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Syntheses and Structures of (Pentamethylcyclopentadienyl)iridium Amidinate Complexes

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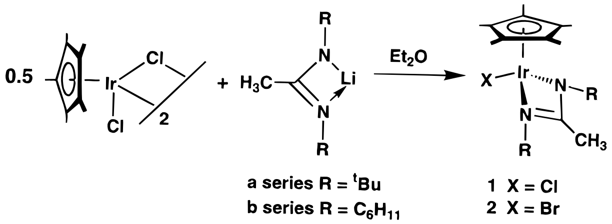
*Summary: Reaction of [Cp*IrCl$_2$] with lithium amidinates provides an entry to a series of Cp*Ir(RNR′CNR)X (**1**, X = Cl; **2**, X = Br) complexes. Alkyl or hydride derivatives are formed by addition of a variety of Grignard reagents or sodium isopropoxide to **1** or **2**. Cationic complexes may be obtained by the interaction of **2** with AgSbF$_6$ in the presence of an appropriate ligand. In all of these compounds, the amidinate ligand adopts a symmetrical, bidentate coordination geometry.*

There is a growing interest in organometallic complexes bearing nitrogen ligands.[1] These compounds catalyze a wide variety of reactions, such as olefin polymerization,[2] ketone and aldehyde reductions,[3] and the water gas shift reaction.[4] For the later transition metals, most of this work has focused on the use of poly(pyrazolyl)borate-, pyridine-, and porphyrin-based ligand environments.[1] Amidinates (RNR′CNR) are a class of ligands which have undergone a recent renaissance,[5] especially for early transition metals, actinides, and lanthanides.[6−11] They have been employed much less frequently with the later transition metals.[12,13] There are a number of dinuclear iridium complexes supported by amidinate ligands,[14] but to date there are no reported mononuclear iridium complexes.[15−18] This paper describes the synthesis and some reactivity of amidinato iridium complexes of the type Cp*Ir(RNR′CNR)X (Cp* = η^5-C$_5$Me$_5$). Maitlis and co-workers prepared analogous formamidinato rhodium(III) complexes[19] and other groups have investigated their reactivity.[20]

Results and Discussion

Complexes of the type Cp*IrX(CH$_3$C(NR)$_2$) (**a**, R = C(CH$_3$)$_3$, **b**, R = C$_6$H$_{11}$; **1**, X = Cl; **2**, X = Br) are prepared by the reaction of [Cp*IrCl$_2$]$_2$ with the lithium amidinates (CH$_3$C(NC(CH$_3$)$_3$)$_2$Li or CH$_3$C(NC$_6$H$_{11}$)$_2$Li·LiBr) in ether solvents (eq 1). The yields of the reactions depend upon the substituents on the nitrogen atoms of the amidinate ligand. The less hindered cyclohexyllithium amidinate reacts faster and in higher yield than the *tert*-butyl-substituted ligand. Both complexes are bright orange crystalline solids which may be stored in air for several weeks without noticeable decomposition. The formation of the bromide **2b** arises from halogen exchange with the LiBr which cocrystalized with the lithium amidinate. The combustion analysis fits quite well with the formation of **2b**, however, indivdual crystals may not reflect the composition of the bulk material (see Supporting Information). Bands in the IR spectra of **1a** and **2b** at 1499 and 1516 cm^{-1} are characteristic of chelating amidinate ligands.[20] The ^{1}H NMR spectrum of **1a** consists of three singlets at δ 2.02, 1.62, and 1.33 ppm in a 1:5:6 ratio, as expected for a symmetrical structure at room temperature. A weak signal at 174.4 in the ^{13}C{^{1}H} NMR spectrum is assigned to the central quaternary carbon of the amidinate ligand. A crystal structure determination of **2b** confirms that the amidinate ligand is planar and symmetrically bound to the iridium (Ir−N$_1$ = 2.125(7); Ir−N$_3$ = 2.127(7) Å). The details of this study are contained in the Supporting Information.



(1)

The halide complexes **1a** and **2b** are excellent precursors for a variety of iridium amidinato complexes (Scheme 1). Reaction of **1** or **2** with various Grignard reagents affords the alkyl derivatives **3−5** in excellent yields as yellow-orange crystalline solids which slowly

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[1] Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497−526.

