Novel Amido-Bridged Dinuclear Iridium(III) and Iridium(II) Complexes. Synthesis and Characterization of $[\mathrm{Cp^*Ir}(\mu_2\text{-}\mathrm{NHC_6H_4R}\text{-}p)_3\mathrm{IrCp^*}]\mathrm{Cl}$ ($\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$; R = Me, H, Cl, $\mathrm{CF_3}$), $[\mathrm{Cp^*Ir}\{(\mu_2\text{-}\mathrm{NH})_2\mathrm{C_{10}H_6}\text{-}1,8\}(\mu_2\text{-}\mathrm{X})\mathrm{IrCp^*}]\mathrm{X}$ (X = Cl, Br), $\mathrm{Cp^*Ir}\{(\mu_2\text{-}\mathrm{NH})_2\mathrm{C_{10}H_6}\text{-}1,8\}\mathrm{IrCp^*}$, and $[\mathrm{Cp^*Ir}\{(\mu_2\text{-}\mathrm{NH})_2\mathrm{C_{10}H_6}\text{-}1,8\}(\mu_2\text{-}\mathrm{H})\mathrm{IrCp^*}]\mathrm{O_2CCF_3}$

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Received June 12, 1997⊗

Summary: A series of novel amido-bridged dinuclear Ir(III) and Ir(II) complexes of the forms $[\mathrm{Cp^*Ir}(\mu_2\text{-}\mathrm{NHC_6H_4R}\text{-}p)_3\mathrm{IrCp^*}]\mathrm{Cl}$ *(**2**·Cl: **2a**, R = Me; **2b**, R = H; **2c**, R = Cl; **2d**, R =* $\mathrm{CF_3}$*),* $[\mathrm{Cp^*Ir}\{(\mu_2\text{-}\mathrm{NH})_2\mathrm{C_{10}H_6}\text{-}1,8\}(\mu_2\text{-}\mathrm{X})\mathrm{IrCp^*}]\mathrm{X}$ *(**4a**, X = Cl; **4b**, X = Br),* $\mathrm{Cp^*Ir}\{(\mu_2\text{-}\mathrm{NH})_2\mathrm{C_{10}H_6}\text{-}1,8\}\mathrm{IrCp^*}$ *(**5**), and* $[\mathrm{Cp^*Ir}\{(\mu_2\text{-}\mathrm{NH})_2\mathrm{C_{10}H_6}\text{-}1,8\}(\mu_2\text{-}\mathrm{H})\mathrm{IrCp^*}]\mathrm{O_2CCF_3}$ *(**6**) were prepared from* $[\mathrm{Cp^*IrX}(\mu_2\text{-}\mathrm{X})]_2$ *(**1a**, X = Cl; **1b**, X = Br) and the corresponding LiNHR species. The molecular structures of **2a**·*$\mathrm{ClO_4}$ *and **5** have been determined by X-ray crystallography.*

Although amido complexes of the late transition metals are not as common as those for the early transition elements, recent progress of the chemistry of these complexes suggests that they may have a rich chemistry, as has been elucidated for metal alkyl, aryl, and hydrido derivatives.[1] We report herein the preparation and characterization of a series of novel amido-bridged dinuclear iridium complexes.[2,3]

Treatment of $[\mathrm{Cp^*IrCl}(\mu_2\text{-}\mathrm{Cl})]_2$ (**1a**) with 3 equiv of LiNHR in THF at −90 °C to room temperature gave the novel amido-bridged cationic dinuclear Ir(III) complexes $[\mathrm{Cp^*Ir}(\mu_2\text{-}\mathrm{NHC_6H_4R}\text{-}p)_3\mathrm{IrCp^*}]\mathrm{Cl}$ (**2**·Cl: **2a**, R = Me; **2b**, R = H; **2c**, R = Cl; **2d**, R = $\mathrm{CF_3}$) as yellow precipitates in good yield (Scheme 1), which were spectroscopically characterized.[4] The structure of **2a**·$\mathrm{ClO_4}$ has been further determined by X-ray diffraction analysis.[5] In the ^{1}H NMR spectrum of **2a**·Cl, the resonances due to both the methyl (δ 2.36, 2.32, 2.31) and the NH protons (δ 5.82, 5.26, 3.53) of NHTol groups are observed as three inequivalent signals, whereas the Cp* protons appear as one singlet at δ 1.18. These spectral features are fully consistent with the crystal structure of **2a**·$\mathrm{ClO_4}$ (vide infra). The ^{1}H NMR data for **2b**·Cl−**2d**·Cl are essentially similar to those for **2a**·Cl.

