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Synthesis and Reactivity of Ir(I) and Ir(III) Complexes with $MeNH_2$, $Me_2C{=}NR$ (R = H, Me), *C,N*-$C_6H_4\{C(Me){=}N(Me)\}$-2, and *N,N′*-$RN{=}C(Me)CH_2C(Me_2)NHR$ (R = H, Me) Ligands

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Complexes $[Ir(Cp^*)Cl_n(NH_2Me)_{3-n}]X_m$ (*n* = 2, *m* = 0 (**1**), *n* = 1, *m* = 1, X = Cl (**2a**), *n* = 0, *m* = 2, X = OTf (**3**)) are obtained by reacting $[Ir(Cp^*)Cl(\mu\text{-}Cl)]_2$ with $MeNH_2$ (1:2 or 1:8) or with $[Ag(NH_2Me)_2]OTf$ (1:4), respectively. Complex **2b** (*n* = 1, *m* = 1, X = ClO_4) is obtained from **2a** and $NaClO_4 \cdot H_2O$. The reaction of **3** with MeC(O)Ph at 80 °C gives $[Ir(Cp^*)\{C,N\text{-}C_6H_4\{C(Me){=}N(Me)\}\text{-}2\}(NH_2Me)]OTf$ (**4**), which in turn reacts with RNC to give $[Ir(Cp^*)\{C,N\text{-}C_6H_4\{C(Me){=}N(Me)\}\text{-}2\}(CNR)]OTf$ (R = ^{t}Bu (**5**), Xy (**6**)). $[Ir(\mu\text{-}Cl)(COD)]_2$ reacts with $[Ag\{N(R){=}CMe_2\}_2]X$ (1:2) to give $[Ir\{N(R){=}CMe_2\}_2(COD)]X$ (R = H, X = ClO_4 (**7**); R = Me, X = OTf (**8**)). Complexes $[Ir(CO)_2(NH{=}CMe_2)_2]ClO_4$ (**9**) and $[IrCl\{N(R){=}CMe_2\}(COD)]$ (R = H (**10**), Me (**11**)) are obtained from the appropriate $[Ir\{N(R){=}CMe_2\}_2(COD)]X$ and CO or Me_4NCl, respectively. $[Ir(Cp^*)Cl(\mu\text{-}Cl)]_2$ reacts with $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$ (1:2) to give $[Ir(Cp^*)(\mu\text{-}Cl)(NH{=}CMe_2)]_2(ClO_4)_2$ (**12**) which in turn reacts with PPh_3 or Me_4NCl (1:2) to give $[Ir(Cp^*)Cl(NH{=}CMe_2)(PPh_3)]ClO_4$ (**13**) or $[Ir(Cp^*)Cl_2(NH{=}CMe_2)]$ (**14**), respectively. Complex **14** hydrolyzes in a CH_2Cl_2/Et_2O solution to give $[Ir(Cp^*)Cl_2(NH_3)]$ (**15**). The reaction of $[Ir(Cp^*)Cl(\mu\text{-}Cl)]_2$ with $[Ag(NH{=}CMe_2)_2]ClO_4$ (1:4) gives $[Ir(Cp^*)(NH{=}CMe_2)_3](ClO_4)_2$ (**16a**), which reacts with PPNCl (PPN = $Ph_3P{=}N{=}PPh_3$) under different reaction conditions to give $[Ir(Cp^*)(NH{=}CMe_2)_3]XY$ (X = Cl, *Y* = ClO_4 (**16b**); X = *Y* = Cl (**16c**)). Equimolar amounts of **14** and **16a** react to give $[Ir(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (**17**), which in turn reacts with PPNCl to give $[Ir(Cp^*)Cl(H\text{-}imam)]Cl$ (R-imam = *N,N′*-N(R)=C(Me)CH_2C(Me)$_2$NHR (**18a**)]. Complexes $[Ir(Cp^*)Cl(R\text{-}imam)]ClO_4$ (R = H (**18b**), Me (**19**)) are obtained from **18a** and $AgClO_4$ or by refluxing **2b** in acetone for 7 h, respectively. They react with $AgClO_4$ and the appropriate neutral ligand or with $[Ag(NH{=}CMe_2)_2]ClO_4$ to give $[Ir(Cp^*)(R\text{-}imam)L](ClO_4)_2$ (R = H, L = ^{t}BuNC (**20**), XyNC (**21**); R = Me, L = MeCN (**22**)) or $[Ir(Cp^*)(H\text{-}imam)(NH{=}CMe_2)](ClO_4)_2$ (**23a**), respectively. The later reacts with PPNCl to give $[Ir(Cp^*)(H\text{-}imam)(NH{=}CMe_2)]Cl(ClO_4)$ (**23b**). The reaction of **22** with XyNC gives $[Ir(Cp^*)(Me\text{-}imam)(CNXy)](ClO_4)_2$ (**24**). The structures of complexes **15**, **16c** and **18b** have been solved by X-ray diffraction methods.

Introduction

Our interest in the study of metal imino complexes is mainly based on the fact that imines participate in many interesting chemical transformations including carbon−carbon bond formation and ring construction processes.[1] In particular, although acetimine can be obtained from acetone/ammonia mixtures or from α-aminonitriles it is rather unstable and decomposes quickly on storage (even at 0 °C) to give acetonine (2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine) with ammonia loss.[2] In turn, N-methyl substi-

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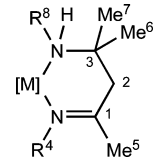
tuted imines RR′C═NMe are very difficult to prepare from azides,[3,4] silazanes or silyl amines,[5] N-chloroalkylamines or α-aminonitrile[6] and tend to polymerize.[4] The difficulties in preparing and handling these imines Me_2C═NR (R = H, Me) must be associated with the scarcity of their metal complexes which have been obtained through a variety of methods none of them using the free ligands or being of general application. Therefore, the synthesis of [M]-N(R)═CMe_2 complexes offers an effective means for studying the properties of these ligands. A different type of NH-imines, R(R′O)C═NH, R(R′NH)C═NH, and R{R′C(O)(Ph_3P═)C}-C═NH, also unstable in the free state, has been obtained by nucleophilic additions to metal-bound nitriles.[7]

We have previously described a family of acetimino complexes of Ag(I),[8] Au(I, III),[9−11] Pt(II, IV),[12] and Rh(I, III)[8,13,14] as well as the N-methylacetimino derivatives [Au{N(Me)═CMe_2}(PPh_3)]OTf[10] and [Ag{N(Me)═CMe_2}$_2$]-X (X = ClO_4, OTf)[15] which, along with [Pt(*N,C,N*-L){N(Me)═CMe_2}]OTf[16] [LH = 1,3-bis(piperidylmethyl)-benzene], are the only N-methylacetimino complexes reported so far. We have also reported the synthesis of the first heteronuclear complexes bearing a bridging acetimido ligand, namely *cis*- and *trans*-[PtCl{μ-N(AuPPh$_3$)═CMe_2}(PPh_3)$_2$]-ClO_4,[12] and the first intramolecular aldol-like condensation of two acetimino ligands into a 2-methyl-2-amino-4-imino-pentano ligand that we found to occur at a Rh(III) center.[13,14] With these precedents we intended the synthesis of acetimino and N-methylacetimino complexes of Ir, which were unprecedented, with the aim of finding new reactivity patterns. This paper describes the first iridium complexes with the imino ligands Me_2C═NR (R = H, Me), *C,N*-C_6H_4{C(Me)═NMe}-2, and *N,N*′-RN═C(Me)CH_2C(Me_2)NHR (R-imam, R = H, Me) as well as some new methylamino derivatives that we prepared with the purpose to use them as precursors of N-methylacetimino complexes.

Chart 1



Experimental Section

When not stated, the reactions were carried out at room temperature without precautions to exclude light or atmospheric oxygen or moisture. Melting points were determined on a Reichert apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer. Molar conductivities were measured on about 5×10^{-4} mol·L^{-1} acetone solutions with a Crison Micro CM2200 conductimeter. IR spectra were recorded on a Perkin-Elmer 16F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets. When not stated otherwise, NMR spectra were recorded at room temperature in Bruker 200, 300, or 400 NMR spectrometers. Chemical shifts are referred to TMS (^{1}H, ^{13}C), or H_3PO_4 (^{31}P). In some cases the assignments were performed with the help of APT, HMBC, and HMQC experiments and those of the R-imam complexes **18**−**24** follow the atom numbering scheme depicted in Chart 1. [IrCl(COD)]$_2$[17] (COD = 1,5-cyclooctadiene), [Ir(Cp*)Cl(μ-Cl)]$_2$[18] (Cp* = pentamethylcyclopentadienyl), [Ag(NH_2Me)$_2$]X[15] (X = ClO_4, CF_3SO_3 (OTf)), [Ag{N(R)═CMe_2}$_2$]X (R = H, X = ClO_4,[8] R = Me, X = ClO_4, OTf[15]), and [Au(NH═CMe_2)(PPh_3)]ClO_4[10] were prepared according to literature methods. TlOTf was obtained from OTfH and Tl_2CO_3 (Fluka). XyNC (Xy = $C_6H_3Me_2$-2,6), ^{t}BuNC, PPh_3 (Fluka), $MeNH_2$ (33% wt in abs EtOH), and $AgClO_4 \cdot H_2O$ (Aldrich) were purchased and used as received. CH_2Cl_2 and acetone were distilled under nitrogen before use from CaH_2 and B_2O_3, respectively. The reactions involving silver compounds were carried out protected from light.

Caution! *Perchlorate salts of organic cations may be explosive. Preparations on a larger scale than that reported herein should be avoided.*

Synthesis of [Ir(Cp*)Cl_2(NH_2Me)] (1). To a suspension of [Ir(Cp*)Cl(μ-Cl)]$_2$ (100 mg, 0.13 mmol) in acetone (15 mL) was added $MeNH_2$ (31 μL, 0.26 mmol). The reaction mixture was stirred for 4 h and filtered through Celite. The solution was concentrated to 1 mL and Et_2O (25 mL) was added. The resulting suspension was filtered and the solid was washed with Et_2O (3 × 5 mL) and suction dried to give **1** as an orange powder. Yield: 100 mg, 0.23 mmol, 93%. Mp: 185 °C (dec). Molar conductivity: 1.1 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{11}H_{20}Cl_2IrN$: C, 30.77; H, 5.69; N, 3.26. Found: C, 30.73; H, 5.92; N, 3.02. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.70 (s, 15 H, Me, Cp*), 2.77 (t, 3 H, Me, $^3J_{HH}$ = 6.7 Hz), 3.65 (br, 2 H, NH_2). ^{13}C{^{1}H} NMR, APT (75 MHz, $CDCl_3$, δ): 9.2 (Me, Cp*), 32.9 (Me), 84.8 (C, Cp*).

Synthesis of [Ir(Cp*)Cl(NH_2Me)$_2$]Cl (2a). To a solution of [Ir(Cp*)Cl(μ-Cl)]$_2$ (300 mg, 0.38 mmol) in CH_2Cl_2 (10 mL) was added $MeNH_2$ (374 μL, 3.04 mmol). The resulting suspension was stirred for 30 min and filtered. The solid was washed with Et_2O (3 × 5 mL) and suction dried to give **2a**, as a lemon-yellow powder. Yield: 325 mg, 0.71 mmol, 94%. Mp: 185 °C (dec). Anal. Calcd for $C_{12}H_{25}Cl_2IrN_2$: C, 31.30; H, 5.47; N, 6.08. Found: C, 31.36; H,

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5.58; N, 6.07. ^{1}H NMR (200 MHz, dmso-d$_6$, δ): 1.62 (s, 15 H, Me, Cp*), 2.46 (t, 6 H, Me, $^3J_{HH}$ = 6.0 Hz), 5.02 (br, 2 H, NH$_2$), 5.14 (br, 2 H, NH$_2$). ^{13}C{^{1}H} NMR, APT (100 MHz, dmso-d$_6$, δ): 8.4 (Me, Cp*), 32.8 (Me), 84.8 (C, Cp*).

Synthesis of [Ir(Cp*)Cl(NH$_2$Me)$_2$]ClO$_4$ (2b). To a suspension of **2a** (500 mg, 1.09 mmol) in acetone (30 mL) was added NaClO$_4$·H$_2$O (610 mg, 4.34 mmol). The reaction mixture was stirred for 30 min and concentrated to dryness. The residue was stirred with CH_2Cl_2 (15 mL), and the resulting suspension was filtered through Celite. The solution was concentrated to 2 mL, Et_2O (25 mL) was added, and the resulting suspension was filtered. The solid was washed with Et_2O (3 × 5 mL) and suction dried to give **2b**, as a yellow powder. Yield: 474 mg, 0.90 mmol, 83%. Mp: 176 °C (dec). Molar conductivity: 158 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{12}H_{25}Cl_2IrN_2O_4$: C, 27.48; H, 4.80; N, 5.34. Found: C, 27.67; H, 4.72; N, 5.68. ^{1}H NMR (200 MHz, acetone-d$_6$, δ): 1.75 (s, 15 H, Me, Cp*), 2.75 (t, 6 H, Me, $^3J_{HH}$ = 6.4 Hz), 4.63 (br, 4 H, NH$_2$). ^{13}C{^{1}H} NMR, APT (50 MHz, acetone-d$_6$, δ): 8.4 (Me, Cp*), 33.1 (Me), 86.2 (C, Cp*).