[2] Wang, L.; Lau, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999−7000.

[3] Mestroni, G.; Zassinovich, G.; Camus, A. *J. Organomet. Chem.* **1977**, *140*, 63−72.

[4] Ziessel, R. *J. Am. Chem. Soc.* **1993**, *115*, 118−127.

[5] Juvinall, G. L. *J. Am. Chem. Soc.* **1964**, *86*, 4202−4203.

[6] Hagadorn, J. R.; Arnold, J. *J. Am. Chem. Soc.* **1996**, *117*, 893−894.

[7] Gómez, R.; Duchateau, R.; Chernega, A. N.; Meetsma, A.; Edelmann, F. T.; Teuben, J. H.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1995**, 217−225.

[8] Duchateau, R.; Wee, C. T. v.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931−4932.

[9] Berno, P.; Hao, S.; Minhas, R.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 7417−7418.

[10] Roesky, H. W.; Meller, B.; Noltemeyer, M.; Schmidt, H.-G.; Scholz, U.; Shledrick, G. M. *Chem. Ber.* **1988**, *121*, 1403−1406.

[11] Wedler, M.; Knösel, F.; Noltemeyer, M.; Edelmann, F. T.; Behrens, U. *J. Organomet. Chem.* **1990**, *388*, 21−45.

[12] Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *113*, 219−300.

[13] Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 430−481.

[14] Cotton, F. A.; Walton, R. A. In *Multiple Bonds Between Metal Atoms*; Oxford: New York, 1993; pp 502−507.

[15] A substructure search of *Chemical Abstracts* for Ir−N−C−N metallacycles produced the following three references.

[16] Beck, W.; Rieber, W.; Cenini, S.; Porta, F.; Monica, F. L. *J. Chem. Soc., Dalton Trans.* **1974**, 298−304.

[17] Ciriano, M. A.; Perez-Torrente, J. J.; Oro, L. A. *J. Organomet. Chem.* **1993**, *445*, 267−271.

[18] Ciriano, M. A.; Perez-Torrente, J. J.; Oro, L. A. *J. Organomet. Chem.* **1993**, *445*, 273−281.

[19] Rigby, W.; Lee, H.-B.; Bailey, P. M.; McCleverty, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 387−394.

[20] Piraino, P.; Bruno, G.; Tresoldi, G.; Faraone, G.; Bomieri, G. *J. Chem. Soc., Dalton Trans.* **1983**, 2391−2395.

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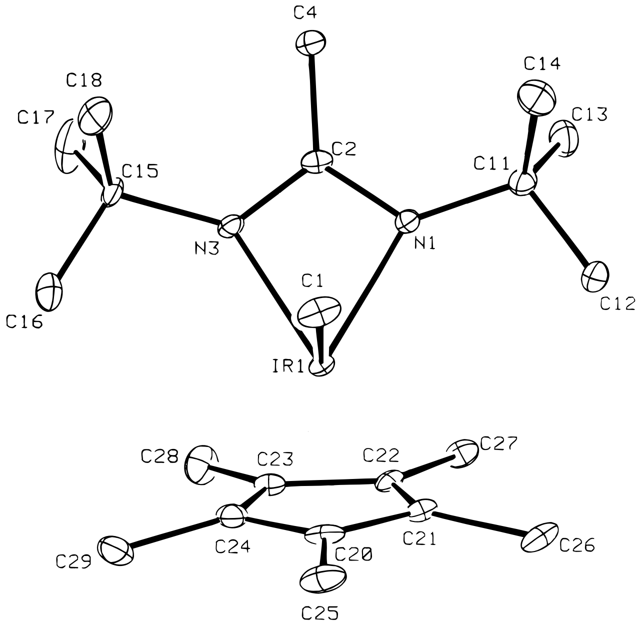
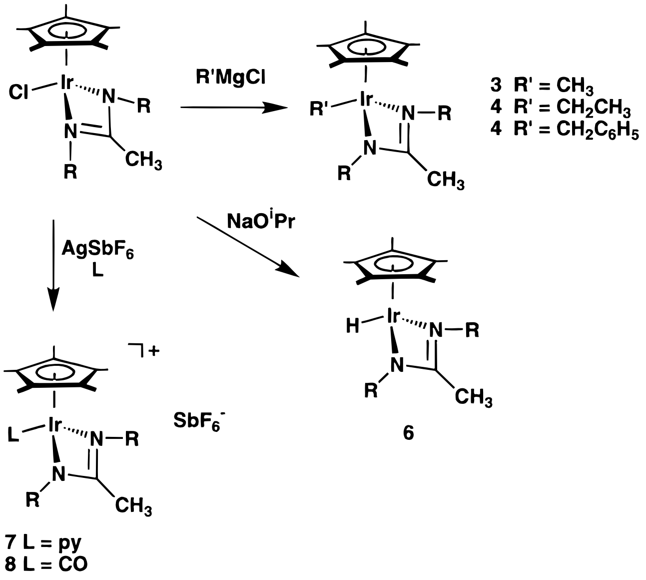