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⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1997.

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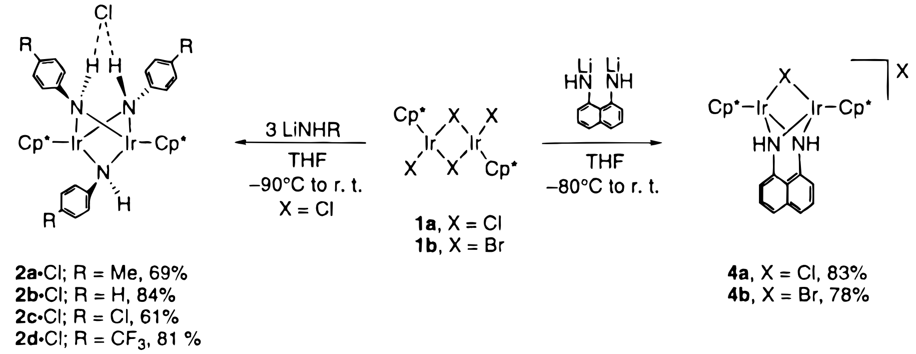
(4) The typical procedure is as follows. LiNHTol was prepared in situ by treatment of a THF (30 mL) solution of *p*-toluidine (1.78 g, 16.56 mmol) with 1.57 M $\mathrm{Bu^nLi}$ in hexane (10.6 mL, 16.56 mmol). To this suspension was added a THF (75 mL) suspension of **1a** (4.00 g, 5.02 mmol) at −90 °C, and the resultant mixture was gradually warmed to room temperature, during which time the original orange suspension turned to a red-brown suspension. After filtration, the remaining solid was washed with THF (10 mL, two times), dried in vacuo, and extracted with $\mathrm{CH_2Cl_2}$ (20 mL, five times). Removal of the solvent gave **2a**·Cl as a yellow crystalline solid (3.483 g, 69%), which was recrystallized from $\mathrm{CHCl_3}$−hexane to afford yellow columnar crystals. **2a**·Cl: yield 69%; IR (KBr) ν_{NH} 3430 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.34−6.95 (m, 12H, aryl), 5.82, 5.26, 3.53 (br s, 1H each, NH), 2.36, 2.32, 2.31 (s, 3H each, $\mathrm{C_6H_4Me}$), 1.18 (s, 30H, Cp*). Anal. Calcd for $\mathrm{C_{41}H_{54}ClN_3Ir_2\cdot CHCl_3}$: C, 44.72; H, 4.91; N, 3.72. Found: C, 44.71; H, 5.11; N, 3.82. Complexes **2b**·Cl−**2d**·Cl were prepared analogously. **2b**·Cl: yield, 84%; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.47−6.90 (m, 15H, aryl), 6.00, 5.46, 3.62 (br s, 1H each, NH), 1.19 (s, 30H, Cp*). Anal. Calcd for $\mathrm{C_{38}H_{48}ClN_3Ir_2\cdot 0.5CH_2Cl_2}$: C, 45.82; H, 4.89; N, 4.16. Found: C, 46.05; H, 4.99; N, 4.10. **2c**·Cl: yield, 61%; IR (KBr) ν_{NH} 3380 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.37−7.01 (m, 12H, aryl), 6.11, 5.60, 3.41 (br s, 1H each, NH), 1.20 (s, 30H, Cp*). Anal. Calcd for $\mathrm{C_{38}H_{45}Cl_4N_3Ir_2\cdot 0.5CHCl_3}$: C, 40.93; H, 4.06; N, 3.72. Found: C, 41.03; H, 4.58; N, 3.77. **2d**·Cl: yield 81%; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 8.02−6.91 (m, 12H, aryl), 6.45, 5.94, 3.61 (br s, 1H each, NH), 1.19 (s, 30H, Cp*). Anal. Calcd for $\mathrm{C_{41}H_{45}ClF_9N_3Ir_2\cdot 0.5CHCl_3}$: C, 40.51; H, 3.73; N, 3.42. Found: C, 40.97; H, 3.65; N, 3.36. **2a**·$\mathrm{ClO_4}$: IR (KBr) ν_{NH} 3260 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.21−6.98 (m, 12H, aryl), 3.93, 3.63, 3.61 (br s, 1H each, NH), 2.37 (s, 3H, $\mathrm{C_6H_4Me}$), 2.33 (br s, 6H, $\mathrm{C_6H_4Me}$), 1.14 (s, 30H, Cp*). Anal. Calcd for $\mathrm{C_{41}H_{54}ClIr_2N_3O_4\cdot CH_2Cl_2}$: C, 43.57; H, 4.88; N, 3.63. Found: C, 43.91; H, 4.86; N, 3.67.