Synthesis of [Ir(Cp*)(NH$_2$Me)$_3$](OTf)$_2$ (3). To a suspension of [Ir(Cp*)Cl(μ-Cl)]$_2$ (103 mg, 0.13 mmol) in acetone (15 mL) was added [Ag(NH$_2$Me)$_2$]OTf[15] (165 mg, 0.52 mmol). The resulting suspension was stirred for 30 min and filtered through Celite. The solution was concentrated to 2 mL and Et_2O (25 mL) was added. The resulting suspension was filtered and the solid washed with Et_2O (3 × 5 mL) and suction dried to give **3**, as a pale tan powder. Yield: 156 mg, 0.22 mmol, 84%. Mp: 180 °C (dec). Molar conductivity: 165 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{15}H_{30}F_6IrN_3O_6S_2$: C, 25.07; H, 4.21; N, 5.85; S, 8.92. Found: C, 25.40; H, 4.49; N, 5.76; S, 8.70. ^{1}H NMR (300 MHz, acetone-d$_6$, δ): 1.81 (s, 15 H, Me, Cp*), 2.76 (t, 9 H, Me, $^3J_{HH}$ = 6.4 Hz), 4.93 (br, 6 H, NH$_2$). ^{13}C{^{1}H} NMR, APT (75 MHz, acetone-d$_6$, δ): 8.6 (Me, Cp*), 34.1 (Me), 88.4 (C, Cp*).

Synthesis of [Ir(Cp*){C,N−C$_6$H$_4$C(Me)=N(Me)-2}(NH$_2$Me)]OTf·H$_2$O (4·H$_2$O). A yellow suspension of **3** (110 mg, 0.15 mmol) in acetophenone (3 mL) was stirred at 80 °C for 4 h. The resulting orange suspension was filtered through Celite, and the filtrate was concentrated to 1 mL. Upon the addition of n-pentane (20 mL) an oily solid formed. The mother liquor was decanted, and the residue was stirred with Et_2O (10 mL). The suspension was filtered, and the solid was recrystallized from CH_2Cl_2/Et_2O (1:10 mL) and dried, first under nitrogen and then under vacuum for 4 h to give **4**·H$_2$O, as a dark yellow powder. Yield: 75 mg, 0.11 mmol, 76%. Mp: 127 °C. Molar conductivity: 136 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{21}H_{32}F_3IrN_2O_4S$: C, 38.35; H, 4.90; N, 4.25; S, 4.87. Found: C, 37.96; H, 4.70; N, 4.51; S, 4.92. ^{1}H NMR (200 MHz, $CDCl_3$, δ): 1.70 (s, 2 H, H_2O), 1.74 (s, 15 H, Me, Cp*), 2.16 (t, 3 H, *Me*NH$_2$, $^3J_{HH}$ = 6.4 Hz), 2.56 (s, 3 H, C*Me*), 3.91 (s, 3 H, N*Me*), 7.13 (dt, 1 H, CH, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 7.23 (dt, 1 H, CH,$^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 7.47 (dd, 1 H, CH, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 7.71 (dd, 1 H, CH, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz). ^{13}C{^{1}H} NMR, APT (100 MHz, $CDCl_3$, δ): 9.0 (Me, Cp*), 15.1 (C*Me*), 34.6 (*Me*NH$_2$), 46.2 (N*Me*), 89.2 (C, Cp*), 122.9 (CH), 128.6 (CH), 132.0 (CH), 134.5 (CH), 147.8 (*ipso*-C, Ar), 164.7 (C−Ir), 183.7 (C=N).

[Ir(Cp*){C,N−C$_6$H$_4$C(Me)=N(Me)-2}(CNR)]OTf·nH$_2$O [R = ^{t}Bu, *n* = 1 (5·H$_2$O); R = Xy, *n* = 0 (6)]. To a solution of **4**·H$_2$O (for **5**: 60 mg, 0.09 mmol; for **6**: 50 mg, 0.08 mmol) in $CHCl_3$ (20 mL) was added the appropriate RNC (for **5**: R = ^{t}Bu, 65 μL, 0.58 mmol; for **6**: R = Xy, 15.4 mg, 0.12 mmol) and the reaction mixture was heated in a Carius tube for 5 h at 75 °C (**5**) or refluxed for 8 h (**6**). The resulting suspension was allowed to cool to room temperature and then filtered through Celite. The filtrate was concentrated to 1 mL and Et_2O (25 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and suction dried to give **5**·H$_2$O or **6** as a yellow powder.

5·H$_2$O: Yield: 45 mg, 0.07 mmol, 69%. Mp: 157 °C. Molar conductivity: 125 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{25}H_{36}F_3IrN_2O_4S$: C, 42.30; H, 5.11; N, 3.95; S, 4.52. Found: C, 42.46; H, 4.88; N, 4.45; S, 4.38. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.33 (s, 9 H, Me, ^{t}Bu), 1.57 (s, 2 H, H_2O), 1.88 (s, 15 H, Me, Cp*), 2.63 (s, 3 H, C*Me*), 3.90 (s, 3 H, N*Me*), 7.16−7.26 (m, 2 H, CH), 7.49−7.52 (m, 2 H, CH). ^{13}C{^{1}H} NMR, APT (100 MHz, $CDCl_3$, δ): 9.1 (Me, Cp*), 15.6 (C*Me*), 30.7 (Me, ^{t}Bu), 48.4 (N*Me*), 58.4 (C, ^{t}Bu), 96.2 (C, Cp*), 123.6 (CH), 129.0 (CH), 132.1 (CH), 135.0 (CH), 147.7 (*ipso*-C, Ar), 155.4 (C−Ir), 184.5 (C=N).

6: Yield: 47.5 mg, 0.06 mmol, 78%. Mp: 165 °C (dec). Molar conductivity: 156 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{29}H_{34}F_3IrN_2O_3S$: C, 47.08; H, 4.63; N, 3.79; S, 4.33. Found: C, 46.71; H, 4.46; N, 3.92; S, 4.40. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.97 (s, 15 H, Me, Cp*), 2.04 (s, 6 H, Me, Xy), 2.66 (s, 3 H, C*Me*), 3.98 (s, 3 H, N*Me*), 7.04 (d, 2 H, CH, Xy, $^3J_{HH}$ = 8.0 Hz), 7.14 (m, 1 H, CH, Xy), 7.21 (td, 1 H, CH, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 7.28 (td, 1 H, CH, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz), 7.53 (dd, 1 H, CH, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz), 7.60 (dd, 1 H, CH, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$, δ): 9.3 (Me, Cp*), 15.7 (C*Me*), 18.2 (Me, Xy), 48.7 (N*Me*), 97.4 (C, Cp*), 124.1 (CH), 128.1 (*meta*-C, Xy), 129.2 (CH), 129.2 (*para*-C, Xy), 132.5 (CH), 134.7 (*ortho*-C, Xy), 135.4 (CH), 147.9 (*ipso*-C, Ph), 154.6 (C−Ir), 185.3 (C=N)

Synthesis of [Ir(NH=CMe$_2$)$_2$(COD)]ClO$_4$·H$_2$O (7·H$_2$O). To a solution of [IrCl(COD)]$_2$ (313 mg, 0.47 mmol) in CH_2Cl_2 (20 mL) was added [Ag(NH=CMe$_2$)$_2$]ClO$_4$ (300 mg, 0.93 mmol) under nitrogen atmosphere. A suspension immediately formed which was stirred for 30 min and filtered through Celite. The solution was concentrated to 2 mL, Et_2O (30 mL) was added, and the resulting suspension was filtered. The solid was washed with Et_2O (2 × 3 mL) and dried, first by suction and then in an oven at 60 °C for 24 h, to give **7**·H$_2$O, as a lemon-yellow solid. Yield: 438 mg, 0.82 mmol, 88%. Mp: 162 °C (dec). Molar conductivity: 163 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{14}H_{28}ClIrN_2O_5$: C, 31.73; H, 4.93; N, 5.37; Found: C, 31.60; H, 5.30; N, 5.27. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.62 (br, 2 H, H_2O), 1.66 (m, 4 H, CH_2), 2.22 (s, 6 H, Me), 2.26 (m, 4 H, CH_2), 2.44 (s, 6 H, Me), 3.73 (br, 4 H, CH), 9.60 (br, 2 H, NH). ^{13}C{^{1}H} NMR, APT (75 MHz, $CDCl_3$, δ): 28.1 (Me), 29.3 (Me), 31.1 (CH_2), 67.6 (CH), 184.5 (C=N).

Synthesis of [Ir{N(Me)=CMe$_2$}$_2$(COD)]OTf·H$_2$O (8·H$_2$O). A solution containing AgOTf (125 mg, 0.47 mmol) and MeNH$_2$ (121 μL, 0.97 mmol) in acetone (10 mL) was stirred in the dark for 1 h. The solvent was removed under vacuum and CH_2Cl_2 (15 mL) and [IrCl(COD)]$_2$ (150 mg, 0.22 mmol) were succesively added to the oily residue ([Ag{N(Me)=CMe$_2$}$_2$]OTf) under a nitrogen atmosphere. A suspension immediately formed which was stirred for 30 min and filtered through Celite. The solution was concentrated to 2 mL, Et_2O (30 mL) was added, and the suspension was filtered under nitrogen. The solid was recrystallized from CH_2Cl_2/Et_2O (2:25 mL), washed with Et_2O (2 × 3 mL), and suction dried to give **8**·H$_2$O, as a yellow powder. Yield: 167 mg, 0.28 mmol, 63%. Mp: 125 °C (dec). Molar conductivity: 147 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{17}H_{32}F_3IrN_2O_4S$: C, 33.49; H, 5.29; N, 4.59; S, 5.26. Found: C, 33.93; H, 5.39; N, 4.62; S, 4.67. ^{1}H NMR (300 MHz, acetone-d$_6$, δ): Molar ratio A:B = 2.25:1. Isomer A: 1.48−1.84 (m, 4 H, CH_2, overlapped with CH_2 of isomer B), 2.11 (s, 6 H, C*Me*, overlapped with Me of isomer B), 2.19−2.43 (m, 4 H, CH_2, overlapped with CH_2 of isomer B), 2.81 (br, 2 H, H_2O), 2.93 (s, 6 H, C*Me*), 3.34 (s, 6 H, N*Me*), 3.61 (m, 2 H, CH), 3.91 (m, 2 H,

CH). Isomer B: 1.48−1.84 (m, 4 H, CH_2, overlapped with CH_2 of isomer A), 2.11 (s, 6 H, C*Me*, overlapped with Me of isomer A), 2.19−2.43 (m, 4 H, CH_2, overlapped with CH_2 of isomer A), 2.71 (s, 6 H, C*Me*), 2.78 (br, 2 H, H_2O), 3.48 (s, 6 H, N*Me*), 3.68 (m, 2 H, CH), 3.83 (m, 2 H, CH). (300 MHz, acetone-d_6, 10 °C, δ): Molar ratio A:B = 2.25:1. Isomer A: 1.48−1.84 (m, 4 H, CH_2, overlapped with CH_2 of isomer B), 2.10 (s, 6 H, C*Me*), 2.19−2.43 (m, 4 H, CH_2, overlapped with CH_2 of isomer B), 2.93 (q, 6 H, C*Me*, $^5J_{HH}$ =1.2 Hz), 3.34 (s, 6 H, N*Me*), 3.59 (m, 2 H, CH), 3.87 (m, 2 H, CH). Isomer B: 1.48−1.84 (m, 4 H, CH_2, overlapped with CH_2 of isomer A), 2.09 (s, 6 H, C*Me*), 2.19−2.43 (m, 4 H, CH_2, overlapped with CH_2 of isomer A), 2.71 (s, 6 H, C*Me*), 3.47 (s, 6 H, N*Me*), 3.66 (m, 2 H, CH), 3.80 (m, 2 H, CH). (300 MHz, acetone-d_6, 50 °C, δ): 1.69 (br, 4 H, CH_2), 2.13 (s, 6 H, C*Me*), 2.34 (br, 4 H, CH_2), 2.93 (br, 6 H, C*Me*), 3.39 (br, 6 H, N*Me*), 3.64 (br, 2 H, CH), 3.91 (br, 2 H, CH). $^{13}C\{^1H\}$ NMR, APT (100 MHz, $CDCl_3$, δ): Isomer A: 22.6 (C*Me*), 30.7 (CH_2), 31.2 (CH_2), 31.3 (C*Me*), 43.7 (N*Me*), 66.6 (CH), 67.2 (CH), 180.2 (C=N). Isomer B: 22.6 (C*Me*), 31.0 (CH_2), 31.1 (CH_2), 31.6 (C*Me*), 43.3 (N*Me*), 65.9 (CH), 67.7 (CH), 180.2 (C=N).

