Synthesis and Characterization of a Dicationic Dihydrogen Complex of Iridium with a Bis-carbene Ligand Set

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Received December 3, 2004

Reaction of $[Cp^*Ir(CH_3CN)_3][PF_6]_2$ with methylenebis(*N*-methylimidazolium) iodide in the presence of Et_3N affords $[Cp^*Ir(C-C)I]PF_6$ (**1**) (C−C = bis-carbene). The structure of complex **1** was confirmed by X-ray crystallography. The chloride analogue $[Cp^*Ir(C-C)Cl]X$ (**2**) was similarly prepared from $[Cp^*Ir(CH_3CN)_3][PF_6]_2$ (X = PF_6) or $[Cp^*IrCl_2]_2$ (X = Cl) and methylenebis(*N*-methylimidazolium) chloride. Reaction of **2** (X = Cl) with $Et_3SiB(C_6F_5)_4$ under hydrogen gas gives the dicationic dihydrogen complex $[Cp^*Ir(C-C)(H_2)]^{2+}$ (**3**). Complex **3** is identified as a dihydrogen complex based on $T_{1(min)} = 37$ ms for the hydride resonance (240 K, 750 MHz) and $J_{HD} = 23.5$ Hz in the partially deuterated analogue.

N-Heterocyclic carbenes[1] have attracted considerable recent attention in homogeneous catalysis as robust alternatives to phosphine ligands. Efficient catalysis by carbene complexes of several reactions has been reported, including hydrogenation,[2] olefin metathesis,[3] transfer hydrogenation,[4] C−H activation reactions,[5] and carbonylation of alkyl halides.[6] Most of the carbene complexes reported to date employ monodentate carbene ligands, with a smaller number of examples of bidentate bis-carbene ligands.[7] Among the many complexes that have been reported, there are very few hydride complexes[2] and no examples to date of dihydrogen complexes with carbene co-ligands.

We have previously reported the preparation and novel properties of dicationic elongated dihydrogen complexes of Ir of the form $[Cp^*Ir(P-P)(H_2)]^{2+}$.[8,9] These dicationic complexes are extremely acidic, which makes their isolation very challenging. We anticipated that replacement of the chelating phosphine ligand with stronger donor chelating bis-carbene ligands would lead to more tractable complexes. We now report the synthesis and characterization of $[Cp^*Ir(C-C)(H_2)]^{2+}$ (**3**), which exhibits a much shorter H−H distance than its bis-phosphine analogues.

Results

Reaction of $[Cp^*Ir(CH_3CN)_3](PF_6)_2$[10] with methylenebis(*N*-methylimidazolium) iodide in the presence of Et_3N affords $[Cp^*Ir(C-C)I]PF_6$ (**1**) (C−C = bis-carbene) in 78% yield (Scheme 1).

Complex **1** exhibits the expected ^1H NMR spectrum. In addition to resonances for the Cp* and carbene moieties, the CH_2 protons of the methylene bridge give quite different chemical shifts at $\delta = 6.13$ ppm and $\delta = 5.71$ ppm, with geminal coupling $^2J = 13$ Hz. Crystals of complex **1** suitable for diffraction studies were obtained by concentration of a methylene chloride solution. The ORTEP diagram of the cationic portion of the molecule is shown in Figure 1.

The chloride analogue $[Cp^*Ir(C-C)Cl]X$ (**2**) was prepared by reaction of methylenebis(*N*-methylimidazolium) chloride with $[Cp^*Ir(CH_3CN)_3][PF_6]_2$ (X = PF_6) or $[Cp^*IrCl_2]_2$ (X = Cl). The latter reaction proceeds via an observable intermediate (see discussion). The spectroscopic data for **2** are similar to **1**. The structure of complex **2** was confirmed by X-ray diffraction (see Supporting Information).