(5) $\mathrm{C_{41}H_{54}ClN_3O_4Ir_2\cdot CH_2Cl_2}$: $P2_1/n$ (monoclinic), $a = 19.656(4)$ Å, $b = 16.991(2)$ Å, $c = 13.835(6)$ Å, $\beta = 109.67(3)°$, $V = 4351(3)$ Å^3, $Z = 4$, $D = 1.767$ g/cm^{-3}; Mo Kα radiation ($\lambda = 0.710\ 69$ Å); R (R_{w}) = 8.4% (7.7%) for 5249 reflections ($I > 3\sigma(I)$) collected with $5.0 < 2\theta < 50°$ at 298 K. Bond distances (Å): Ir(1)−N(1), 2.31(2); Ir(1)−N(2), 2.16(2); Ir(1)−N(3), 2.13(2); Ir(2)−N(1), 2.01(2); Ir(2)−N(2), 2.07(2); Ir(2)−N(3), 2.19(2). Bond angles (deg): Ir(1)−N(1)−Ir(2), 90.8(8); Ir(1)−N(2)−Ir(2), 93.6(9); Ir(1)−N(3)−Ir(2), 91.6(0)°.

S0276-7333(97)00499-8 CCC: $14.00

Scheme 1



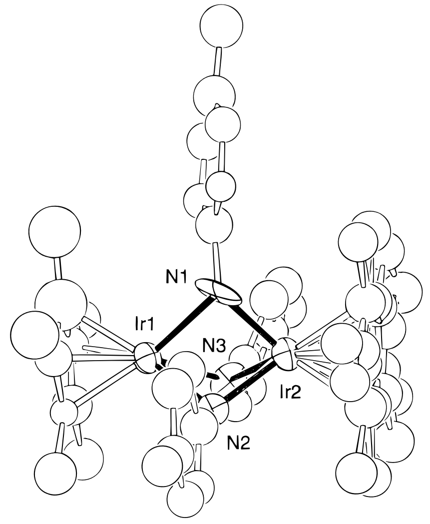


Figure 1. ORTEP drawing of the cationic part of **2a**$\cdot$ClO$_4$.

Figure 1 shows an ORTEP drawing of the cationic part in **2a**$\cdot$ClO$_4$, having a dinuclear structure where two Cp*Ir units are bridged by three *p*-tolylamido groups. Two of the three μ_2-NHTol groups are hydrogen-bonded to the perchlorate anion, which lies in the outer coordination sphere and is not bound to the metal.[6] The intramolecular distance between two Ir atoms is 3.08(1) Å, which indicates the absence of metal–metal bonding interactions.

The monomeric imido complexes Cp*IrNR (**3**, R = Bu^t, SiMe$_2$Bu^t, 2,6-Me$_2$C$_6$H$_3$, 2,6-Pr$^i{}_2$C$_6$H$_3$) were previously reported, which were prepared from **1a** with 4 equiv of LiNHR in THF at 0 °C.[7] It should be noted that complexes **3** are isolable only with the bulky R groups described above. Reaction of **1a** with LiNHPh under similar conditions led only to intractable materials. It is in sharp contrast that a series of amido-bridged dinuclear complexes **2**$\cdot$Cl were readily obtained in good yield, as reported herein. Formation of the corresponding monomeric imido complexes Cp*IrN(C$_6$H$_4$R-*p*) was not observed under our conditions. More recently the dinuclear imido- or imido/amido-bridged compounds [Cp*Ir(μ_2-NC$_5$H$_9$)]$_2$ and [Cp*Ir(μ_2-NC$_6$H$_{11}$)(μ_2-NHC$_6$H$_{11}$)IrCp*]Cl were isolated by treatment of **1a** with LiNHC$_5$H$_9$ and LiNHC$_6$H$_{11}$, respectively.[3a] It is interesting to note that reaction of **1a** with LiNHR is surprisingly sensitive to the conditions employed and produces a variety of structures.