Figure 1. ORTEP diagram of $Cp^*IrCH_3(CH_3C(NC(CH_3)_3)_2)$ (**3a**).

Scheme 1



decompose in air. The IR spectra of all of these derivatives display an absorption at *ca*. 1500 cm^{-1}, again characteristic of an η^2-amidinate ligand. The NMR spectra of these complexes are unexceptional and are consistent with a symmetrical η^2-amidinate ligand.

Crystals suitable for an X-ray diffraction study were obtained by slow cooling of a saturated Et_2O solution of **3a** to −30 °C. An ORTEP diagram is shown in Figure 1, selected distances and angles in Tables 2 and 3. The Ir−N distances, as well as the geometries about the amidinate ligand and iridium center, are quite similar to those found in **2b**. There is a very slight asymmetry in the bonding of Ir to the Cp* ligand, with the Ir−C distances varying from 2.252(6) to 2.181(6) Å. The Ir−CH_3 bond length is 2.107(5) Å, comparable to the distances observed in other Cp*Ir methyl complexes.[21,22]

Table 1. Crystal Data and Collection Parameters for Compound 3a

	3a
formula	$C_{21}H_{39}IrN_2$
fw	511.78
cryst dimens (mm)	0.28 × 0.21 × 0.27
space group	$P2_1/n$ (No. 14)
temp (°C)	−70
a (Å)	9.191(1)
b (Å)	16.942(2)
c (Å)	13.979(1)
V (Å^3)	2161.3
β (deg)	96.50(1)
Z	4
d_{calcd} (g/cm^3)	1.572
diffractometer	CAD4
radiation	Mo Kα (0.710 69 Å)
monchromator	graphite
scan type (deg)	ω (1.20−2.20°)
data collected	h,k,l
2θ range (deg)	2.4−57.0
transmission factors	0.24−0.29
μ (cm^{-1})	61.58
no. of data collected	11257
no. of duplicates	2915
R-merge (%)	2.2
no. of unique refln ($I > 3\sigma$)	3508
no. of param refined	217
R (%)	3.4
R_w (%)	2.7
error of fit	0.83

Table 2. Selected Intramolecular Distances (Å) for 3a

Ir(1)−N(1)	2.119(5)	Ir(1)−N(3)	2.107(5)
Ir(1)−C(1)	2.107(5)	Ir(1)−C(20)	2.181(6)
Ir(1)−C(21)	2.177(6)	Ir(1)−C(22)	2.241(5)
Ir(1)−C(23)	2.252(6)	Ir(1)−C(24)	2.190(6)
N(1)−C(2)	1.320(7)	N(1)−C(11)	1.476(7)
N(3)−C(2)	1.338(7)	N(3)−C(15)	1.487(7)

Table 3. Selected Intramolecular Angles (deg) for 3a

Ir(1)-N(1)-C(2)	95.6(4)	Ir(1)-N(3)-C(15)	135.7(4)
Ir(1)-N(1)-C(11)	137.0(4)	N(1)-C(2)-N(3)	107.6(5)
Ir(1)-N(3)-C(2)	95.6(3)		