Reaction of complex **2** with 2 equiv of $Et_3SiB(C_6F_5)_4$ under hydrogen affords a new complex, **3**, which exhibits a broad hydride resonance at $\delta = -7.25$ ppm. Integration of this resonance with respect to the Cp* resonance is consistent with two H atoms. The relaxation time (T_1) for the hydride resonance in complex **3** was determined at 750 MHz at temperatures ranging from 200 to 280 K. The minimum value of T_1 (maximum rate of relax-

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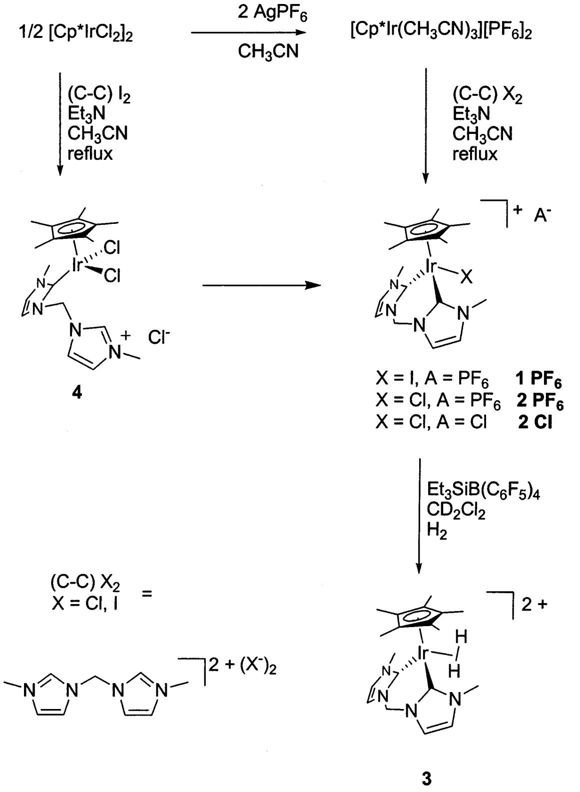
10.1021/om049045p CCC: $30.25

Scheme 1



ation) was found to be 37 ms at 240 K. When the preparative reaction was repeated under HD gas, **3**-d_1 was obtained. Complex **3**-d_1 exhibits a 1:1:1 triplet resonance at −7.25 ppm with J_{HD} = 23.5 Hz (see Figure 2). The partially deuterated species could also be obtained by treating complex **3** with D_2 gas.

Complex **3** is strongly acidic. Facile deprotonation was observed in the presence of water or diethyl ether, affording the monohydride [Cp*Ir(C−C)H]$^+$, identified by a hydride resonance in the ^{1}H NMR spectrum at −14.4 ppm. Complex **3** was regenerated by treatment of the monohydride with 1 equiv of triflic acid.

Discussion

The synthesis of the bis-carbene halide complexes is similar to the procedure employed by Peris and coworkers in the preparation of *p*-cymene complexes of ruthenium with chelating bis-carbene ligands.[11] In the ruthenium studies, it was demonstrated that an intermediate monocarbene complex could be observed in the reaction between [(η-*p*-cymene)RuCl$_2$]$_2$ and methylenebis(*N*-methylimidazolium) iodide, which ultimately leads to the bis-carbene complex. Although we observe no intermediates in the reaction of the imidazole salt with [Cp*Ir(CH$_3$CN)$_3$]$^{2+}$, the intermediate species Cp*Ir-(κ^1-C−C)Cl$_2$ (**4**) is observed in the reaction between [Cp*IrCl$_2$]$_2$ and methylenebis(*N*-methylimidazolium) chloride, which was carried out in acetonitrile solution at reflux (see Scheme 1). Complex **4** was characterized by ^{1}H NMR and could be obtained from solution after brief heating, accompanied by varying amounts of **2** (Scheme 1). Along with the resonances corresponding to the Cp* (s at 1.62 ppm) and CH$_3$ groups (s at 4.04 and 4.12 ppm), complex **4** exhibits a singlet at 5.62 ppm assigned to the CH$_2$ group bridging the two imidazolylidene rings and a singlet at 8.33 ppm attributed to the proton in the 2′ position of the uncoordinated ring. The latter resonance and the presence of four additional singlets (7.37, 7.83, 7.65, and 7.32 ppm) for the protons in the 4 and 5 positions of each imidazole ring are indicative of the loss of the 2-fold symmetry of the bis-carbene ligand. Complete conversion from compound **4** to **2** is achieved by heating at reflux for 12 h.