***cis*-[Ir(NH=CMe$_2$)$_2$(CO)$_2$]ClO$_4$ (9).** CO was bubbled for 10 min through a solution of **7**·H_2O (400 mg, 0.75 mmol) in CH_2Cl_2 (20 mL). The solution was stirred for 20 min, concentrated to 1 mL, and Et_2O (20 mL) was added. The suspension was filtered under nitrogen, and the solid was suction dried to give **9**, as a pale yellow solid. Yield: 332 mg, 0.72 mmol, 96%. Mp: 126 °C (dec). Molar conductivity: 123 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_8H_{14}ClIrN_2O_6$: C, 20.80; H, 3.06; N, 6.07. Found: C, 20.54; H, 3.03; N, 6.42. ^1H NMR (400 MHz, $CDCl_3$, δ): 2.38 (s, 3 H, Me), 2.47 (s, 3 H, Me), 9.64 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR, APT (100 MHz, $CDCl_3$, δ): 29.1 (Me), 29.5 (Me), 171.5 (CO), 193.4 (C=N).

Synthesis of [IrCl(NH=CMe$_2$)(COD)]·H$_2$O (10·H$_2$O). A suspension containing Me_4NCl (15 mg, 0.13 mmol) in acetone (60 mL) was treated for 5 min in an ultrasound bath. **7**·H_2O (60 mg, 0.11 mmol) was then added, and the reaction mixture was stirred under nitrogen atmosphere for 5 h and concentrated under vacuum to dryness. The residue was extracted with Et_2O (2 × 20 mL), and the suspension was filtered through Celite. The filtrate was concentrated under vacuum to dryness, and the residue was stirred with n-pentane (10 mL). The suspension was filtered, and the solid was recrystallized from CH_2Cl_2/pentane (2:25 mL), and suction dried to give **10**·H_2O as a yellow powder. Yield: 35 mg, 0.09 mmol, 82%. Mp: 149 °C (dec). Molar conductivity: 1.7 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{11}H_{21}ClIrNO$: C, 32.15; H, 5.11; N, 3.41. Found: C, 32.33; H, 4.92; N, 3.76. ^1H NMR (400 MHz, $CDCl_3$, δ): 1.53 (br, 4 H, CH_2), 1.73 (br, 2 H, H_2O), 2.19 (s, 3 H, Me), 2.22 (m, 4 H, CH_2), 2.48 (s, 3 H, Me), 3.27 (br, 2 H, CH), 4.30 (br, 2 H, CH), 8.99 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR, APT (75 MHz, $CDCl_3$, δ): 27.5 (Me), 30.2 (Me), 31.0 (CH_2), 32.0 (CH_2), 57.4 (CH), 70.0 (CH), 183.2 (C=N).

Synthesis of [IrCl{N(Me)=CMe$_2$}(COD)]·0.5H$_2$O (11·0.5H$_2$O). To a solution of **8**·H_2O (91 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) was added PPNCl (88.3 mg, 0.15 mmol). The reaction mixture was stirred for 5 h and concentrated under vacuum to dryness. Et_2O (30 mL) was added, and the resulting suspension was filtered through Celite. The filtrate was concentrated to dryness, and the residue was stirred with n-pentane (10 mL). The suspension was filtered under a nitrogen atmosphere, and the solid collected was suction dried to give **11**·0.5H_2O as a yellow powder. Yield: 40 mg, 0.10 mmol, 64%. Mp: 133 °C (dec). Molar conductivity: 1.5 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{12}H_{22}ClIrNO_{0.5}$: C, 34.65; H, 5.33; N, 3.37. Found: C, 34.89; H, 5.32; N, 3.22. ^1H NMR (400 MHz, $CDCl_3$, δ): 1.48 (m, 4 H, CH_2), 1.83 (s, 1 H, H_2O), 2.04 (s, 3 H, Me), 2.25 (m, 4 H, CH_2), 2.69 (s, 3 H, Me), 3.13 (m, 1 H, CH), 3.26 (m, 1 H, CH), 3.32 (s, 3 H, N*Me*), 4.29 (m, 2 H, CH). $^{13}C\{^1H\}$ NMR, APT (100 MHz, $CDCl_3$, δ): 22.2 (Me), 30.7 (Me), 30.8 (CH_2), 31.0 (CH_2), 31.9 (CH_2), 32.3 (CH_2), 42.5 (N*Me*), 57.2 (CH), 57.3 (CH), 68.4 (CH), 68.9 (CH), 175.3 (C=N).

Synthesis of [Ir(Cp*)(μ-Cl)(NH=CMe$_2$)]$_2$(ClO$_4$)$_2$ (12). To a solution of [Ir(Cp*)Cl(μ-Cl)]$_2$ (300 mg, 0.375 mmol) in CH_2Cl_2 (4 mL) was added [Au(NH=CMe$_2$)(PPh$_3$)]ClO_4 (463 mg, 0.751 mmol). The reaction mixture was stirred for 1 h and filtered. The solid was washed with CH_2Cl_2 (2 mL) and suction dried to give **12**, as an orange powder. Yield: 280 mg, 0.27 mmol, 72%. Mp: 190 °C (dec). Anal. Calcd for $C_{26}H_{44}Cl_4N_2O_8Ir_2$: C, 30.06; H, 4.27; N, 2.70. Found: C, 29.79; H, 4.14; N, 2.87. ^1H NMR (300 MHz, dmso-d_6, δ): 1.65 (s, 15 H, Me, Cp*), 2.34 (s, 3 H, Me), 2.49 (s, 3 H, Me), 10.49 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR, APT (75 MHz, dmso-d_6, δ): 8.2 (Me, Cp*), 27.0 (Me), 28.2 (Me), 93.8 (C, Cp*), 191.2 (C=N).

Synthesis of [Ir(Cp*)Cl(NH=CMe$_2$)(PPh$_3$)]ClO$_4$ (13). To a suspension of **12** (140 mg, 0.13 mmol) in CH_2Cl_2 (20 mL) was added PPh_3 (70.7 mg, 0.27 mmol). The reaction mixture was stirred for 2 h and filtered through Celite. The solution was concentrated to 1 mL, and Et_2O (25 mL) was added. The suspension was filtered, and the solid was suction dried to give **13**, as a yellow powder. Yield: 180 mg, 0.23 mmol, 85%. Mp: 198 °C (dec). Molar conductivity: 150 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{31}H_{37}Cl_2IrNO_4P$: C, 47.63; H, 4.77; N, 1.79. Found: C, 47.68; H, 4.72; N, 1.93. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.51 (d, 15 H, Me, Cp*, $^4J_{HP}$ = 2.4 Hz), 2.00 (d, 3 H, Me, $^4J_{HH}$ = 0.9 Hz), 2.22 (s, 3 H, Me), 7.48 (br, 15 H, Ph), 9.14 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR, APT (75 MHz, $CDCl_3$, δ): 8.7 (Me, Cp*), 26.5 (Me), 29.9 (Me), 94.2 (d, C, Cp*, $^2J_{CP}$ = 2 Hz), 128.6 (d, *ortho*-Ph, $^2J_{CP}$ = 15 Hz), 131.4 (*meta*-Ph), 134.7 (*para*-Ph,), 190.10 (C=N). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, δ): 8.9.

Synthesis of [Ir(Cp*)Cl$_2$(NH=CMe$_2$)]·H$_2$O (14·H$_2$O). A suspension containing **12** (168 mg, 0.16 mmol) and Me_4NCl (43 mg, 0.39 mmol) in acetone (40 mL) was stirred under nitrogen for 6 h. The reaction mixture was concentrated to dryness, and the residue was stirred with CH_2Cl_2 (10 mL). The resulting suspension was filtered through Celite, the solution was concentrated to 1 mL, and n-pentane (25 mL) was added. The suspension was filtered, the solid was recrystallized from CH_2Cl_2/Et_2O (2:25 mL), and dried, first by suction and then in an oven at 60 °C for 14 h, to give **14**·H_2O, as a yellow powder. Yield: 120 mg, 0.26 mmol, 81%. Mp: 167 °C (dec). Molar conductivity: 1.5 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{13}H_{24}Cl_2IrNO$: C, 32.98; H, 5.11; N, 2.96. Found: C, 32.83; H, 4.98; N, 3.09. ^1H NMR (400 MHz, $CDCl_3$, δ): 1.61 (s, 2 H, H_2O), 1.66 (s, 15 H, Me, Cp*), 2.38 (d, 3 H, Me, $^4J_{HH}$ = 1.3 Hz), 2.38 (s, 3 H, Me), 9.35 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR, APT (100 MHz, $CDCl_3$, δ): 9.1 (Me, Cp*), 26.0 (Me), 30.5 (Me), 85.6 (C, Cp*), 184.4 (C=N).

Synthesis of [Ir(Cp*)Cl$_2$(NH$_3$)] (15). In an attempt to grow single crystals of **14**·H_2O by the liquid diffusion method, using CH_2Cl_2 and Et_2O, orange crystals of the hydrolysis product **15** grew instead which allowed its crystal structure to be determined. Additionally, after washing a crop of crystals with n-pentane and drying them under nitrogen, they were used to obtain the data reported below. Mp: 182 °C (dec). Anal. Calcd for $C_{10}H_{18}Cl_2NIr$: C, 28.91; H, 4.37; N, 3.37. Found: C, 28.91; H, 4.26; N, 3.30. ^1H NMR (300 MHz, $CDCl_3$, δ): 1.71 (s, 15 H, Me, Cp*), 3.19 (br, 3 H, NH_3).

Synthesis of [Ir(Cp*)(NH=CMe$_2$)$_3$](ClO$_4$)$_2$ (16a). To a suspension of [Ir(Cp*)Cl(μ-Cl)]$_2$ (180 mg, 0.225 mmol) in acetone (10 mL) was added [Ag(NH=CMe$_2$)$_2$]ClO_4 (302 mg, 0,901 mmol). The

reaction mixture was stirred for 5 min, filtered through Celite, and the yellow solution was concentrated to 2 mL. Et_2O (25 mL) was added, the resulting suspension was filtered, and the solid was recrystallized from acetone/Et_2O (5 × 25 mL), washed successively with $CHCl_3$ (3 × 5 mL) and Et_2O (3 × 5 mL), and suction dried to give **16a**, as a pale tan solid. Yield: 298 mg, 0.427 mmol, 90%. Mp: 195 °C (dec). Molar conductivity: 185 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{19}H_{36}Cl_2IrN_3O_8$: C, 32.71; H, 5.20; N, 6.02. Found: C, 32.34; H, 5.52; N, 5.89. ^{1}H NMR (200 MHz, acetone-d$_6$, δ): 1.74 (s, 15 H, Me, Cp*), 2.16 (d, 9 H, Me, $^4J_{HH}$ = 0.6 Hz), 2.54 (d, 9 H, Me, $^4J_{HH}$ = 1.4 Hz), 10.25 (br, 3 H, NH). ^{13}C{^{1}H} NMR, APT (100 MHz, acetone-d$_6$, δ): 8.8 (Me, Cp*), 26.2 (Me), 29.5 (Me), 91.0 (C, Cp*), 192.8 (C=N).

Synthesis of [Ir(Cp*)(NH=CMe$_2$)$_3$]Cl(ClO$_4$) (16b). To a suspension of **16a** (141 mg, 0.20 mmol) in acetone (5 mL) was added PPNCl (116 mg, 0.20 mmol). After 2 h of stirring, the suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and suction dried to give **16b**, as a white powder. Yield: 109 mg, 0.17 mmol, 85%. Mp: 180 °C (dec). Molar conductivity: 133 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{19}H_{36}Cl_2IrN_3O_4$: C, 36.02; H, 5.73; N, 6.63. Found: C, 36.11; H, 5.90; N, 6.66. ^{1}H NMR (300 MHz, dmso-d$_6$, δ): 1.60 (s, 15 H, Me, Cp*), 1.83 (s, 9 H, Me), 2.39 (s, 9 H, Me), 11.38 (br, 3 H, NH). (300 MHz, dmf-d$_7$, δ): 1.73 (s, 15 H, Me, Cp*), 2.02 (s, 9 H, Me), 2.52 (s, 9 H, Me), 12.04 (br, 3 H, NH). (300 MHz, dmf-d$_7$, −58 °C, δ): 1.63 (br, 3 H, Me), 1.72 (s, 15 H, Me, Cp*), 2.16 (s, 6 H, Me), 2.33 (br, 3 H, Me), 2.48 (s, 6 H, Me), 10.94 (br, 1 H, NH), 12.52 (br, 2 H, NH). ^{13}C{^{1}H} NMR, APT (400 MHz, dmso-d$_6$, δ): 8.2 (Me, Cp*), 25.4 (Me), 28.2 (Me), 89.0 (C, Cp*), 188.9 (C=N). MS (FAB$^+$): (*m*/*z*, %) [M$^+$] 534.1, 34; [M$^+$ − Cl − Me$_2$C=NH] 441.2, 100.0.