All of the alkyl complexes are extremely stable and show little reactivity of the Ir−C bond. No reactions were observed when these compounds were treated with CO, ethylene, $C_6H_5C{\equiv}CH$, or PMe_3. No signs of decomposition were observed upon heating C_6D_6 solutions of **3**−**5** for several months at 100 °C. The Ir−C bonds in complexes **3**−**5** react rapidly with added acids. Addition of 1.0 equiv of HCl to a C_6D_6 solution of **4a** produces ethane and **1a** in 63 and 92% yield by ^1H NMR. If excess acid is added, protonation of the amidinate ligand occurs and the only identifiable product is $[Cp^*IrCl_2]_2$. Addition of CF_3SO_3H to solutions of **3**−**5** in various solvents results in formation of the expected hydrocarbon product and several iridium containing products (vide infra).

Addition of a variety of hydride donor reagents ($LiBHEt_3$, $LiBH_4$, $LiAlH_4$) to **1a** results in the formation of several Cp* and hydride containing products. The only identifiable compound in these mixtures is the previously reported polyhydride Cp^*IrH_4.[23] The formation of this product demonstrates that under some conditions the amidinate ligand may be lost from the iridium center. The desired hydride Cp*Ir(^{t}BuN-

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(21) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462−10463.

(22) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970−1973.

(23) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3508−3516.

$(CH_3C)N^tBu)H$ (**6a**) is produced from the reaction of **1a** with an excess of NaO^iPr in isopropyl alcohol. Recrystalization from CH_3CN at −35 °C gave a 45% yield of **6a** as pale yellow needles. A slightly broadened singlet at δ −10.43 ppm is assigned to the signal of the hydride in the ^1H NMR spectrum. The Ir−H stretch occurs at 2063 cm^{-1} in the infrared spectrum. This band shifts to a value of 1480 cm^{-1} when isopropyl alcohol-d_8 is used as the solvent for the reaction, confirming that isopropoxide serves as the hydride source.

The hydride complex **6a** is very unreactive. No detectable change is observed when C_6D_6 solutions of **6a** were treated with CH_2CH_2, $(CH_3)_2C{=}C{=}CH_2$, $PhC{\equiv}CH$, CO, CO_2, or PMe_3.

Halide abstraction with $AgSbF_6$ in the presence of excess ligand yields the yellow, cationic complexes **7b** and **8b**. If no added ligand is present, complicated mixtures of products are formed. The pyridine ligand in **7b** is very tightly bound; no exchange with solvent was observed when solutions of **7b** in py-d_5 were heated at 100 °C for several days.

The cationic carbonyl complex **8b** is produced when halide abstraction is performed under an atmosphere of CO. The CO stretching frequency of 2042 cm^{-1} is in the range observed by Wang and Angelici for their series of $[Cp^*Ir(CO)(PR_3)H]^+$ (2038−2051 cm^{-1}) and $Cp^*Ir(CO)(PR_3)CH_3]^+$ (2030−2032 cm^{-1}) complexes.[24] In contrast to $Cp^*RhCl(CH_3C_6H_4N(CH)NC_6H_4CH_3)$, which reacts with CO to form the acyl−formamidinato complex $Cp^*RhCl(COCH_3C_6H_4N(CH)NC_6H_4CH_3)$,[20] there is no evidence for CO insertion into the Ir−N bond during the reaction of **2b** with CO and silver salts or if **1** or **2** is treated with CO under conditions similar to those used to effect CO insertion for the rhodium formamidinato complex. The molecular structure of **8b** (contained in the Supporting Information) is quite similar to those previously described. The Ir−N distances are slightly shorter than those found in **2b**, 2.115 and 2.116(5) Å, while the distances and angles within the amidinate ligand are essentially unchanged. The Ir−CO distance is 1.863(10) Å.

In summary, the reaction of $[Cp^*IrCl_2]$ with lithium amidinates provides an entry to a series of $Cp^*Ir(RNR'CNR)X$ complexes. Alkyl derivatives are formed by addition of a variety of Grignard reagents. Cationic complexes may be obtained by the addition of $AgSbF_6$ in the presence of an appropriate ligand. In all of these compounds, the amidinate ligand adopts a symmetrical, bidentate coordination geometry. The base-free cations $[Cp^*Ir(RNR'CNR)]^+$, which could not be isolated, are isoelectronic to $[Cp^*Rh(acac)]^+$ (acac = acetylacetonate) prepared by Maitlis.[19] In the solid state, the rhodium complex achieves an 18-electron configuration by adopting a dimeric structure with a μ-η^2,η^1-acac ligand. The bulky substituents on the amidinate nitrogens may prevent the formation of a similar dimeric structure. The hydride and alkyl derivatives are quite unreactive, undoubtedly due to the coordinative saturation at the iridium center.