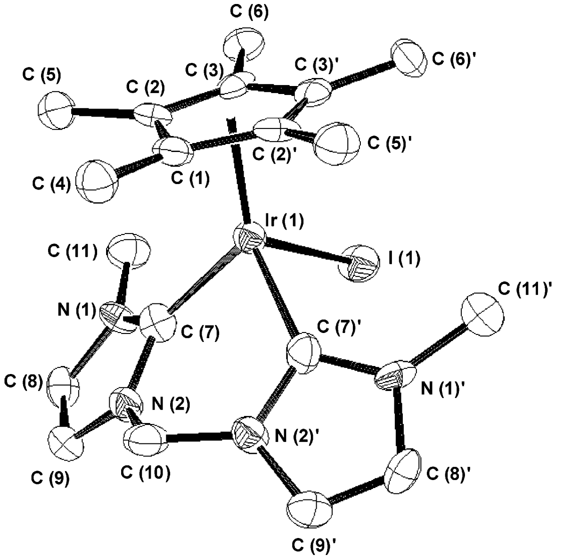


Figure 1. ORTEP diagram of the cationic portion of complex **1**. 50% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity. Relevant bond distances (Å) and angles (deg) include Ir−I = 2.6962(8), Ir−C7 = 2.019(8), Ir−Cp*(centroid) = 1.874, C7−Ir−C7′ = 86.4(4), C7−Ir−I = 91.3(2), Cp*−Ir−C7 = 128.2, and Cp*−Ir−I = 120.2.

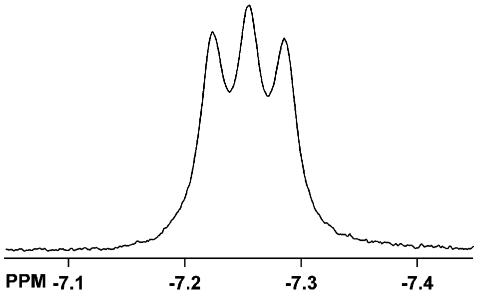


Figure 2. Partial (hydride region) ^{1}H NMR spectrum of **3**-d_1 obtained with a 180−τ−90 pulse sequence (τ = 30 ms, 750 MHz, 280 K, CD$_2$Cl$_2$).

The structure of complex **1** can be compared to closely related Ir(III) complexes with bis-phosphine ligands. For example, [Cp*Ir(dmpm)Cl]$^+$ (dmpm = 1,2-bis(dimethylphosphino)methane) has an angle of 135.93° between the Cp* ring centroid, the iridium center, and the bound P atoms,[9] while complex **1** has an angle of 128.19° between the Cp* ring centroid, the iridium atom, and the bound C atoms of the carbene ligand. This may be driven by steric interactions between the N-Me groups and the Cp* ligand, which would tend to favor a more acute angle. Other aspects of the geometry of complex **1** are similar to previously reported bis-carbene complexes.[1b] The C−M−C angle in **1** is 86.4°, essentially

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identical to the corresponding angle in an Ir(III) complex reported by Crabtree and co-workers[12] and very similar to a Pd(II) complex reported by Hermann and co-workers.[5] The X-ray structure shows no unusual contacts between the anion PF_6^- and the cationic complex, with the closest C···F distances being 3.321 and 3.427 Å (3.395 and 3.705 Å for **2**). The Ir−I bond distance is 2.69 Å (Ir−Cl: 2.407 Å in $[Cp^*Ir(C-C)Cl]^+$), which is slightly shorter than the one in the related cationic iridium(III) complex $[Cp^*Ir(CO)_2I]^+$ (2.71 Å).[13] Interestingly, the C−Ir−C bond angle in **1** (86.4°) lies between the corresponding values reported for $[Cp^*Ir(dmpm)Cl]^+$ (P−Ir−P = 71.8°) and $[Cp^*Ir(CO)_2I]^+$ (C−Ir−C = 92°). Since Ir−C bonds are shorter than Ir−P bonds and the angles between the Cp* ring, the iridium center, and the carbene ligands are smaller than their phosphine analogues, the bis-carbene ligands are closer to the Cp* ring.

