_3)$_2$]PF_6 (322 mg, 0.33 mmol) and 7,8-benzoquinoline (60 mg, 0.33 mmol) were dissolved in freshly distilled dichloromethane (10 mL). The resulting red solution was allowed to cool to 0 °C. Trimethylacetaldehyde was added (36 μL, 0.33 mmol). Dihydrogen gas was bubbled for 5 min with constant stirring to give a yellow solution. The solution was allowed to warm to room temperature and gave a pale orange solution. Then, dry diethyl ether (100 mL) was added dropwise. The solution was filtered in vacuo to give a yellow precipitate, which was dried in vacuo to yield 84 mg of **7H** as a powder (22%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K, ppm): δ −16.05 (m 1H, Ir−H), 0.66 (br s, 18H, coord + free CH_3), 6.75−9.40 (m, 38H), 9.20 (s, 2H, coord + free CH). ^{1}H NMR (CD_2Cl_2, 500 MHz, 183 K, ppm): δ −15.86 (t, 1H, $^2J_{H-P}$ = 13.92 Hz, Ir−H), 0.22 (s, 9H, coord CH_3), 0.97 (s, 9H, free CH_3), 6.00−9.40 (m, 38H), 8.78 (s, 1H, coord CH), 9.42 (s, 1H, free CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 125 MHz, 293 K, ppm): δ 18.03 (s). IR (thin-film, cm^{-1}): ν, 1645.9 (C═O), 2171.1 (Ir−H). Anal. Calcd for $C_{54}H_{49}NOP_3F_6Ir\cdot2.75(CH_2Cl_2)$: C, 50.06, H, 4.03, N, 1.03. Found: C, 50.15, H, 3.84, N, 1.36.

(2-Amino-7,8-benzoquinolinato)hydrido(dimethylformamide)bis(triphenylphosphine)iridium(III) Hexafluorophosphate (8). [Ir(cod)(PPh_3)$_2$]PF_6 (291 mg, 0.30 mmol) and 2-amino-7,8-benzoquinoline (58 mg, 0.30 mmol) were dissolved in freshly distilled dichloromethane (10 mL). The resulting red solution was allowed to cool to 0 °C. Dimethylformamide was added (233 μL, 3.0 mmol). Dihydrogen gas was bubbled for 15 min with constant stirring to give a brown-yellowish solution. The ice bath was removed, and dihydrogen gas was allowed to bubble for an additional 15 min.Then, degassed heptane (100 mL) was added dropwise. After 30 min, a brown oil was decanted under an atmosphere of argon, which was dried in vacuo to yield 124 mg of **8** as a powder (37%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K, ppm): δ −16.59 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 2.30 (s, 3H, coord CH_3), 2.35 (s, 3H, coord CH_3), 2.85 (s, 3H, free CH_3), 2.94 (s, 3H, free CH_3), 6.50 (s, 1H, coord CH), 6.60−7.90 (m, 39H), 8.00 (s, 1H, free CH). ^{1}H NMR (CD_2Cl_2, 500 MHz, 183 K, ppm): δ −16.43 (t, 1H, $^2J_{H-P}$ = 14.65 Hz, Ir−H), 2.17 (s, 3H, coord CH_3), 2.23 (s, 3H, coord CH_3), 2.81 (s, 3H, free CH_3), 2.91 (s, 3H, free CH_3), 6.21 (s, 1H, NH_b), 6.31 (s, 1H, coord CH), 6.50−7.40 (m, 39H), 7.51 (s, 1H, NH_a), 7.95 (s, 1H, free CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 125 MHz, 293 K, ppm): δ 20.23 (s). IR (thin-film, cm^{-1}): ν, 1640.6 (C═O), 2182.2 (Ir−H), 3345.7 (NH), 3479.6 (NH). Anal. Calcd for $C_{52}H_{47}N_3OP_3F_6Ir\cdot0.5(CH_2Cl_2)$: C, 53.82, H, 3.96, N, 3.57. Found: C, 54.20, H, 3.97, N, 3.74.

(7,8-Benzoquinolinato)hydrido(dimethylformamide)bis(triphenylphosphine)iridium(III) Hexafluorophosphate (8H). [Ir(cod)(PPh_3)$_2$]PF_6 (313 mg, 0.32 mmol) and 7,8-benzoquinoline (57 mg, 0.32 mmol) were dissolved in freshly distilled dichloromethane (10 mL). The resulting red solution was allowed to cool to 0 °C. Dimethylformamide was added (250 mL, 3.2 mmol). Dihydrogen gas was bubbled for 15 min with constant stirring to give a yellow solution. The ice bath was removed, and dihydrogen gas was allowed to bubble for an additional 15 min.Then, degassed heptane (100 mL) was added dropwise. The solution was filtered in vacuo to give a yellow precipitate, which was dried in vacuo to yield 244 mg of **8H** as a powder (67%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 293 K, ppm): δ −16.21 (t, 1H, $^2J_{H-P}$ = 15.87 Hz, Ir−H), 2.27 (s, 3H, coord CH_3), 2.55 (s, 3H, coord CH_3), 2.82 (s, 3H, free CH_3), 2.92 (s, 3H, free CH_3), 6.43 (s, 1H, coord CH), 6.65−9.17 (m, 38H), 7.97 (s, 1H, free CH). ^{1}H NMR (CD_2Cl_2, 500 MHz, 183 K, ppm): δ −16.13 (t, 1H, $^2J_{H-P}$ = 15.87 Hz, Ir−H), 2.15 (s, 3H, coord CH_3), 2.54 (s, 3H, coord CH_3), 2.78 (s, 3H, free CH_3), 2.88 (s, 3H, free CH_3), 6.16 (s, 1H, coord CH), 6.60−9.14 (m, 38H), 7.91 (s, 1H, free CH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 125 MHz, 293 K, ppm): δ 17.14 (s). IR (thin-film, cm^{-1}): ν, 1656.1 (C═O), 2140.1 (Ir−H). Anal. Calcd for $C_{52}H_{46}N_2OP_3F_6Ir\cdot0.5(CH_2Cl_2)$: C, 54.52, H, 4.09, N, 2.42. Found: C, 54.44, H, 4.04, N, 2.23.

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Supporting Information Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic displacement coefficients, and hydrogen atom coordinates for the structural analyses of compound **2**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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