[Ir(Cp*)(NH=CMe$_2$)$_3$]Cl$_2$ (16c). In an attempt to grow single crystals of **16b** by slow diffusion of an acetone solution of **16a** through another of PPNCl in the same solvent, crystals of **16c** grew instead which were used for measuring its ^{1}H NMR spectrum (300 MHz, dmso-d$_6$, δ: 1.60 (s, 15 H, Me, Cp*), 1.83 (s, 9 H, Me), 2.40 (s, 9 H, Me), 11.54 (br, 3 H, NH)) and for an X-ray diffraction study.

Synthesis of [Ir(Cp*)Cl(NH=CMe$_2$)$_2$]ClO$_4$ (17). A suspension containing **14**·H_2O (185 mg, 0.39 mmol) and **16a** (271 mg, 0.39 mmol) in CH_2Cl_2 (25 mL) was stirred for 24 h. It was then filtered through Celite, the solution was concentrated to 2 mL, and Et_2O (25 mL) was added. The resulting suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and suction dried to give **17**, as a yellow powder. Yield: 413 mg, 0.72 mmol, 92%. Mp: 147 °C. Molar conductivity: 156 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{16}H_{29}Cl_2IrN_2O_4$: C, 33.33; H, 5.07; N, 4.86. Found: C, 33.12; H, 5.55; N 4.72. ^{1}H NMR (400 MHz, acetone-d$_6$, δ): 1.66 (s, 15 H, Me, Cp*), 2.43 (s, 6 H, Me), 2.47 (d, 6 H, Me, $^4J_{HH}$ = 1.1 Hz), 9.83 (br, 2 H, NH). ^{13}C{^{1}H} NMR, APT (100 MHz, acetone-d$_6$, δ): 9.0 (Me, Cp*), 26.7 (Me), 29.9 (Me), 88.1 (C, Cp*), 190.3 (C=N).

Synthesis of [Ir(Cp*)Cl(H-imam)]Cl (18a). To a solution of **17** (90 mg, 0.156 mmol) in acetone (3 mL) was added PPNCl (89.6 mg, 0.156 mmol), and the reaction mixture was stirred for 24 h. The resulting suspension was filtered, and the solid washed with Et_2O (3 × 5 mL) and suction dried to give **18a** as a yellow powder. Yield: 36 mg, 0.07 mmol, 45%. Mp: 230 °C (dec). **18a** is not soluble enough in acetone for conductivity measurements. Anal. Calcd for $C_{16}H_{29}Cl_2IrN_2$: C, 37.49; H, 5.70; N, 5.47. Found: C, 37.75; H, 5.88; N, 5.36. ^{1}H NMR (300 MHz, dmso-d$_6$, δ): 0.92 (s, 3 H, Me6), 1.39 (s, 3 H, Me7), 1.66 (s, 15 H, Me, Cp*), 2.36 (s, 3 H, Me5), 2.40 (s, 1 H, CH$_2$), 2.42 (s, 1 H, CH$_2$), 4.21 (d, 1 H, NH$_2$, $^2J_{HH}$ = 12 Hz), 5.67 (d, 1 H, NH$_2$, $^2J_{HH}$ = 12 Hz), 11.27 (br, 1 H, NH). ^{13}C{^{1}H} NMR, APT, HMQC, HMBC (75 MHz, dmso-d$_6$, δ): 8.4 (Me, Cp*), 23.6 (Me6), 29.3 (Me7), 29.6 (Me5), 46.4 (C2), 47.3 (C3), 86.9 (C, Cp*), 183.0 (C1).

Synthesis of [Ir(Cp*)Cl(H-imam)]ClO$_4$ (18b). To a suspension of **18a** (100 mg, 0.19 mmol) in acetone (20 mL) was added $NaClO_4$·H_2O (109 mg, 0.77 mmol), and the reaction mixture was stirred for 1 h. It was then concentrated under vacuum to dryness, the residue was stirred with CH_2Cl_2 (20 mL), and the resulting suspension was filtered through Celite. The solution was concentrated to 2 mL, Et_2O (25 mL) was added, the suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and suction dried to give **18b** as a yellow powder. Yield: 103 mg, 0.18 mmol, 91%. Mp: 232 °C (dec). Molar conductivity: 157 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{16}H_{29}Cl_2IrN_2O_4$: C, 33.33; H, 5.07; N, 4.86. Found: C, 33.72; H, 5.33; N, 4.93. ^{1}H NMR (400 MHz, acetone-d$_6$, δ): 1.19 (s, 3 H, Me6), 1.54 (s, 3 H, Me7), 1.75 (s, 15 H, Me, Cp*), 2.36 (d, 3 H, Me5, $^4J_{HH}$ = 2 Hz), 2.63 (s, 2 H, CH$_2$), 4.21 (br, 1 H, NH$_2$), 5.31 (br, 1 H, NH$_2$), 10.84 (br, 1 H, NH). Crystals of **18b** suitable for an X-ray diffraction study grew from acetone/Et_2O by the liquid diffusion method.

Synthesis of [Ir(Cp*)Cl(Me-imam)]ClO$_4$ (19). A solution of **2b** (161 mg, 0.31 mmol) in acetone (15 mL) was refluxed for 7 h, and the reaction mixture was filtered through Celite. The solution was concentrated to 2 mL, and Et_2O (25 mL) was added. The resulting suspension was filtered, and the solid washed with Et_2O (3 × 5 mL) and suction dried to give **19** as a yellow powder. Yield: 174 mg, 0.29 mmol, 94%. Mp: 200 °C (dec). Molar conductivity: 158 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{18}H_{33}Cl_2IrN_2O_4$: C, 35.76; H, 5.50; N, 4.63. Found: C, 35.39; H, 5.35; N, 4.36. ^{1}H NMR (400 MHz, acetone-d$_6$, δ): Molar ratio A:B = 1:1.7. Isomer A: 0.99 (s, 3 H, Me6), 1.51 (s, 3 H, Me7), 1.68 (s, 15 H, Me, Cp*), 2.38 (d, 1 H, CH$_2$, $^2J_{HH}$ = 15 Hz), 2.55 (s, 3 H, Me5), 2.79 (d, 3 H, Me8, $^3J_{HH}$ = 6 Hz), 2.94 (d, 1 H, CH$_2$, $^2J_{HH}$ = 15 Hz), 3.70 (br, 1 H, NH), 3.76 (s, 3 H, Me4). Isomer B: 1.36 (s, 3 H, Me6), 1.46 (s, 3 H, Me7), 1.73 (s, 15 H, Me, Cp*), 2.35 (d, 1 H, CH$_2$, $^2J_{HH}$ = 13 Hz), 2.58 (s, 3 H, Me5), 2.93 (d, 3 H, Me8, $^3J_{HH}$ = 6 Hz), 3.13 (d, 1 H, CH$_2$, $^2J_{HH}$ = 13 Hz), 3.64 (s, 3 H, Me4), 5.13 (br, 1 H, NH). ^{13}C{^{1}H} NMR, APT, HMQC, HMBC (100 MHz, acetone-d$_6$, δ): Isomer A: 8.6 (Me, Cp*), 19.6 (Me6), 25.8 (Me5), 26.4 (Me7), 36.9 (Me8), 48.6 (Me4), 55.2 (C2), 56.6 (C3), 88.3 (C, Cp*), 183.6 (C1). Isomer B: 9.7 (Me, Cp*), 25.1 (Me5 + Me6), 25.5 (Me7), 37.1 (Me8), 47.3 (Me4), 58.1 (C2), 60.0 (C3), 88.2 (C, Cp*), 184.4 (C1).

Synthesis of [Ir(Cp*)(H-imam)(CNR)](ClO$_4$)$_2$ (R = ^{t}Bu, 20; Xy, 21). To a solution of **18b** (for **20**: 25 mg, 0.04 mmol; for **21**: 48 mg, 0.08 mmol) in acetone (10 mL) were successively added equimolar amounts of $AgClO_4$ and RNC. The resulting suspension was stirred for 1 h and filtered through Celite. The solution was concentrated to 1 mL, Et_2O (25 mL) was added, the suspension was filtered, and the solid collected was washed with Et_2O (3 × 5 mL) and suction dried to give **20** or **21** as a white powder.

20: Yield: 25 mg, 0.03 mmol, 80%. Mp: 162 °C (dec). Molar conductivity: 210 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{21}H_{38}Cl_2IrN_3O_8$: C, 34.86; H, 5.29; N, 5.81. Found: C, 34.65; H, 5.58; N, 5.57. ^{1}H NMR (400 MHz, dmso-d$_6$, δ): 1.13 (s, 3 H, Me6), 1.21 (s, 3 H, Me7), 1.53 (s, 9 H, Me, ^{t}Bu), 1.85 (s, 15 H, Me, Cp*), 2.26, 2.53 (AB system, 2 H, CH$_2$, J_{AB} = 17 Hz), 2.40 (s, 3 H, Me5), 4.77 (d, 1 H, NH$_2$, $^2J_{HH}$ = 12 Hz), 6.19 (d, 1 H, NH$_2$, $^2J_{HH}$ = 12 Hz), 11.02 (br, 1 H, NH). ^{13}C{^{1}H} NMR, APT, HMQC, HMBC (100 MHz, dmso-d$_6$, δ): 8.2 (Me, Cp*), 25.9 (Me6 + Me7), 29.5 (Me, ^{t}Bu), 30.0 (Me5), 47.3 (C2), 49.2 (C3), 59.4 (C, ^{t}Bu), 94.8 (C, Cp*), 187.6 (C1).

21: Yield: 59 mg, 0.07 mmol, 92%. Mp: 150 °C (dec). Molar conductivity: 206 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{25}H_{38}Cl_2IrN_3O_8$: C, 38.91; H, 4.96; N, 5.45. Found: C, 38.80; H, 5.18; N, 5.31. ^{1}H NMR, (300 MHz, acetone-d$_6$, δ): 1.34 (s, 3 H, Me6), 1.51 (s, 3 H, Me7), 2.09 (s, 15 H, Me, Cp*), 2.48 (s, 6 H, Me, Xy), 2.62 (d, 3 H, Me5, $^4J_{HH}$ = 1 Hz), 2.80, 2.96 (AB system, 2 H, CH$_2$, J_{AB} = 18 Hz), 4.80 (d, 1 H, NH$_2$, $^2J_{HH}$ = 9 Hz), 6.08 (d, 1 H, NH$_2$, $^2J_{HH}$ = 9 Hz), 7.26−7.36 (m, 3 H, CH, Xy), 10.89 (br, 1 H, NH). ^{13}C{^{1}H} NMR, APT, HMQC, HMBC (75 MHz, acetone-d$_6$, δ): 8.2 (Me, Cp*), 18.0 (Me, Xy), 24.9 (Me6), 26.7 (Me7), 30.1 (Me5), 47.9 (C2), 50.1 (C3), 97.1 (C, Cp*), 128.1 (*meta*-C), 130.2 (*para*-C), 136.2 (*ortho*-C, Xy), 189.6 (C1).

Synthesis of [Ir(Cp*)(Me-imam)(NCMe)](ClO$_4$)$_2$·H$_2$O (22·H$_2$O). To a solution of **19** (150 mg, 0.25 mmol) in MeCN (15 mL) was added $AgClO_4$ (51.4 mg, 0.25 mmol). The resulting suspension was stirred for 2 h, filtered through Celite, and the solution concentrated to 2 mL. Et$_2$O (25 mL) was added, and the suspension was filtered. The solid collected was washed with Et$_2$O (3 × 5 mL) and suction dried to give **22**·H$_2$O as a pale tan powder. Yield: 158 mg, 0.22 mmol, 87%. Mp: 161 °C (dec). Molar conductivity: 130 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{20}H_{38}Cl_2IrN_3O_9$: C, 33.01; H, 5.26; N, 5.77. Found: C, 33.20; H, 5.03; N, 5.93. ^{1}H NMR (300 MHz, acetone-d$_6$, δ): Molar ratio A:B = 1.7:1. Isomer A: 1.02 (s, 3 H, Me6), 1.58 (s, 3 H, Me7), 1.82 (s, 15 H, Me, Cp*), 2.34 (d, 1 H, CH$_2$, $^2J_{HH}$ = 16 Hz), 2.62 (s, 3 H, Me5), 2.84 (br, 2 H, H$_2$O), 2.94 (s, 3 H, Me, MeCN), 2.95 (d, 3 H, Me8, $^3J_{HH}$ = 6 Hz), 3.09 (d, 1 H, CH$_2$, $^2J_{HH}$ = 16 Hz), 3.92 (s, 3 H, Me4), 5.28 (br, 1 H, NH). Isomer B: 1.35 (s, 3 H, Me6), 1.50 (s, 3 H, Me7), 1.83 (s, 15 H, Me, Cp*), 2.20 (d, 1 H, CH$_2$, $^2J_{HH}$ = 14 Hz), 2.55 (s, 3 H, Me5), 2.89 (s, 3 H, Me, MeCN), 2.96 (d, 3 H, Me8, $^3J_{HH}$ = 5 Hz), 3.19 (d, 1 H, CH$_2$, $^2J_{HH}$ = 14 Hz), 3.75 (s, 3 H, Me4), 4.68 (br, 1 H, NH). ^{13}C{^{1}H} NMR, APT, HMQC, HMBC (75 MHz, acetone-d$_6$, δ): Isomer A: 4.4 (*Me*CN), 8.7 (Me, Cp*), 19.8 (Me6), 26.0 (Me7), 26.2 (Me5), 38.9 (Me8), 49.4 (Me4), 55.5 (C2), 57.2 (C3), 92.1 (C, Cp*), 187.4 (C1). Isomer B: 4.8 (*Me*CN), 9.6 (Me, Cp*), 24.6 (Me7), 24.8 (Me6), 25.3 (Me5), 38.1 (Me8), 47.9 (Me4), 58.3 (C2), 60.3 (C3), 91.7 (C, Cp*), 187.4 (C1).