Halide abstraction from complex **2** in the presence of hydrogen affords a new dicationic hydride species **3**. Integration of the ^1H NMR spectrum is consistent with the presence of two hydrogen atoms. As expected for a dication, complex **3** is strongly acidic, with complete deprotonation observed in the presence of weak bases to afford a cationic monohydride derivative. Reprotonation to regenerate **3** is observed with 1 equiv of triflic acid.

A distinction between a dihydride and a dihydrogen structure for **3** can be made by the measurement of dipole−dipole relaxation rates in the ^1H NMR resonance for the hydride signal. At the temperature where the maximum rate of relaxation is observed ($T_{1(\mathrm{min})}$), use of the methodology developed by Halpern and co-workers[14] allows the determination of the H−H distance in a dihydrogen or dihydride complex. For complex **3**, the minimum relaxation time measured for the hydride resonance is 37 ms at 240 K (750 MHz). Assuming the slow rotation regime, the H−H distance derived by this method is 1.11 Å.

Confirmation of complex **3** as a dihydrogen rather than a dihydride complex comes from the observation of a significant H−D coupling in **3**-d_1, prepared by reaction of **2** with $Et_3SiB(C_6F_5)_4$ under HD gas. The HD coupling measured is 23.5 Hz (Figure 2), which corresponds[15] to a H−H distance of 1.04 Å. The HD coupling in **3** is independent of the observation temperature (220−300 K), in contrast to previous observations on $[Cp^*Ir(dmpm)(H_2)]^{2+}$ and $[Cp^*Ru(dppm)(H_2)]^+$, where significant temperature dependence was observed. Interestingly, there is no noticeable isotope shift between the resonances of **3** and **3**-d_1.

There are significant structural differences between bis-carbene complex **3** and the previously studied bis-phosphine species $[Cp^*Ir(dmpm)(H_2)]^{2+}$. The phosphine complex exhibits an equilibrium between a *cisoid* dihydrogen and a *transoid* dihydride structure, with the former predominant (97:3). This equilibrium between a nominally Ir(III) dihydrogen complex and an Ir(V) dihydride is similar to the situation observed for related monocationic Ru complexes, where the equilibrium composition is a complex function of the steric and electronic parameters of the ligand set. In contrast, complex **3** has only the dihydrogen structure, with no evidence for a *transoid* dihydride form. We attribute this to steric interactions between the imidazole methyl groups and the methyl groups of the Cp* ligand, which are diminished in the *cisoid* geometry.

The other important structural difference between complex **3** and the dmpm analogue is the HH distance in the bound hydrogen ligand. In complex **3**, this distance is 1.04 Å, while the corresponding distance in $[Cp^*Ir(dmpm)(H_2)]^{2+}$ is 1.45 Å. The latter is an example of a highly elongated dihydrogen complex, also known as a compressed dihydride species.[8,9] Elongation of the H−H distance to this extent is usually seen to be the result of donation from the HH σ bond to a metal-centered acceptor orbital combined with back-donation from filled metal d orbitals to the σ^* orbital of the H_2 ligand.

In the more extensively studied Ru monocations of the form $[Cp^*Ru(PP)(H_2)]^+$, the role of back-donation is clearly demonstrated by the longer H−H distances observed for more basic phosphine ligands. For example, the dppm complex has an HH distance of 1.10 Å, while the more basic ligand dmpm gives a complex with a longer HH distance of 1.17 Å.[16] Using a Tolman parameter analysis, Hermann and co-workers concluded that NHC ligands are usually thought to be better donors than alkyl phosphine ligands.[17] Consistent with the greater donor ability of the carbene ligand set, complex **3** is significantly less acidic than the dmpm analogue $[Cp^*Ir(dmpm)(H_2)]^{2+}$. This is demonstrated by the protonation of $[Cp^*Ir(C-C)H]^+$ by triflic acid, while the corresponding phosphine monohydride complex $[Cp^*Ir(dmpm)H]^+$ does not react with triflic acid.[9]

Based on these considerations, it was expected that the HH distance in complex **3** would be ca. 1.5 Å. The actual distance is *much* shorter than expected. To explain this surprising observation, we postulate that in extremely electron-deficient dicationic hydrogen complexes such as **3**, the interaction between the metal center and the bound H_2 may be dominated by donation from the HH σ bond to a metal-centered acceptor orbital, with a relatively minor contribution from metal to ligand back-donation. This could explain the counter intuitive observation that a better donor ligand set leads to a much shorter HH bond distance in **3** compared to closely related phosphine analogues.