Experimental Section

General Considerations. Unless otherwise stated, all manipulations were conducted using standard Schlenk-line and glovebox techniques. Tetrahydrofuran, diethyl ether, hexane, and toluene were distilled from sodium/benzophenone. Dichloromethane and pyridine were distilled from activated molecular sieves. C_6D_6 was vacuum-transferred from sodium/benzophenone, while CD_2Cl_2 and $CDCl_3$ were vacuum-transferred from activated molecular sieves. Unless otherwise stated, all reagents were used as received from standard chemical suppliers. The complex $[Cp^*IrCl_2]_2$ was prepared by the method of Maitlis.[25] The amidinate ligands were prepared by addition of a slight deficiency of methyllithium to a hexane solution of the corresponding carbodiimide. The resulting white precipitate was collected on a frit under N_2 and washed with hexane. In the case of the cyclohexyl amidinate (**b** series) 1 equiv of lithium bromide precipitated with the ligand. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at ambient temperature at 301.5 and 75.71 MHz, respectively. Proton chemical shifts are referenced relative to residual protiated solvent at δ 7.26 ($CDCl_3$), 7.15 (C_6D_6), and 5.32 (CD_2Cl_2) ppm; ^{13}C shifts are referenced to solvents peaks at δ 77.0 ($CDCl_3$), 128.0 (C_6D_6), and 53.2 (CD_2Cl_2) ppm. Complexes bearing the cyclohexyl-substituted amidinate ligand (**b** series) have several broad resonances between δ 2.0 and 1.0 ppm which are not included in the subsequent spectral data. Coupling constants are reported in Hertz. All IR samples were prepared as KBr pellets. Elemental analyses were performed by Galbraith Laboratories.

$Cp^*IrCl(CH_3C(NC(CH_3)_3)_2)$ (1a). A 250 mL Schlenk flask was charged with 797 mg (1.0 mmol) of $[Cp^*IrCl_2]_2$ and 100 mL of Et_2O and cooled to −78 °C. A solution of $(CH_3C(NC(CH_3)_3)_2)Li$ (352 mg, 2.0 mmol, 2.0 equiv) in 50 mL of THF was added via cannula to the rapidly stirred slurry of the iridium complex. As the reaction mixture was allowed to warm to room temperature, the solution became homogeneous. It was allowed to stir at ambient temperature for 12 h. After this time, the dark red-brown solution was evaporated under reduced pressure. At this point, all subsequent manipulations were performed in the air. The brown residue was extracted with 3 × 25 mL of toluene and filtered through Celite, then the volatile materials were removed using a rotory evaporator. The resulting sticky brown residue was collected on a frit and washed with cold (−78 °C) methanol to yield bright orange crystals of **1a** (458 mg, 43%). ^1H NMR ($CDCl_3$): δ 2.02 (s, 3H), 1.62 (s, 15H), 1.33 (s, 18H) ppm. $^{13}C\{^1H\}$ ($CDCl_3$): δ 174.4, 82.9, 53.7, 33.9, 25.3, 10.7. IR: 2960 (m), 1499 (m), 1375 (s), 1359 (s), 1100 (s), 793 (s). Anal. Calcd for $C_{20}H_{36}ClIrN_2$: C, 45.14; H, 6.82; N, 5.26; Cl, 6.66. Found: C, 45.04; H, 6.82; N, 5.28.