On the other hand, addition of 1 equiv of **1a** or its bromide analogue **1b** to a THF solution of (LiNH$_2$)$_2$C$_{10}$H$_6$-1,8 at −80 °C to room temperature resulted in the precipitation of the bis-amido-bridged dinuclear Ir(III) complexes [Cp*Ir{(μ_2-NH)$_2$C$_{10}$H$_6$-1,8}(μ_2-X)IrCp*]X (**4a**, X = Cl; **4b**, X = Br), which were obtained as yellow-brown microcrystalline solids in about 80% yield and spectroscopically characterized (Scheme 1).[8] The ^{1}H NMR spectrum of **4a** exhibits a singlet at δ 1.18 (s, 30H) due to the Cp* groups and a resonance at δ 5.67 (br s, 2H) assignable to the NH protons, together with those attributable to the naphthyl moiety. Furthermore, the electronic conductivity of **4** in chloroform (31−34 S cm^2 mol^{-1}) corresponds well to that of a chloroform solution of [Bu^{n}N]$_4$BF$_4$ (23 S cm^2 mol^{-1}). These features suggest the triply bridged structure of **4** shown in Scheme 1.

Reduction of **4b** with excess Na/Hg in THF at room temperature afforded the dinuclear Ir(II) complex Cp*Ir{(μ_2-NH)$_2$C$_{10}$H$_6$-1,8}IrCp* (**5**), which was isolated as dark red columnar crystals and both spectroscopically[9] and crystallographically[10] characterized (Scheme 2). The ^{1}H NMR spectrum of **5** exhibits a singlet attributable

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(6) Distances between hydrogen-bonded atoms (Å); N(2)−O(3), 3.04; N(3)−O(3), 2.87.

(7) Glueck, D. S.; Wu, J.; Hollander, J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041.

(8) 1,8-(LiNH)$_2$C$_{10}$H$_6$ was prepared in situ by treatment of a THF (1.5 mL) solution of 1,8-(NH$_2$)$_2$C$_{10}$H$_6$ (40 mg, 0.253 mmol) with 1.65 M Bu^{n}Li in hexane (0.3 mL, 0.506 mmol) at −80 °C. To this solution was added a THF (6.5 mL) suspension of **1a** (168 mg, 0.211 mmol) at −80 °C and the resultant mixture was gradually warmed to room temperature, during which time the original orange suspension turned to a green-brown suspension. After filtration, the remaining solid was washed with THF (4 mL, two times), dried in vacuo, and extracted with CHCl$_3$ (5 mL, two times). Removal of the solvent gave **4a** as a brown powder, which was recrystallized from CHCl$_3$−hexane (3−10 mL) to afford brown columnar crystals (148 mg, 83%): IR (KBr) ν_{NH} 3418 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.77 (d, 2H, J = 7.1 Hz, aryl), 7.45 (d, 2H, J = 8.3 Hz, aryl), 7.24 (dd, 2H, J = 8.3, 7.1 Hz, aryl), 5.67 (br s, 2H, NH), 1.18 (s, 30H, Cp*). Anal. Calcd for C$_{30}$H$_{38}$Cl$_2$Ir$_2$N$_2$$\cdot$0.5CHCl$_3$: C, 38.90; H, 4.12; N, 2.97. Found: C, 38.13; H, 4.12; N, 2.76. Complex **4b** was obtained analogously: yield 78%; ^{1}H NMR (CDCl$_3$) δ 7.72 (d, 2H, J = 7.3 Hz, aryl), 7.45 (d, 2H, J = 8.3 Hz, aryl), 7.25 (dd, 2H, J = 8.3, 7.3 Hz, aryl), 5.52 (br s, 2H, NH), 1.19 (s, 30H, Cp*). Anal. Calcd for C$_{30}$H$_{38}$Br$_2$Ir$_2$N$_2$$\cdot$0.5CHCl$_3$: C, 35.55; H, 3.77; N, 2.72. Found: C, 35.97; H, 3.61; N, 2.85.