Conclusion

The present investigations of a new class of iridium complexes with the Cp* moiety and a chelating bis-carbene ligand show unexpected properties. In contrast to its bis-phosphine iridium and ruthenium analogues $[Cp^*M(PP)(H_2)]^{n+}$ (M = Ru, Ir; PP = dmpm, dppm),

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complex **3** exhibits a small degree of activation of the H_2 ligand, resulting in a much shorter HH distance. Even though it is well accepted that carbene ligands are better electron-donating ligands than phosphines, the *trans* dihydride Ir(V) complex is not accessible in this case due to steric interactions with the Cp* ring.

We are continuing to investigate the properties and reactivity of complexes of the type $[Cp^*M(C-C)]^{n+}$ (M = Ru, Rh, Ir), with a view to understanding the binding and activation of σ bond donors by these electrophilic metal centers.

Experimental Section

General Procedures. Unless stated otherwise, all manipulations were carried out under nitrogen using Schlenk techniques. Methylimidazole and methylene iodide (Sigma-Aldrich) were used as received. Hydrogen gas was purchased from Airgas. HD(g) and D_2(g) were used as received from Cambridge Isotopes Laboratories. $[Cp^*IrCl_2]_2$,[18] $[Cp^*Ir(CH_3CN)_3][PF_6]_2$,[19] and methylenebis(*N*-methyl)imidazolium diiodide[20] were prepared according to literature procedures. Elemental analyses were performed by Galbraith. NMR spectra were recorded on Bruker AV-300, DRX-499, AV-500, and DMX-750 spectrometers. Proton NMR spectra were referenced to the solvent resonance with chemical shifts reported relative to TMS. The NMR studies were carried out in high-quality 5 mm NMR tubes, utilizing deuterated solvents distilled from standard drying agents. The conventional inversion−recovery method ($180-\tau-90$) was used to determine the relaxation times T_1. In each experiment the waiting period was longer than 10 times the expected relaxation rate. More than 18 variable delays were employed, utilizing appropriate pulse widths. Spectra used for precise measuring of coupling constants were zero-filled prior to Fourier transform. Mass spectra were recorded on a Bruker Esquire ion trap mass spectrometer with electrospray, APCI and nanospray ionization sources using acetonitrile as mobile phase solvent. Nitrogen was employed as drying and nebulizing gas. Isotope experimental patterns were compared with theoretical patterns obtained using the Bruker Daltronics Esquire LC4.5 data analysis version 3.0 software. In all cases there was excellent agreement between the experimental and calculated isotopic mass distributions.

Methylenebis(*N*-methyl)imidazolium Dichloride. $AgOOCCH_3$ (10 mmol, 1.67 g) was added to a vigorously stirred solution of methylenebis(*N*-methyl)imidazolium diiodide (5 mmol, 2.18 g) in 20 mL of H_2O/MeOH (1:1). The mixture was stirred for 1 h in the absence of light. The resulting yellowish precipitate was filtered off, and the clear solution was treated with 5 mL of HCl (10 M). The solvents were evaporated under vacuum to give a white powder, which was then redissolved in dry ethanol and dried under vacuum. This procedure was repeated three times. Drying via high vacuum for 48 h at 50 °C gave 1.14 g (92%) of methylenebis(*N*-methyl)imidazolium dichloride as a colorless hygroscopic powder. ^1H NMR, δ (DMSO, 300 MHz, 298 K): 9.78 (s, 2 H, NCHN), 8.20, 7.8 (s, 2 H, CH_{imid}), 6.85 (s, 2 H, $NCH_{2\ linker}$), 3.90 (s, 6 H, NCH_3). Electrospray MS, capillary exit 60 V, *m/z*: 89.2 $[M]^{2+}$.