$Cp^*IrBr(CH_3C(NC_6H_{11})_2)$ (2b). A 250 mL flask was charged with 2.60 g (3.26 mmol) of $[Cp^*IrCl_2]_2$ and 100 mL of THF. The orange slurry was cooled to −30 °C. A solution of 2.07 g (6.6 mmol, 2.1 equiv) of $((C_6H_{11})N)_2C(CH_3)Li{\cdot}LiBr$ in THF (50 mL) was added via cannula to the reaction flask. The solution darkened and was allowed to warm to room temperature. After the reaction mixture was stirred for 2 h, the volatile materials were removed *in vacuo* and the residue extracted with 3 × 30 mL hexane and filtered through a pad of Celite. The combined hexane extracts were concentrated to 50 mL and cooled to −30 °C overnight. The bright orange crystals were collected on a frit and washed with cold hexane to yield 2.24 g (60%) of analytically pure **2b**. Combustion analysis indicates that the chlorides originally present on the iridium exchanges with the lithium bromide. ^1H NMR ($CDCl_3$): δ 3.1 (m, 2H), 2.50 (bm, 2H), 1.57 (s, 15H), 1.55 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 174.9, 82.8, 56.3, 37.5, 34.6, 26.0, 25.9, 25.7, 16.3, 10.8 ppm. IR: 2982 (s), 2850 (s), 1516 (m), 1450 (m), 1359 (m), 1201 (m), 1047 (m), 1026 (m) cm^{-1}. Anal. Calcd for $C_{24}H_{40}BrIrN_2$: C, 45.85; H, 6.41; N, 4.46; Br, 12.71; Cl, 0.00. Found: C, 46.01; H, 6.14; N, 4.56; Br, 11.68; Cl, 0.01.

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(24) Wang, D.; Angelici, R. J. *Inorg. Chem.* **1996**, *35*, 1321−1331.

(25) White, C.; Yates, A.; Maitlis, P. M. In *Inorganic Syntheses*; Grimes, R. N., Ed.; John Wiley & Sons: New York, 1992; Vol. 29, pp 228−234.

General Procedure for the Synthesis of Alkyl Complexes 3−5. A solution of 480 mg (0.902 mmol) of **1a** in 30 mL of Et_2O was cooled to −30 °C. CH_3MgCl (350 μL of a 3.0 M solution, 1.05 mmol, 1.2 equiv) was added to the bright orange solution. The reaction mixture rapidly turned yellow, and a dull tan precipitate began to form. After the reaction mixture was warmed to room temperature and stirred for 1 h, the volatile materials were removed. The product was extracted with hexane (3 × 5 mL), filtered through Celite and concentrated to volume of ∼2 mL. Cooling to −30 °C for 12 h afforded plate-like orange crystals (420 mg, 91%) of analytically pure **3a**.

$Cp^*IrCH_3(CH_3C(NC(CH_3)_3)_2)$ (3a). ^1H NMR (C_6D_6): δ 1.84 (s, 3H), 1.59 (s, 15H), 1.36 (s, 3H), 1.28 (s, 18H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.0, 83.0, 52.9, 34.3, 34.2, 25.1, 10.7, −11.2 ppm. IR: 2913 (s), 2794 (m), 1504 (s), 1454 (m), 1439 (m), 1235 (s), 1199 (s). Anal. Calcd for $C_{21}H_{39}IrN_2$: C, 49.19; H, 7.67; N, 5.47. Found: C, 48.80; H, 7.78; N, 5.46.

$Cp^*IrCH_3(CH_3C(NC_6H_{11})_2)$ (3b). ^1H NMR (C_6D_6): δ 2.95 (m, 4H), 1.72 (s, 15H), 1.60 (s, 3H), 1.25 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 167.4, 82.6, 56.6, 37.4, 34.9, 26.6, 26.5, 26.3, 15.5, 10.8, −5.6 ppm. IR 2931 (s), 1527 (s), 1450 (m), 1363 (m), 1201 (m), 1093 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{43}IrN_2$: C, 53.25; H, 7.69; N, 4.97. Found: C, 52.88; H, 7.77; N, 4.96.