(9) To Na/Hg (0.3%; 355 mg, 15.5 mmol) was added a THF (90 mL) suspension of **4b** (500 mg, 0.515 mmol) at room temperature, and the resultant mixture was stirred for 2 days. The resulting reddish brown suspension was filtered, and the solvent was removed in vacuo. The residual solid was extracted with THF (20 mL, two times). Evaporation of the solvent afforded **5** as a spectroscopically pure reddish brown powder (354 mg, 85%). Dark red columnar crystals suitable for structural analysis were obtained by recrystallization from hexane at −20 °C: IR (KBr) ν_{NH} 3401 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 7.42 (d, 2H, J = 7.8 Hz, aryl), 6.99 (dd, 2H, J = 7.8 Hz, aryl), 6.90 (d, 2H, J = 7.8 Hz, aryl), 4.08 (br s, 2H, NH), 1.82 (s, 30H, Cp*). Anal. Calcd for C$_{30}$H$_{38}$Ir$_2$N$_2$: C, 44.43; H, 4.72; N, 3.45. Found: C, 44.27; H, 4.88; N, 3.76.

(10) C$_{30}$H$_{38}$N$_2$Ir$_2$: $P2_12_12_1$ (orthorhombic), a = 14.6337(7) Å, b = 18.6916(6) Å, c = 10.2601(6) Å, V = 2806.4 Å^3, Z = 4, D = 1.920 g/cm^{-3}; Mo Kα radiation (λ = 0.710 69 Å); R (R_w) = 5.8% (6.1%) for 2373 reflections ($I > 3\sigma(I)$) collected with $5.0 < 2\theta < 49.5°$ at 298 K. Ir(1)−Ir(2), 2.584(1); Ir(1)−N(1), 2.02(1); Ir(1)−N(2), 2.10(2); Ir(2)−N(1), 2.11(1); Ir(2)−N(2), 2.08(3). Bond angles (deg): Ir(1)−N(1)−Ir(2), 77.4(5); Ir(1)−N(2)−Ir(2), 76.4(8).

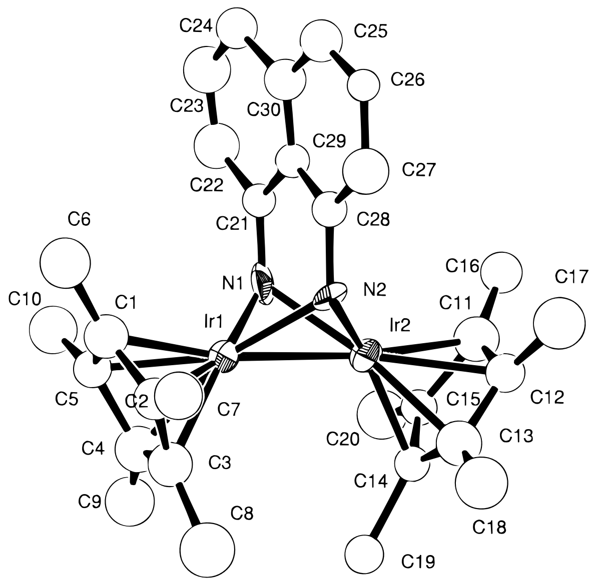
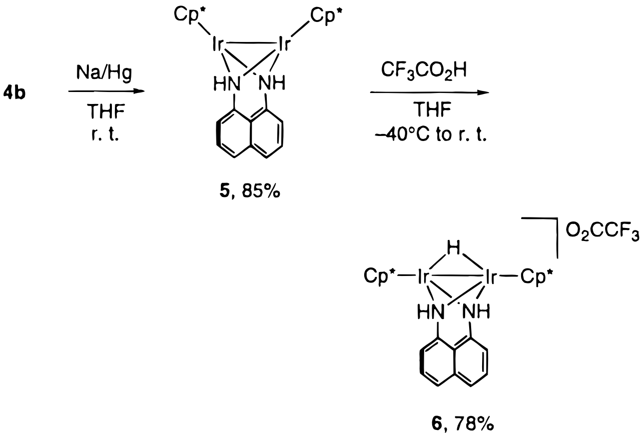


Figure 2. ORTEP drawing of **5**.