$[Cp^*Ir(C-C)I]PF_6$ (C−C = methylenebis(*N*-methyl)imidazolium biscarbene) (1). A 100 mL Schlenk flask was charged with $[Cp^*Ir(CH_3CN)_3][PF_6]_2$ (285 mg, 0.39 mmol) and methylenebis(*N*-methyl)imidazolium diiodide (167 mg, 0.39 mmol). Addition of 30 mL of CH_3CN and Et_3N (107 μL, 0.77 mmol) gave a dark orange solution. After heating for 48 h at 60 °C, the solvent was evaporated and 10 mL of $CHCl_3$ was added. The resulting suspension was stirred for 1 h at −78 °C to give a yellow solid, which was isolated by filtration, washed with diethyl ether, and dried under high vacuum. Yield: 238 mg, 78%. ^1H NMR, δ (CD_2Cl_2, 300 MHz, 298 K): 7.38, 7.17 (d, 2 H, $^2J_{HH}$ = 1.8 Hz, CH_{imid}), 6.13, 5.71 (d, 1 H, $^2J_{HH}$ =13.2 Hz, $NCH_{2\ linker}$), 3.81 (s, 6 H, NCH_3), 1.97 (s, 15 H, Cp*), Electrospray MS, capillary exit 100 V, *m/z*: 631 $[M^+]$. Anal. Calcd for $C_{19}H_{27}F_6IIrN_4P$: C 29.43, H 3.51, N 7.22. Found: C 29.21; H 3.65, N 7.04.

$[Cp^*Ir(C-C)Cl]PF_6$ (2PF$_6$) was prepared as above for **1** but using methylenebis(*N*-methyl)imidazolium dichloride (34 mg, 0.14 mmol), $[Cp^*Ir(CH_3CN)_3][PF_6]_2$ (100 mg, 0.14 mmol), and 2 equiv of triethylamine (0.28 mmol, 40 μL). Additional purification of complex **2** was achieved by dissolution in methylene chloride, filtration through Celite, and recrystallization from methylene chloride/diethyl ether at 0 °C. Complex **2** was obtained as a bright yellow powder, which was washed with diethyl ether and hexanes and dried under vacuum for 24 h. Yield: 56 mg, (58%). ^1H NMR, δ (CD_2Cl_2, 500 MHz, 298 K): 7.41, 7.14 (d, 2 H, $^2J_{HH}$ = 2.0 Hz, CH_{imid}), 6.18, 5.58 (d, 1 H, $^2J_{HH}$ = 13.2 Hz, $NCH_{2\ linker}$), 3.88 (s, 6 H, NCH_3), 1.85 (s, 15 H, Cp*). Electrospray MS, capillary exit 100 V, *m/z*: 539 $[M^+]$. Anal. Calcd for $C_{19}H_{27}F_6ClIrN_4P$: C 33.36, H 3.98, N 8.19. Found: C 32.56, H 3.97, N 7.75

$[Cp^*Ir(C-C)Cl]Cl$ (2Cl). A 150 mL round-bottom flask was charged with 30 mg of $[Cp^*IrCl_2]_2$ (0.0376 mmol), methylenebis(*N*-methyl)imidazolium dichloride (20 mg, 0.0828 mmol), Et_3N (104 μL, 0.752 mmol), and 30 mL of O_2-free acetonitrile. After 10 h of reflux, the solvent was removed in vacuo. The resulting yellow powder was redissolved in CH_2Cl_2, layered with Et_2O, and left overnight at −26 °C to precipitate the ammonium salt formed. Et_3NHCl was filtered off through glass wool. Recrystallization in CH_2Cl_2/Et_2O (50/50) affords complex **2Cl** in 60% yield. ^1H NMR, δ (acetone-d_6, 500 MHz, 298 K): 7.83, 7.57 (d, 1 H, $^2J_{HH}$ = 2.0 Hz, CH_{imid}), 7.03, 5.85 (d, 1 H, $^2J_{HH}$ = 13.2 Hz, $NCH_{2\ linker}$), 4.04 (s, 6 H, NCH_3), 2.02 (s, 15 H, Cp*). Anal. Calcd for $C_{19}H_{27}Cl_2IrN_4$: C 39.72, H 4.74, N 9.75. Found: C 39.03, H 4.72, N 9.48.