Synthesis of [Ir(Cp*)(H-imam)(NH=CMe$_2$)](ClO$_4$)$_2$ (23a). To a solution of **18b** (60 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was added [Ag(NH=CMe$_2$)$_2$]ClO$_4$ (33.5 mg, 0.10 mmol). The resulting suspension was stirred for 1 h and filtered through Celite. The solution was concentrated to 1 mL, Et$_2$O (25 mL) was added, the suspension was filtered, and the solid collected was washed with Et$_2$O (3 × 5 mL) and suction dried to give **23a** as a white powder. Yield: 66 mg, 0.09 mmol, 91%. Mp: 217 °C (dec). Molar conductivity: 180 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{19}H_{36}Cl_2IrN_3O_8$: C, 32.71; H, 5.20; N, 6.02. Found: C, 32.64; H, 5.43; N, 5.92. ^{1}H NMR (400 MHz, acetone-d$_6$, δ): 1.17 (s, 3 H, Me6), 1.55 (s, 3 H, Me7), 1.81 (s, 15 H, Me, Cp*), 2.23 (d, 1 H, CH$_2$, $^2J_{HH}$ = 17 Hz), 2.34 (s, 3 H, Me *trans*-Ir), 2.46 (d, 3 H, Me5, $^4J_{HH}$ =1 Hz), 2.52 (d, 3 H, Me *trans*-H, $^4J_{HH}$ = 1 Hz), 2.70 (d, 1 H, CH$_2$, $^2J_{HH}$ = 17 Hz), 4.61 (d, 1 H, NH$_2$, $^2J_{HH}$ = 11 Hz), 5.36 (d, 1 H, NH$_2$, $^2J_{HH}$ = 11 Hz), 10.10 (br, 1 H, NH), 11.08 (br, 1 H, NH). ^{13}C{^{1}H} NMR APT, HMQC, HMBC (100 MHz, acetone-d$_6$, δ): 8.7 (Me, Cp*), 24.1 (Me6), 26.8 (Me, *trans*-Ir), 29.7 (Me7 + Me *trans*-H), 31.0 (Me5), 47.5 (C2), 49.6 (C3), 90.3 (C, Cp*), 188.2 (C1), 193.2 (C=N).

Synthesis of [Ir(Cp*)(H-imam)(NH=CMe$_2$)]Cl(ClO$_4$) (23b). To a solution of **23a** (50 mg, 0.07 mmol) in acetone (10 mL) was added PPNCl (41.2 mg, 0.07 mmol). The resulting suspension was stirred for 4 h and filtered. The solid collected was washed with Et$_2$O (3 × 5 mL) and suction dried to give **23b** as a white powder. Yield: 37 mg, 0.06 mmol, 81%. Mp: 185 °C (dec). Molar conductivity: **23b** is poorly soluble in acetone. Anal. Calcd for $C_{19}H_{36}Cl_2IrN_3O_4$: C, 36.02; H, 5.73: N, 6.63. Found: C, 35.96; H, 6.03; N, 6.43. ^{1}H NMR (300 MHz, dmso-d$_6$, δ): 0.82 (s, 3 H, Me6), 1.49 (s, 3 H, Me7), 1.67 (s, 15 H, Me, Cp*), 1.77 (d, 1 H, CH$_2$, $^2J_{HH}$ = 15 Hz), 2.04 (s, 3 H, Me), 2.29 (s, 3 H, Me5), 2.38 (s, 3 H, Me), 5.32 (d, 1 H, NH$_2$, $^2J_{HH}$ = 12 Hz), 6.03 (d, 1 H, NH$_2$, $^2J_{HH}$ = 12 Hz), 11.50 (br, 1 H, NH), 11.56 (br, 1 H, NH). ^{13}C{^{1}H} NMR, APT, HMQC, HMBC (75 MHz, dmso-d$_6$, δ): 8.2 (Me, Cp*), 23.0 (Me6), 25.7 (Me), 28.3 (Me), 28.7 (Me7), 29.5 (Me5), 46.5 (C2), 47.3 (C3), 88.2 (C, Cp*), 184.9 (C1), 188.7 (C=N).

Synthesis of [Ir(Cp*)(Me-imam)(CNXy)](ClO$_4$)$_2$ (24). To a solution of **22**·H$_2$O (60 mg, 0.08 mmol) in acetone (10 mL) was added XyNC (11 mg, 0.08 mmol). The reaction mixture was stirred for 2 h, filtered through Celite, and the solution was concentrated to 2 mL. Et$_2$O (25 mL) was added, and the suspension was filtered. The solid collected was washed with Et$_2$O (3 × 5 mL) and suction dried to give **24** as a pale tan powder. Yield: 62 mg, 0.077 mmol, 92%. Mp: 157 °C (dec). Molar conductivity: 218 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{27}H_{42}Cl_2N_3IrO_8$: C, 40.55; H, 5.29; N, 5.25. Found: C, 40.60; H, 5.59; N, 5.36. ^{1}H NMR (300 MHz, dmso-d$_6$, δ): Molar ratio A:B = 3.7:1. Isomer A: 0.90 (s, 3 H, Me6), 1.47 (s, 3 H, Me7), 1.88 (s, 15 H, Me, Cp*), 2.01 (d, 1 H, CH$_2$, $^2J_{HH}$ = 16 Hz), 2.47 (s, 6 H, Me, Xy), 2.52 (s, 3 H, Me5), 2.92 (d, 3 H, Me8, $^3J_{HH}$ = 5 Hz), 3.00 (d, 1 H, CH$_2$, $^2J_{HH}$ = 16 Hz), 3.80 (s, 3 H, Me4), 5.42 (q, 1 H, NH, $^3J_{HH}$ = 5 Hz), 7.34−7.43 (m, 3 H, CH, Xy). Isomer B: 1.16 (s, 3 H, Me6), 1.30 (s, 3 H, Me7), 1.89 (s, 15 H, Me, Cp*), 2.49 (br, 3 H, Me5), 2.51 (s, 6 H, Me, Xy), 2.80 (d, 3 H, Me8, $^3J_{HH}$ = 6 Hz), 3.10 (d, 1 H, CH$_2$, $^2J_{HH}$ = 14 Hz), 3.73 (s, 3 H, Me4), 6.34 (br, 1 H, NH), 7.34−7.43 (m, 3 H, CH, Xy). ^{13}C{^{1}H} NMR, APT, HMQC (75 MHz, dmso-d$_6$, δ): Isomer A: 8.5 (Me, Cp*), 18.7 (Me, Xy), 19.2 (Me6), 24.5 (Me7), 26.3 (Me5), 43.2 (Me8), 52.6 (Me4), 54.1 (C2), 56.3 (C3), 97.4 (C, Cp*), 126.6 (*ipso*-C), 128.4 (*meta*-C), 130.5 (*para*-C), 136.0 (*ortho*-C), 188.5 (C1). Isomer B: 9.3 (Me, Cp*), 18.6 (Me, Xy), 23.9 (Me6), 24.0 (Me7), 24.9 (Me5), 39.9 (Me8), 52.0 (Me4), 57.0 (C2), 60.0 (C3), 96.8 (C, Cp*), 128.4 (*meta*-C), 129.4 (*ipso*-C), 131.1 (*para*-C), 136.4 (*ortho*-C), 187.1 (C1).

X-ray Structure Determinations of 15, 16c, and 18b. Crystal data and refinement details for **15** and **16c** are presented in Table 1. The three crystals were measured on a Bruker Smart APEX diffractometer. Data were collected using monochromated Mo Kα radiation in ω scan mode. Absorption corrections were applied on the basis of multiscans (Program SADABS). All of the non-hydrogen atoms were refined anisotropically on F^2 (program SHELX-97, G. M. Sheldrick, University of Göttingen, Göttingen, Germany). The NH hydrogens were refined freely with SADI, the methyl groups were refined using rigid groups (AFIX 137), and the other hydrogens were refined using a riding model. *Special features:* For **18b**, the crystal structure of **18b** was solved in *Pna2*$_1$ (a = 26.6907(53) Å, b = 8.1806(16) Å, c = 27.9305(56) Å, orthorhombic, T = 100(2) K, Z = 12, 67515 reflections measured, 14190 unique (R_{int} = 0.038). Although the connectivity of the cation could be established unambiguously, some irregularities in the bond distances and angles of the different molecules made it impossible to refine the structure properly. The pseudosymmetry problem along with the presence of heavy atoms, impeded the direct location of the hydrogen atoms.

Discussion

Synthesis of Imino Iridium Complexes. To prepare iridium imino complexes we have studied two alternative methods, the reaction of iridium methylamino complexes

Table 1. Crystal Data and Structure Refinement of **15** and **16c**

	15	**16c**
formula	$C_{10}H_{18}Cl_2IrN$	$C_{19}H_{36}Cl_2IrN_3$
fw	415.35	569.61
T(K)	100(2)	298(2) K
cryst syst	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/n$
a (Å)	8.6828(6)	10.6457(6)
b (Å)	7.7401(5)	13.6922(7)
c (Å)	19.4092(13)	15.9691(8)
β (deg)	101.791(2)	99.821(2)
V (Å^3)	1276.89(15)	2293.6(2)
Z	4	4
ρ_{calcd} (Mg m^{-3})	2.161	1.650
μ(Mo Kα) (mm^{-1})	10.839	6.061
F(000)	784	1128
cryst size (mm)	0.08 × 0.07 × 0.06	0.29 × 0.27 × 0.09
θ range (deg)	2.14 to 28.13	1.97 to 28.09
reflns collected	14215	25654
independent reflns (R_{int})	2964 (0.021)	5278 (0.020)
max. and min. transmsn	0.562 and 0.478	0.611 and 0.272
restraints/parameters	3/144	3/249
goodness-of-fit on F^2	1.134	1.051
R1 ($I > 2\sigma(I)$]	0.0208	0.0187
wR2 (all reflns)	0.0465	0.0471
largest diff. peak and hole (e Å^{-3})	1.563 and −0.762	0.795 and −0.534
largest diff. peak and hole (e Å^{-3})	1.563 and −0.762	0.795 and −0.534

with ketones and the transmetalation of imino ligands from silver or gold imino complexes to iridium chloro complexes.

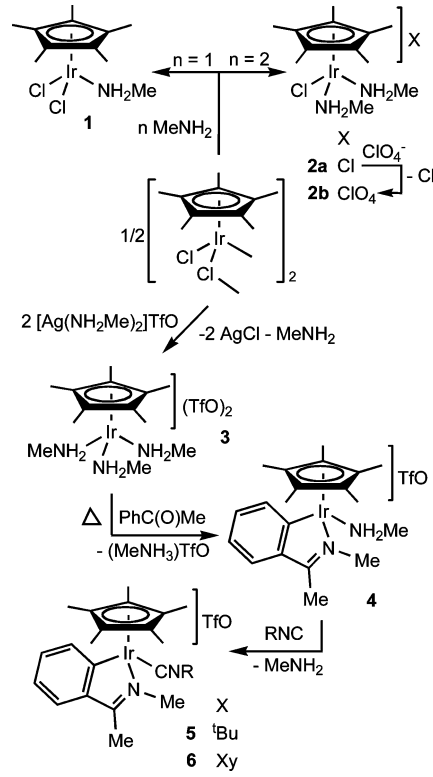
(1) Synthesis of Methylamino Iridium(III) Complexes and their Reactions with Ketones. In contrast with the many methylamino complexes described for transition elements, only two iridium derivatives have been reported, namely [Ir{*C,C*-$C_4(CO_2Me)_4$}H(NH_2Me)(PPh_3)$_2$][19] and [Ir(=CH=C=CH_2)Cl(CO)(NH_2Me)(PPh_3)$_2$][20] prepared by reacting the appropriate precursors with $MeNH_2$.

On reaction of [Ir(Cp*)Cl(μ-Cl)]$_2$ with $MeNH_2$ in a 1:2 molar ratio in CH_2Cl_2, the amino complex [Ir(Cp*)Cl_2(NH_2Me)] (**1**) was prepared (Scheme 1). Complex **1** was also obtained using acetone as solvent and was recovered unchanged after refluxing it in acetone for 6 h. Complex [Ir(Cp*)Cl(NH_2Me)$_2$]Cl (**2a**) precipitated almost quantitatively in CH_2Cl_2 only when an excess of the amine (8:1) was used because, otherwise, it forms along with a small amount of **1**. The reaction of **2a** with an excess of $NaClO_4 \cdot H_2O$ in THF allowed the synthesis of [Ir(Cp*)Cl(NH_2Me)$_2$]ClO_4 (**2b**). Like **1**, complexes **2** do not react with acetone at room temperature, although **2b** converts into an (imino)amino (Me-imam) complex through an aldol-like reaction after refluxing it in acetone for 7 h (see below). This contrasts with the behavior of the Rh homologue [Rh(Cp*)Cl(NH_2Me)$_2$]ClO_4, which converts into the corresponding Me-imam derivative upon stirring it in acetone at room or refluxing temperature for 24 or 2 h, respectively.[15] This difference proves that the metal plays a key role in the aldol-like reaction and that the more inert nature of the Ir metal center is responsible for the slow down of the reaction.