$Cp^*IrCH_2CH_3(CH_3C(NC(CH_3)_3)_2)$ (4a). ^1H NMR (C_6D_6): δ 2.39 (q, $J = 7.6$, 2H), 1.97 (s, 3H), 1.93 (t, $J = 7.6$, 3H), 1.70 (s, 15H), 1.49 (s, 18H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 167.3, 83.6, 52.6, 34.3, 25.2, 22.0, 10.8, 2.62 ppm. IR: 2943 (s), 1500 (s), 1358 (s), 1232 (s), 1197 (s), 1095 (m), 1030 (m) cm^{-1}. Anal. Calcd for $C_{22}H_{41}IrN_2$: C, 50.26; H, 7.86; N, 5.33. Found: C, 50.19; H, 7.94; N, 5.28.

$Cp^*IrCH_2C_6H_5(CH_3C(NC(CH_3)_3)_2)$ (5a). ^1H NMR (C_6D_6): δ 7.44 (d, $J = 6.9$, 2H), 7.25 (t, $J = 7.8$, 2H), 6.96 (t, $J = 6.5$, 1H), 3.72 (s, 2H), 1.84 (s, 3H), 1.37 (s, 15H), 1.31 (s, 18H) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 168.9, 156.2, 129.4, 127.5, 121.7, 84.2, 52.9, 34.5, 25.7, 12.1, 10.9 ppm. IR (KBr): 2914 (s), 1586 (m), 1505 (s), 1486 (s), 1351 (m), 1230 (m), 1197 (s), 1028 (m), 760 (w), 698 (s) cm^{-1}. Anal. Calcd for $C_{27}H_{43}IrN_2$: C, 55.16; H, 7.37; N, 4.77. Found: C, 54.94; H, 7.33; N, 4.83.

$Cp^*IrH(CH_3C(NC(CH_3)_3)_2)$ (6a). In the drybox, a 50 mL flask was charged with 161 mg (0.880 mmol, 4.0 equiv) of NaN(TMS)$_2$ and 20 mL of isopropyl alcohol. The flask was stoppered and allowed to stir for 0.5 h at ambient temperature. After this time, 117 mg (0.220 mmol) of **1a** was added as a solid to the reaction flask. Over the course of 10 min, the orange solid dissolved to give a yellow solution and a white precipitate. After the reaction mixture was stirred for 8 h, the volatile materials were removed *in vacuo*. The product was extracted with 3 × 10 mL of hexane. The combined extracts were filtered through Celite and evaporated. The product was extracted into boiling acetonitrile and slowly cooled to −35 °C. After 2 days, 95 mg (0.19 mmol, 86%) of analytically pure yellow needles of **6a** had formed. ^1H NMR (C_6D_6): δ 1.76 (s, 15H), 1.69 (s, 3H), 1.30 (s, 18H), −10.43 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 169.2, 84.2, 53.1, 33.3, 22.9, 12.0 ppm. IR: 2912 (s), 2035 (m), 1698 (m), 1542 (s), 1338 (s), 1198 (s), 1030 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{37}IrN_2$: C, 48.26; H, 7.49; N, 5.63. Found: C, 48.80; H, 7.78; N, 5.46.

$[Cp^*Ir(py)(CH_3C(NC_6H_{11})_2)]^+SbF_6^-$ (7b). In the drybox, a 100 mL flask was charged with 420 mg (0.668 mmol) of **2b**, 0.5 mL of pyridine, and 10 mL of CH_2Cl_2. $AgSbF_6$ (230 mg, 0.668 mmol, 1.0 equiv) was dissolved in 10 mL of CH_2Cl_2 and added to the stirred solution of **2b**. The reaction mixture turned bright yellow, and a dull tan precipitate rapidly formed. After the reaction mixture was stirred for 1 h at ambient temperature, the solution was filtered through a pad of Celite and the volatile materials removed *in vacuo*. The residue was washed with 3 × 5 mL of Et_2O to yield a tacky yellow solid. This was dissolved in ∼2 mL of CH_2Cl_2, and the resulting solution was layered with ∼15 mL of Et_2O. The solution was cooled to −30 °C for 3 days. The resulting yellow crystals were collected on a frit and washed with Et_2O (3 × 10 mL). Residual solvent was removed *in vacuo*, affording 438 mg (75%) of analytically pure **7b**. ^1H NMR (CD_2Cl_2): δ 8.57 (d, $J = 5.4$, 2H), 7.94 (t, $J = 7.0$, 1H), 7.50 (t, $J = 7.1$, 2H), 3.04 (m, 2H), 1.77 (s), 1.65 (s) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.6, 154.3, 154.0, 139.0, 126.6, 85.3, 57.0, 36.5, 36.4, 25.8, 25.6, 18.5, 10.1 ppm. IR: 2934 (m), 1602 (m), 1523 (m), 1446 (m), 1359 (m), 1203 (m), 1080 (m), 761 (m), 703 (m), 655 (s) cm^{-1}. Anal. Calcd for $C_{29}H_{45}F_6IrN_3Sb$: C, 40.33; H, 5.25; N, 4.87. Found: C, 39.93; H, 5.08; N, 4.81.