When the mixture was heated for 3 h, the intermediate **4** could be isolated accompanied by **2** as identified by ^1H NMR (see Discussion). ^1H NMR, δ (acetone-d_6, 500 MHz, 298 K): 8.33 (s, 1 H, NCHN), 7.83, 7.65 (s, 1 H, free CH_{imid}), 7.37, 7.32 (d, 1 H, coord. CH_{imid}), 5.62 (s, 2 H, $NCH_{2\ linker}$), 4.12 (s, 3 H, free NCH_3), 4.04 (s, 3 H, coord NCH_3), 1.61 (s, 15 H, Cp*).

$[Cp^*Ir(C-C)(H_2)][B(C_6F_5)_4]_2$ (3). An NMR tube fitted with a high-vacuum Kontes valve was charged with 15 mg (0.016 mmol) of $Ph_3CB(C_6F_5)_4$. After addition via vacuum transfer of Et_3SiH (1−2 mL), the resulting yellow mixture was sonicated for 24 h. Excess Et_3SiH was then removed under vacuum to leave a white solid. After addition of 5 mg (0.007 mmol) of **2**, CD_2Cl_2 was vacuum transferred into the tube. The sample was briefly degassed at −78 °C, backfilled with H_2 (or HD) gas, and flame sealed. ^1H NMR, δ (273 K, CD_2Cl_2, 500 MHz): 7.33 (s, 2 H, H_{imid}), 7.15 (s, 2 H, H_{imid}), 6.05(d, 1 H, $^2J_{HH}$ = 13.3 Hz, CH_2), 5.66 (d, 1 H, $^2J_{HH}$ = 13.3 Hz, CH_2), 3.80(s, 6 H, CH_3), 2.16 (s, 15 H, Cp*), −7.22 (br, s, 2 H, Ir(H_2)). Complex **3-d_1** was prepared similarly with HD gas: δ −7.22 (t, J_{HD} = 23.5 Hz).

X-ray Structure of $[Cp^*Ir(C-C)I][PF_6]$. Yellow crystals suitable for X-ray diffraction were obtained by concentration of a solution of $[Cp^*Ir(C-C)I][PF_6]$ in CH_2Cl_2 and mounted on glass capillaries in oil. Diffraction measurements were made on a crystal fragment of dimensions 0.09 × 0.09 × 0.09 mm in a nitrogen stream at 130 K on a Nonius KappaCCD diffractometer using graphite-monochromated radiation (λ = 0.71073 Å). Crystal-to-detector distance was 30 mm, and exposure time was 30 s per degree for all sets. The scan width was 2.0°. Data collection was 95.5% complete to 28.35° and

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99.0% complete to 25° in 2 ϑ. A total of 12 873 partial and complete reflections were collected covering the indices $h = -18$ to 18, $k = -15$ to 15, $l = -17$ to 18. A total of 2945 reflections were symmetry independent, and the $R_{\text{int}} = 0.0796$ indicated that the data were average quality (0.07). Indexing and unit cell refinement indicated an othorhombic *P* lattice. The space group was found to be *Pnma* (No. 62) with cell parameters $a = 13.9510(8)$ Å, $b = 12.2730(8)$ Å, $c = 13.8420(10)$ Å, $\alpha = 90°$, $\beta = 90°$, and $\gamma = 90°$. The cell volume was 2370.0 (3) Å^3, and the calculated density was 2.173 g/cm^3, with $Z = 4$. The data were integrated and scaled using hkl-SCALEPACK. Solution by direct methods produced a complete heavy atom phasing model closely related to the proposed structure. All hydrogen atoms were placed using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. The symmetry of this structure reproduces a full anion and cation from half molecules inside the asymmetric unit (numbered atoms). Tables of data collection, solution, and refinement details, crystal data, atomic coordinates, and anisotropic thermal parameters are included in the Supporting Information.

Acknowledgment. This research was supported by the U.S. National Science Foundation. Acquisition of the 750 MHz NMR spectrometer was supported by the National Science Foundation and the Murdoch Charitable Trust. M.V. would like to acknowledge the Trans Atlantic Science Student Exchange Program (TASSEP) and the "Fritz-ter-Meer" scholarship (Bayer AG) for a fellowship.

Supporting Information Available: Crystallographic data and T_1 data (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM049045P