(19) O′Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232.

(20) Chen, J.-T.; Chen, Y.-K.; Chu, J.-B.; Lee, G.-H.; Wang, Y. *Organometallics* **1997**, *16*, 1476.

Scheme 1

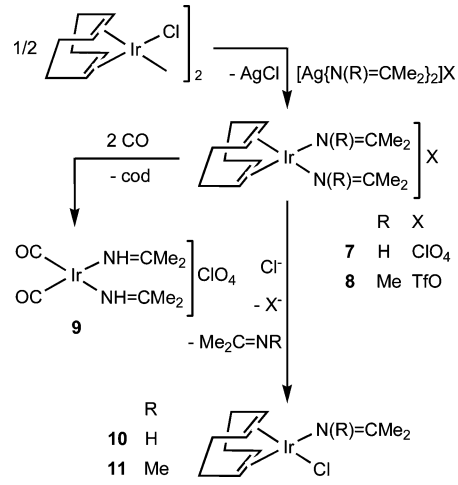


[Ir(Cp*)Cl(μ-Cl)]$_2$ reacts with $MeNH_2$ and MOTf (M = Ag, Tl) (1:6:4, in CH_2Cl_2) to give a mixture of [Ir(Cp*)(NH_2Me)$_3$](OTf)$_2$ (**3**) and [Ir(Cp*)Cl(NH_2Me)$_2$]OTf that we could not separate. However, **3** was obtained in almost quantitative yield by reacting [Ir(Cp*)Cl(μ-Cl)]$_2$ with [Ag(NH_2Me)$_2$]OTf[15] (1:4, in acetone). When solutions of **3** were stirred in acetone for 4 h, at room or refluxing temperature, mixtures formed that we could not separate. Their ^{1}H NMR spectra, showed the presence of **3** and other unidentified species.

When suspensions of **1** or **2a** in MeC(O)Ph were stirred at room or refluxing temperature, formation of [Ir(Cp*)Cl(μ-Cl)]$_2$ took place with $MeNH_2$ loss. Complex **3** was recovered unchanged upon stirring it in MeC(O)Ph for 24 h at room temperature. However, when it was heated in a small volume of MeC(O)Ph at 80 °C for 4 h, the orthometallated complex [Ir(Cp*){*C,N*-C_6H_4{C(Me)=N(Me)}-2}(NH_2Me)]OTf (**4**) formed along with [$MeNH_3$]OTf. Complex **4** results from the condensation reaction of one of the amino ligands in **3** with acetophenone and orthometalation of the phenyl group. These reactions with acetophenone parallel those of their homologue rhodium complexes, previously reported by us.[15]

Complex **4** does not react with RNC (R = ^{t}Bu, Xy) at room temperature, even if a large excess of isocyanide is used. However, complexes [Ir(Cp*){*C,N*-C_6H_4{C(Me)=N(Me)}-2}(CNR)]OTf [R = ^{t}Bu (**5**), Xy (**6**)] can be obtained by refluxing a mixture of **4** and the isocyanide (1:6 or 1:1.5, respectively, in $CHCl_3$, 5 h). The result of these reactions do not change if a larger excess of isocyanide is used (1:12) and the refluxing is prolonged for 24 h which is a difference with respect to its homologue rhodium complex (R = Xy) which, under the same reaction conditions inserts isocyanide

Scheme 2



into the Rh−C_{aryl} bond to give the imino(iminoacyl) complex [Rh(Cp*){*C,N*-C(=NXy)C_6H_4{C(Me)=N(Me)}-2}(CNXy)]OTf.[15]

Apart from our [Rh(Cp*){*C,N*-C_6H_4{C(Me)=N(Me)}-2}(NH_2Me)]OTf,[15] and [Sm(Cp*)$_2${*C,N*-C_6H_4{C(Me)C=N(Me)}-2],[21] no complex of any metal with this orthometallated imino ligand has been reported so far in spite of the existence of a large number of complexes derived from the orthometalation of arylimino ligands, many of them structurally characterized by X-ray crystallography.[22] The related complexes [Ir(C•N)$_2$Cl]$_2$ and [Ir(C•N)$_2$(R-acac)] [C•N = *C,N*-C_6H_3{C(Me)-C=N(Me)}-2-^{t}Bu-5, R-acac = O,O′-OC(Me)CHC(O){$(CH_2)_2$-C_6H_4CH=CH_2-4}] have been used to prepare polymers with interesting optical properties.[23] The samarium complex and its halogenated (X = H, Cl, Br) derivatives [Sm(Cp*)$_2${*C,N*-C_6H_3{C(Me)C=N(Me)}-2}X-4] were obtained by reacting [Sm(Cp*)$_2$H]$_2$ with the appropriate imine C_6H_3{C(Me)C=N(Me)}-2,X-4 in a process producing H_2 evolution.

(2) Synthesis of Imino Iridium Complexes by Transmetalation Reactions. On the basis of our previous experience on the ability of silver and gold complexes [Ag{N(R)=CMe_2}$_2$]X (R = H, X = ClO_4; R = Me, X = ClO_4, OTf)[8,15] and [Au{N(R)=CMe_2}PPh_3]X (R = H, X = ClO_4; R =Me, X = OTf),[10] to act as efficient transmetallating agents toward chloro complexes of Rh(I),[8] Rh(III),[13,14] and Pt(II),[12] we decided to extend this method to the synthesis of [Ir]{N(R)=CMe_2} complexes.

The reaction of the appropriate [Ag{N(R)=CMe_2}$_2$]X complex and [Ir(μ-Cl)(COD)]$_2$ in 2:1 molar ratio, allowed the syntheses of complexes [Ir{N(R)=CMe_2}$_2$(COD)]X (R = H, X = ClO_4 (**7**); R = Me, X = OTf (**8**)) in good yields (Scheme 2). **8** was also obtained directly from AgOTf, $MeNH_2$, and [IrCl(COD)]$_2$ (2:4:1) in acetone. The reaction of **7** with excess CO produces the replacement of COD to give *cis*-[Ir(CO)$_2$(NH=CMe_2)$_2$]ClO_4 (**9**) which is stable in solution under a CO atmosphere but decomposes slowly in the solid state. In an attempt to prepare [Ir(CO)$_2${N-(Me)=CMe_2}$_2$]OTf, we bubbled CO through a solution of **8** in CH_2Cl_2 but, in this case, massive decomposition was observed.

The reaction of **7** or **8** with Me_4NCl (1:1.1) produces the substitution of one imino ligand by chloro to give the neutral mono(imino) derivative [IrCl{N(R)=CMe_2}(COD)] [R = H (**10**) or Me (**11**), respectively] (Scheme 2). When PPNCl or Bu_4NCl were used instead of Me_4NCl, complex **10** or **11** could not be separated from the corresponding ammonium perchlorate even after repeated recrystallizations.

When [Ir(Cp*)Cl(μ-Cl)]$_2$ was reacted with [Au(NH=CMe_2)(PPh_3)]ClO_4[10] (1:2, in CH_2Cl_2), quantitative precipitation of [Ir(Cp*)(μ-Cl)(NH=CMe_2)]$_2$(ClO_4)$_2$ (**12**) occurred. The soluble byproduct, [AuCl(PPh_3)], was removed by filtration (Scheme 3). The homologous Rh(III) complex was prepared by the same method,[13] and both syntheses support our[10,12,13,24] and others'[25] previous observations on the utility of gold(I) complexes as transmetallating agents. The reaction of **12** with PPh_3 or Me_4NCl in 1:2 molar ratio produces complexes [Ir(Cp*)Cl(NH=CMe_2)(PPh_3)]ClO_4 (**13**) or [Ir(Cp*)Cl$_2$(NH=CMe_2)] (**14**), respectively. In an attempt to get single crystals of **14** by the liquid diffusion method, using CH_2Cl_2 and Et_2O, orange crystals of the hydrolysis product [Ir(Cp*)Cl$_2$(NH_3)] (**15**) grew instead.

The reaction of [Ir(Cp*)Cl(μ-Cl)]$_2$ with [Ag(NH=CMe_2)$_2$]ClO_4 (1:4) gives [Ir(Cp*)(NH=CMe_2)$_3$](ClO_4)$_2$ (**16a**). When a 1:2 molar ratio of the same reagents was used, a mixture formed of the expected bis(imino) complex [Ir(Cp*)Cl(NH=CMe_2)$_2$]ClO_4 (**17**) and (**16a**) that we could not separate. The analogous reaction with the corresponding rhodium complex gave only the Rh analog of **17**.[13] The attempt to prepare **17** by reaction of **16a** with PPNCl produces instead the substitution of one perchlorate counteranion by chloride to give [Ir(Cp*)(NH=CMe_2)$_3$]Cl(ClO_4) (**16b**) which precipitated in the reaction mixture. This behavior contrasts with that of the rhodium analog [Rh(Cp*)(NH=CMe_2)$_3$](ClO_4)$_2$, which reacts with PPNCl to give an H-imam complex[13] resulting from the aldol-like condensation of two imino ligands. In an attempt to grow single crystals of **16b** by slow diffusion of an acetone solution of **16a** through another of PPNCl in the same solvent, crystals of [Ir(Cp*)(NH=CMe_2)$_3$]Cl_2 (**16c**) grew instead, which were used for an X-ray diffraction study.

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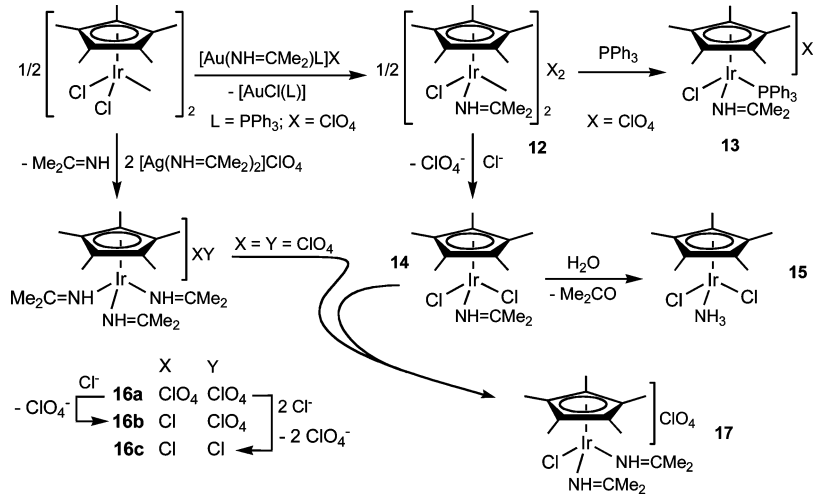
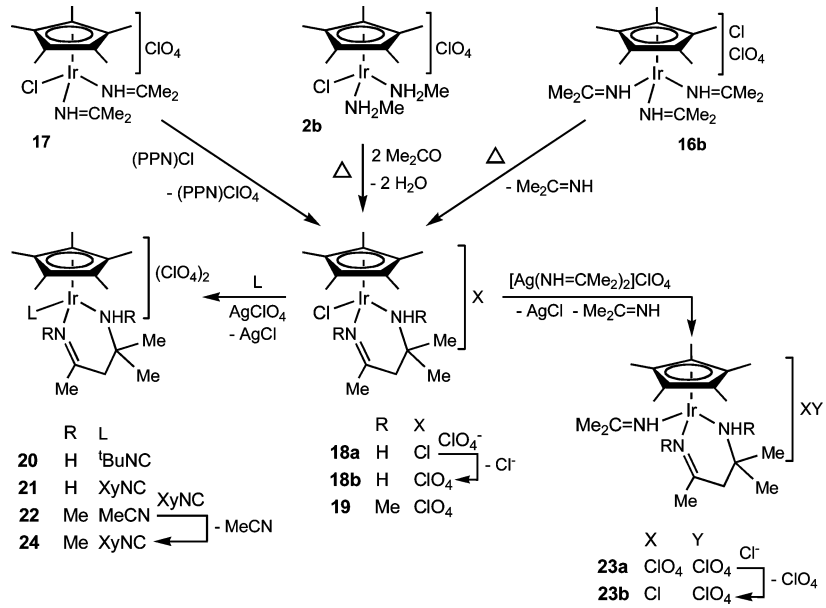
Scheme 3



Scheme 4



The synthesis of the bis(imino)complex **17** was achieved by refluxing in CH_2Cl_2, for 24 h, a mixture containing equimolar amounts of the mono- and tris(imino) derivatives **14** and **16a**, respectively (Scheme 3). When acetone was used instead, condensation processes of the acetimino ligands took place, as we will discuss below.