$[Cp^*Ir(CO)(CH_3C(NC_6H_{11})_2)]^+SbF_6^-$ (8b). Two 100 mL round-bottom flasks equipped with a nitrogen inlet were charged with 323 mg (0.553 mmol) of **2b** and 190 mg (0.533 mmol, 1.0 equiv) of $AgSbF_6$, respectively. The solids were dissolved in 20 mL of acetone, and the flasks were attached to a Schlenk line. The flask containing **2b** was cooled to −78 °C, and CO was bubbled through the solution for 10 min. No color change was observed. The CO addition was momentarily stopped, and the solution of $AgSbF_6$ was added via cannula. A tan precipitate rapidly formed, and the solution turned bright yellow. The reaction mixture was allowed to warm to room temperature, and the volatile materials were removed. The flask was taken into the drybox, and the residue was extracted with 3 × 5 mL of CH_2Cl_2 and filtered through a bed of Celite. The CH_2Cl_2 was removed, and the sticky yellow residue was washed with toluene (3 × 10 mL), dissolved in ∼2 mL of THF, and layered with ∼12 mL of toluene. After this solution was cooled for 4 days, bright yellow crystals were deposited. These were collected on a frit and washed with toluene. Residual solvent was removed *in vacuo* to yield 256 mg (57%) of analytically pure **8b**. ^1H NMR (CD_2Cl_2): δ 2.82 (m, 2H), 2.03 (s, 15H), 1.95 (s, 3H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 183.7, 169.5, 101.2, 58.1, 37.1, 36.4, 25.9, 25.8, 25.7, 17.2, 10.8. IR: 2928 (m), 2042 (vs), 1512 (m), 1488 (m), 1361 (m), 1203 (m), 1183 (m), 1076 (m), 659 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{40}F_6IrN_2OSb$: C, 36.95; H, 4.96; N, 3.45. Found: C, 36.91; H, 5.25; N, 3.53.

X-ray Crystallography $Cp^*IrCH_3(CH_3C(NC(CH_3)_3)_2)$ (3a). Table 1 lists a summary of crystallographic data of compound **3a**. Crystals of sufficient quality for an X-ray diffraction study were obtained by slow cooling of a saturated hexane solution of **3a** to −30 °C for 2 days. The crystal chosen for data collection was transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. It was cooled to −70 °C by a nitrogen-flow low-temperature apparatus. The final cell parameters and specific data collection parameters are given in Table 1.

The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares on F. Scattering factors are from the *International Tables for X-Ray Crystallography*, Vol. IV, including the anomalous term for Ir, biweight $\alpha\ [\sigma^2(I) + 0.0009I^2]^{-1/2}$ (excluded 10). An azimuthal scan with 16.4% variation was used to correct for absorption. All non-hydrogen atoms were refined anisotropically, and all hydrogens were refined as fixed atoms. Refinement of the 217 parameters, data/parameter ratio = 16.12, gave the following agreement factors: $R = 0.034$, $R_w = 0.027$, error of fit = 0.83, max $\Delta/\sigma = 0.00$. Because the methyl hydrogens gave unreasonable bond lengths (0.77−1.39 Å) and thermal parameters larger than desired ($B_{iso} = 15.2$), all of the hydrogens have been idealized close to their previously refined positions. The largest residual density is 1.54 e/Å^3, near Ir$_1$.

Supporting Information Available: Tables of crystal structure information, positional parameters, thermal parameters, and bond distances and angles and ORTEP diagrams for compounds **2b**, **3a**, and **8b** (22 pages). Ordering information is given on any current masthead page.

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