Scheme 2



to the Cp* group at δ 1.82 (30H) together with resonances due to the NH (δ 4.08 (br s, 2H)) and naphthyl protons. An ORTEP drawing of **5** is given in Figure 2, showing a dinuclear structure where two Cp*Ir units are bridged by the $(NH)_2C_{10}H_6$-1,8 moiety. Two Cp* ligands are in a mutually cis configuration. The Ir_2N_2 core is not planar but has a butterfly structure and is puckered with a dihedral angle of 95.72° between the plane including Ir(1), Ir(2), and N(1) atoms and that defined by the Ir(1), Ir(2), and N(2) atoms. The short Ir−Ir distance of 2.584(1) Å clearly indicates the existence of a metal−metal single bond, which is in good accord with the diamagnetic nature of **5**.[3a,c−e,11]

Complex **5** was protonated by CF_3CO_2H to give the hydrido-bridged dinuclear Ir(III) complex [Cp*Ir{(μ_2-NH)$_2$C$_{10}$H$_6$-1,8}(μ_2-H)IrCp*]O_2CCF_3 (**6**; Scheme 2), which was isolated as a reddish brown microcrystalline solid and spectroscopically characterized.[12] The ^{1}H NMR spectrum of **5** exhibits the characteristic hydrido signal at δ −13.39, together with those due to the Cp* (δ 1.74) and naphthyl groups.

Further studies are in progress on the reactivities of these novel amido-bridged diiridium complexes.

Acknowledgment. Professors Munetaka Akita and Yoshihiko Moro-oka of Tokyo Institute of Technology are gratefully acknowledged for collecting diffraction data for **2a**·ClO_4. H.M. acknowledges financial support by a Grant-in-Aid for Scientific Research (Priority Area No. 284-09239240) from The Ministry of Education, Science, Sports and Culture of Japan and by the Nissan Foundation for Promotion of Science.

Supporting Information Available: Text giving experimental details of the preparation of **2a**·ClO_4, and tables giving details of the X-ray structure determinations, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **2a**·ClO_4 and **5**, and an ORTEP drawing of a cationic part of **2a**·ClO_4 with the complete atom numbering scheme (31 pages). Ordering information is given on any current masthead page.

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(11) Dinuclear Rh(I) and Rh(II) complexes with a μ_2-(NH)$_2$C$_{10}$H$_6$-1,8 ligand, [Rh(CO)L]$_2${μ_2-(NH)$_2$C$_{10}$H$_6$-1,8} (L = CO, PPh$_3$) and [RhI(CO)(PPh$_3$)]$_2${μ_2-(NH)$_2$C$_{10}$H$_6$-1,8}, were reported: Oro, L. A.; Fernández, M. J.; Modrego, J. Foces-Foces, C.; Cano, F. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 913.

(12) To a THF (15 mL) solution of **5** (408 mg, 0.503 mmol) was added CF_3CO_2H (0.04 mL, 0.508 mmol) at −40 °C, and the resultant mixture was slowly warmed with stirring for 1 day. The resulting yellow-brown suspension was evaporated to dryness. The residual solid was washed with Et_2O (10 mL, two times) and extracted with $CHCl_3$ (20 mL, two times). Removal of the solvent afforded **6** as a reddish brown powder (364 mg, 78%): ^{1}H NMR (CDCl$_3$) δ 7.55 (d, 2H, J = 9.0 Hz, aryl), 7.52 (d, 2H, aryl, J = 9.2 Hz), 7.13 (dd, 2H, J = 9.2, 9.0 Hz, aryl), 5.30 (br s, 2H, NH), 1.74 (s, 30H, Cp*), −13.39 (s, 1H, Ir−H−Ir). Anal. Calcd for $C_{32}H_{39}F_3N_2O_2Ir_2 \cdot 0.5CHCl_3$: C, 39.64; H, 4.04; N, 2.84. Found: C, 39.71; H, 3.95; N, 3.01.