We have made different unsuccessful attempts to prepare Ir(III) complexes with the $Me_2C{=}NMe$ ligand by transmetalation reactions. Thus $[Ir(Cp^*)Cl(\mu\text{-}Cl)]_2$ was reacted in acetone under nitrogen with $[Ag\{N(Me){=}CMe_2\}_2]ClO_4$ in 1:4 or 1:2 molar ratio to produce, respectively, massive decomposition or mixtures in which $[Ir(Cp^*)Cl_2(NH_2Me)]$ (**1**), $[Ir(Cp^*)Cl(Me\text{-}imam)]ClO_4$ (**19**, Me-imam = *N,N′*-N(Me)=C(Me)CH_2C(Me)$_2$NHMe, see below), and Me_2C-(OH)CH_2C(O)Me were identified by ^{1}H NMR. When the same iridium complex was reacted with $[Au\{(N(Me){=}CMe_2)\}(PPh_3)]ClO_4$ (1:2, in acetone, under nitrogen) a mixture was obtained of $[AuCl(PPh_3)]$ (identified by ^{31}P NMR) along with **1** and **19**. These results suggest that the transmetalation reactions effectively occur producing the expected complexes $[Ir(Cp^*)Cl_2\{N(Me){=}CMe_2\}]$ (**A**) and $[Ir(Cp^*)Cl\{N(Me){=}CMe_2\}_2]ClO_4$ (**B**) that are unstable. Hydrolysis of the imino ligand in **A** would account for the formation of **1**, while **19** would form upon the aldol-like condensation of the two imino ligands in **B**.

(3) Imam Complexes. In an attempt to prepare $[Ir(Cp^*)Cl_2$-$(NH{=}CMe_2)]$ by reacting $[Ir(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (**17**) with PPNCl (1:1, in acetone), a suspension of the complex $[Ir(Cp^*)Cl(H\text{-}imam)]Cl$ (**18a**, H-imam = *N,N′*-NH=C(Me)CH_2C(Me)$_2$$NH_2$), resulting from the aldol-like condensation of two acetimino ligands, was obtained (Scheme 4). The homologue $[Ir(Cp^*)Cl(H\text{-}imam)]ClO_4$ (**18b**) was isolated in almost quantitative yield by reacting **18a** with $NaClO_4.H_2O$ (1:1, acetone, 30 min). Complexes of Rh homologous of **18a**, **b** have been prepared by us using the same method,[13] although Rh and Ir acetimino complexes differ in other aspects. Thus, the reaction of PPNCl with $[M(Cp^*)(NH{=}CMe_2)_3](ClO_4)_2$ (1:1, in acetone) gives, when M = Rh, $[Rh(Cp^*)Cl(H\text{-}imam)]ClO_4$, while when M = Ir (**16a**), it produces the substitution of one perchlorate anion

by chloride to give **16b**, as we have mentioned above. After refluxing a suspension of **16b** in acetone, [Ir(Cp*)Cl(H-imam)]ClO_4 (**18b**) formed as the result of substitution of one acetimino ligand by the chloride counterion and the condensation of two acetimino ligands. On the other hand, [Rh(Cp*)Cl(NH=CMe_2)$_2$]ClO_4 remains unchanged after stirring it in acetone at room temperature for 24 h and converts into [Rh(Cp*)Cl(H-imam)]ClO_4 when it is stirred in acetone for 24 h under a CO atmosphere (1.8 bar), or is treated with a catalytic amount of Ph_2C=NH (1:0.1) or SMe_2 (1:0.1), or when it is reacted with the equimolar amount of $AsPh_3$ in acetone, or when it is heated at 70 °C in solution (CH_2Cl_2 or acetone, in a Carius tube) for 24 h.[15] However, none of these reactions work the same way when starting from its homologue iridium complex **17**, which was recovered unchanged after refluxing it in acetone for 24 h, does not react with CO (3 days) or reacts with $AsPh_3$ to give a mixture containing **17** and **18b** among other products that we could not identify.

When an acetone solution of [Ir(Cp*)Cl(NH_2Me)$_2$]ClO_4 (**2b**) was refluxed in acetone for 7 h, with the purpose of preparing [Ir(Cp*)Cl{N(Me)=CMe_2}$_2$]ClO_4, the complex [Ir(Cp*)Cl(Me-imam)]ClO_4 (**19**) formed instead and was isolated in 91% yield. The reaction is likely to occur through the expected bis(imino) complex that would be unstable toward the intramolecular aldol-like condensation of its two imino ligands. This intermediate, that we have not even detected after measuring the NMR of the reaction mixture at different reaction times, seems to be more reactive than its homologous with acetimine [Ir(Cp*)Cl(NH=CMe_2)$_2$]ClO_4 (**17**) that could be isolated and is stable in acetone solution for 24 h at room temperature.

In all previous reports on the formation of H-imam complexes,[26] the ligand forms from the condensation of acetone or mesityl oxide with ammonia in a base assisted template reaction. The formation of **18a** and its Rh analogue shows for the first time that the H-imam ligand can also form by intramolecular aldol-type condensation of two acetimino ligands, and a reasonable mechanism for this process has been previously proposed by us.[15]

Complexes [Ir(Cp*)Cl(R-imam)]ClO_4 react with $AgClO_4$ and the appropriate neutral ligand or with [Ag(NH=CMe_2)$_2$]ClO_4 to give [Ir(Cp*)(R-imam)L]$(ClO_4)_2$ [R = H, L = ^{t}BuNC (**20**), XyNC (**21**); R = Me, L = MeCN (**22**)] or [Ir(Cp*)(H-imam)(NH=CMe_2)]$(ClO_4)_2$ (**23a**), respectively (Scheme 4).

We reacted **23a** with PPNCl in acetone with the purpose of exploring if a second aldol-like condensation process could take place to give a complex with a tridentate mixed-imam ligand. However, substitution of one of the perchlorate anions by chloride took place to give [Ir(Cp*)(H-imam)(NH=CMe_2)]Cl(ClO_4) (**23b**). When a suspension of this complex was refluxed in acetone for 24 h, the imino ligand was replaced by the chloride counterion to give **18b**.

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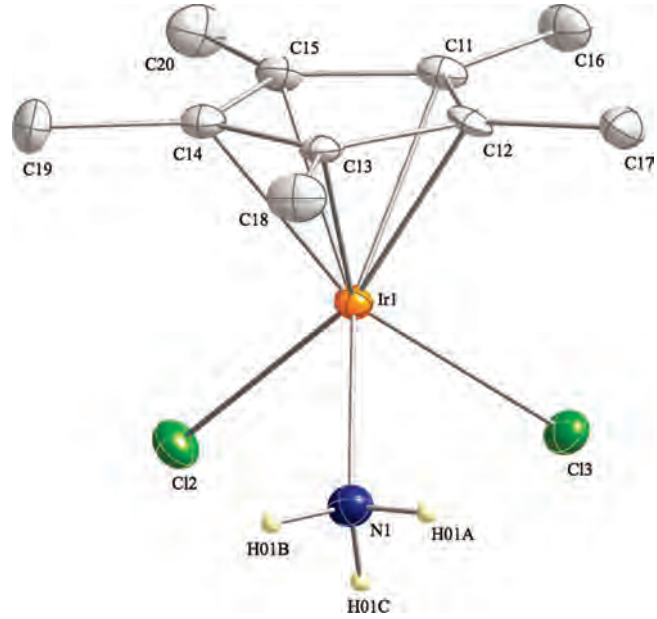

Figure 1. Thermal ellipsoid representation plot (50% probability) of **15**. Me hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(11) 2.165(3), Ir(1)−C(12) 2.133(3), Ir(1)−C(13) 2.122(3), Ir(1)−C(14) 2.139(3), Ir(1)−C(15) 2.164(3), Ir(1)−N(1) 2.127(3), Ir(1)−Cl(2) 2.4271(8), Ir(1)−Cl(3) 2.4289(8), N(1)−Ir(1)−Cl(2) 83.73(9), N(1)−Ir(1)−Cl(3) 82.76(9), Cl(2)−Ir(1)−Cl(3) 88.55(3).

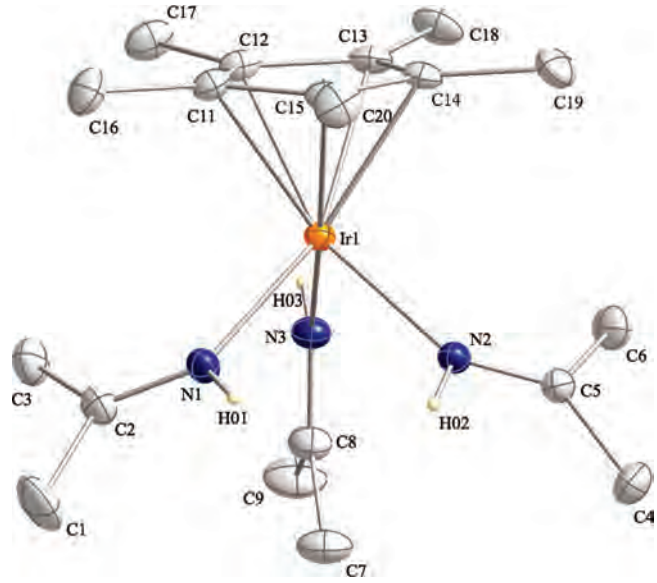

Figure 2. Thermal ellipsoid representation plot (30% probability) of the cation of complex **16c**. Me hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)−C(11) 2.188(2), Ir(1)−C(12) 2.187(2), Ir(1)−C(13) 2.183(2), Ir(1)−C(14) 2.179(2), Ir(1)−C(15) 2.155(2), Ir(1)−N(1) 2.085(2), Ir(1)−N(2) 2.092(2), Ir(1)−N(3) 2.110(2), N(1)−C(2) 1.273(4), N(2)−C(5) 1.272(3), N(3)−C(8) 1.279(3), N(1)−Ir(1)−N(2) 82.60(8), N(1)−Ir(1)−N(3) 87.83(8), N(2)−Ir(1)−N(3) 88.21(8).

The reaction of [Ir(Cp*)(Me-imam)(NCMe)]$(ClO_4)_2$ (**22**) with XyNC produced the replacement of the labile MeCN ligand to give [Ir(Cp*)(Me-imam)(CNXy)]$(ClO_4)_2$ (**24**).

X-ray Crystal Structures. The crystal structures of **15** (Figure 1, Table 1) and **16c** (Figure 2, Table 1) have been solved by X-ray diffraction methods and show the iridium atom in a pseudo-octahedral "three-legged piano stool" environment, with the Cp ligand occupying three *fac* coordination sites. Although the structure of **18b** (Figure 3)

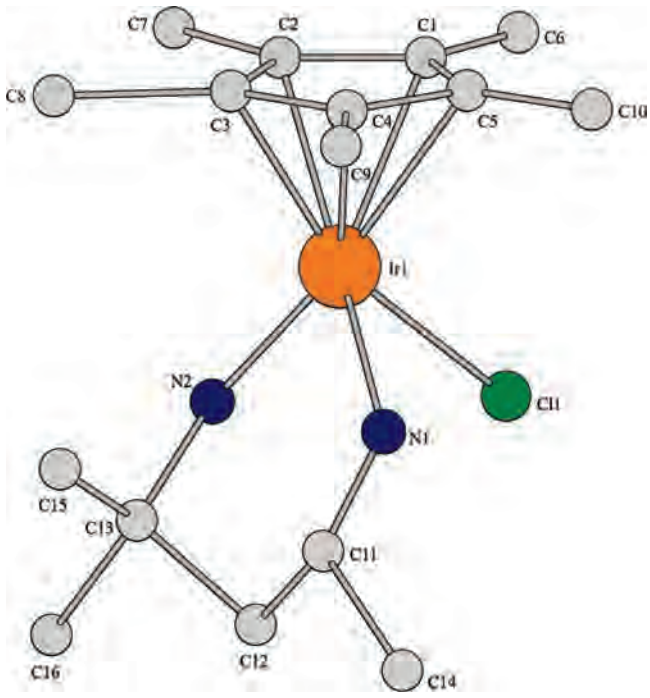

Figure 3. Unrefined structure of the cation in **18b** showing the atom connectivity. Figures 4 and 5 show the various hydrogen bonds present in **15** and **16c**.

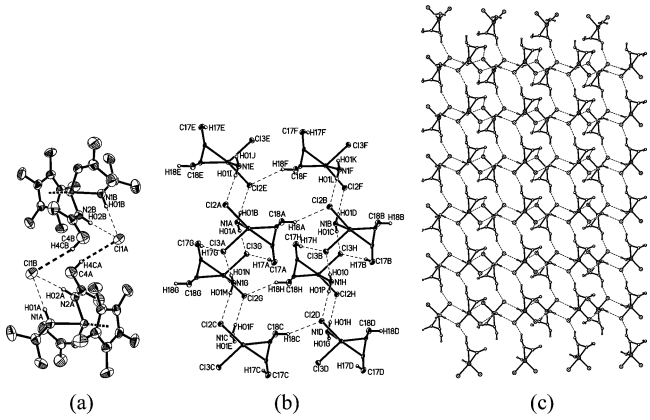

Figure 4. (a) Zig-zag ribbons along the *a* axis in complex **15** formed by intermolecular N−H···Cl interactions. (b) Two-ribbon interactions formed by C−H_{Me}···Cl contacts. Only the two CH groups involved in these contacts are represented. (c) View of the layers.

could not be refined, the atom connectivity in the cation was established unequivocally.

In **15**, the Ir−N and Ir−Cl bond distances are similar to those found in the only two other "Ir(Cp*)$(NH_3)^{2+}$" complexes structurally characterized.[22,27] The C═N bond distances in **16c** are similar to those found in other acetimino complexes (range 1.271(7)−1.285(4) Å)[8,10,12,13,15] regardless of the nature of the metal ions, its formal oxidation state, the charge of the complex, or the other ligands. The Ir−N bond distances in **16c** are similar to those found in the only two other structurally characterized complexes bearing the Ir(Cp*)NH═C fragment, none of which contain an acetimino ligand.[22]

The longest Ir−C_{Cp^*} bond distances in **15** (2.164(3) and 2.165(3) Å) correspond to the widest C_{Cp^*}−Ir−N angles (149.39(13) and 155.02(13)°), that is, to $C_{trans\ to\ N}$−Ir−N angles, while the two shortest ones (2.122(3) and 2.133(3) Å) correspond to C_{Cp^*}−Ir−N angles of 95.43(12) and 110.61(13)°, that is, to $C_{trans\ to\ Cl}$−Ir−N angles. These data suggest that the *trans* influence of chloro is slightly smaller than that of NH_3. In dicationic **16c**, the Ir−C_{Cp^*} bond distances are longer (2.155(2)−2.188(2) Å) than in **15** (2.122(3)−2.165(3) Å), probably because of the decrease of π back-bonding.

Spectroscopic Properties. The ^{1}H NMR spectra of complexes containing $MeNH_2$ ligands (**1**−**4**) show the Me protons as a triplet in the interval 2.16−2.77 ppm with $^3J_{HH}$ coupling constants of 6−7 Hz. As expected, complexes **1** and **3** show only one broad[28] NH resonance at 3.65 and 4.93 ppm, respectively, while in the spectrum of **2a** two NH resonances are observed, at 5.02 and 5.14 ppm. In complex **2b**, both appear together at 4.63 ppm as a broad resonance while in **4** they must be so broad that they cannot be observed. The deshielding of the NH_2 protons in **2a** with respect to those in **2b** suggests the existence of some N−H···Cl interaction in the former. The ^{13}C{^{1}H} NMR spectra of complexes **1**−**3** show one NMe resonance (32.8−34.0 ppm). A broad resonance at 3.19 ppm is observed in the ^{1}H NMR spectrum of **15** because of the NH_3 protons.

In the NMR spectra of complexes **4**−**6**, containing a chelating acetophenone-N-methylimino orthometallated ligand, the resonances due to the N*Me* (3.90−3.98 (^{1}H), 146.2−48.7 (^{13}C) ppm), C-*Me* (2.56−2.66 (^{1}H), 15.1−15.7 (^{13}C) ppm) and *C*═N (183.7−185.3 ppm) fragments are in the same regions as in their rhodium homologues.[15]

The ^{1}H NMR spectrum of free acetimine (in acetonitrile-d_3) has been reported[2] to show one singlet for both Me groups while the NH resonance seems to be absent. With the only exception of **16b**, all the acetimino complexes show one NH (8.99−11.56 ppm), two Me (^{1}H: 1.83−2.54, ^{13}C: 25.7−30.5 ppm) and one C═N (183.2−193.2 ppm) resonances as expected for mono(imino) (**10**, **13**, **14**, **23**) complexes or some bis- (**7**, **9**, **12**) or tris(imino) (**16a**, **c**) derivatives. In some cases, the coupling between the ^{1}H resonance of the Me group trans to the NH proton is observed ($0.9 < {}^4J_{HH} < 1.4$ Hz; **13**, **14**, **16a**, **17**, **23a**); in addition, in **16a** the cis coupling is also observed ($^4J_{HH} = 0.6$ Hz). Similar couplings have been previously observed in acetimino complexes of rhodium,[13] gold,[9,10] or platinum.[12] In contrast to the ^{1}H NMR spectrum of **16a**, which is temperature independent, we have found that each of the resonances observed in the room temperature spectrum of **16b** splits into two signals of 2:1 relative intensities when it is measured at −58 °C (in dmf-d_7, see Experimental Section) showing that one of the imino ligands is inequivalent to the two others probably because of its participation in a N−H···Cl bonding. The *C*═N carbon nuclei are more shielded when the remaining ligands are less electron-withdrawing. This is

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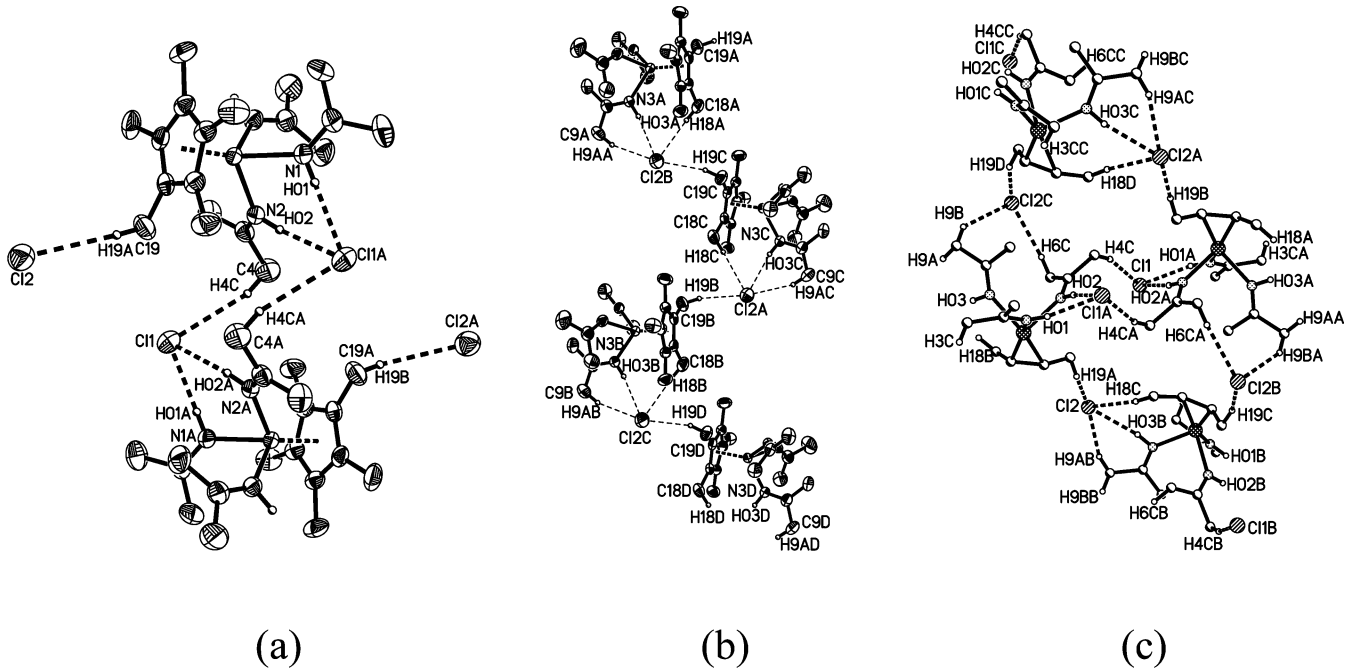
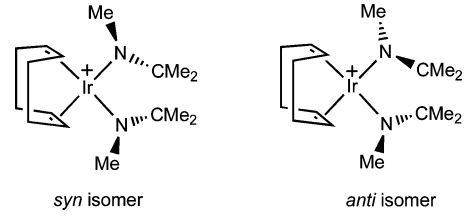


Figure 5. Formation of dimers (a) and chains (b) via C−H···Cl and N−H···Cl contacts between cations and chloride anions in **16c**. (c) View showing contacts between dimers to give a 3D framework.

observed when complex **7** (L_2 = cyclooctadiene, 184.5 ppm) or **14** (L = L′ = Cl, 184.4 ppm) is compared with its homologue **9** (L = CO, 193.4 ppm) or **13** (L = Cl, L′ = PPh_3, 190.1 ppm), respectively.

The ^{1}H NMR spectrum of the free imine Me_2C=NMe[29] shows three signals of 1:1:1 relative intensities. The resonances of the Me groups in cis- or trans- to the NMe group appear as quartets (1.80 ppm, $^5J_{HH}$ = 0.7 Hz; 1.98 ppm, $^5J_{HH}$ =1.3 Hz, respectively) while the N*Me* protons give a multiplet at 3.06 ppm. However, in the ^{1}H NMR spectra of complexes **8** and **11**, the three Me resonances are singlets. The N*Me* nuclei (^{1}H: 3.32−3.48; ^{13}C: 42.5−43.7 ppm) are, as in the free imine, less shielded than the C*Me*$_2$ ones (2.04−2.11, 2.69−2.93 (^{1}H) or 22.2−22.6, 30.7−31.6 (^{13}C) ppm). The NMR spectra of **11** show the expected resonances for the imino ligand (2.04, 2.69, 3.32 (^{1}H), 22.2, 30.7, 42.5, 175.3 (^{13}C) ppm). However, the ^{13}C NMR spectrum shows four resonances for the methylenic (30.8, 31.0, 31.9, 32.3 ppm) and for the olefinic (57.2, 57.3, 68.4, 68.9 ppm) cyclooctadiene carbons which means that the Me_2C=NMe ligand is out of the metal coordination plane, trying to minimize its repulsion with the chloro ligand. As this must also be the case for both imino ligands in **8**, two isomers, *syn* and *anti* (Chart 2), have to be observed in its NMR spectra. In fact, both the imino and cyclooctadiene ^{1}H and ^{13}C NMR resonances are duplicated in **8**. As one of the isomers is more abundant than the other (2.25:1) we could assign the resonances of both isomers except when they coincide accidentally. We tentatively assign the more intense resonances to the *anti* isomer which is less crowded. A VT ^{1}H NMR study shows that at 10 °C one of the Me resonances of the major isomer splits into a quartet (at 2.93 ppm, $^5J_{HH}$ = 1 Hz) while at 50 °C the spectrum shows only one set of

Chart 2. Isomers of Complex **8**



resonances indicating that the activation barrier for the isomerization process is exceeded at that temperature.

The ^{1}H NMR spectra of the R-imam complexes **18**−**24** show the protons of Me5 (Chart 1), bonded to a sp^2 carbon (2.36−2.62 ppm), less shielded than those of Me6 and Me7 (0.90−1.36, 1.21−1.58 ppm, respectively), both attached to a sp^3 carbon, and the same trend is observed in the ^{13}C NMR spectra (24.9−31.0 (Me5), 19.2−25.9 and 24.0−29.3 ppm). The proton resonances are singlet except those of Me5 in **18b**, **20**, and **23a** which are doublet due to coupling to the NH proton ($^4J_{HH}$ 1−3 Hz). The CH_2 protons give two doublets (**19**, **22**−**24**) or an AB system (in the interval 1.77−3.91 ppm, $^2J_{HH}$ 13−18 Hz) except in complexes **18** where they are isocronous (**18b**, 2.63 ppm) or resonate very close to each other (in **18a**, only the central resonances of the expected AB system are observed at 2.40 and 2.42 ppm). The resonances due to the Me4 nuclei (3.64−3.92 (^{1}H), 47.3−52.6 (^{13}C) ppm) and C1 (183.0−189.6 ppm), both bonded to the iminic nitrogen, are considerably less shielded than those of Me8 (2.79−2.97 (^{1}H), 36.9−43.2 (^{13}C) ppm) and C3 (47.3−60.3 ppm) bonded to the aminic nitrogen, respectively.

In the H-imam complexes, the inequivalent NH_2 protons give two doublets (4.21−5.32, 5.21−6.19 ppm; $^2J_{HH}$ 9−12 Hz) with the exception of **18b** which shows two very broad resonances. The iminic NH proton gives a broad signal

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(10.1−11.5 ppm) in the same region where the NH appears in the acetimino complexes. In the Me-imam complexes the aminic NH resonance (3.70−6.34 ppm) is generally broad, although in the spectrum of one of the isomers of **24** it is a quartet due to coupling to the Me8 protons ($^3J_{HH}$ = 5 Hz). Additionally, Me-imam complexes **19**, **22**, and **24** contain two chiral centers, and all the resonances of the RR+SS and RS+SR diastereoisomers could be assigned since they are in different molar ratios (see Experimental Section).

The Me_{Cp^*} (1.5−2.1 (^{1}H), 8.2−9.2 (^{13}C) ppm) and the C_5Me_5 (84.8−97.4 ppm) nuclei give singlet resonances. The position of the latter seems not to depend on the charge of the complex since neutral complexes **1** or **14** compared to cationic **2a** or **17**, respectively, give similar δ values (85−88 ppm). Replacement of Cl in **14** by PPh_3 to give **13** causes the deshielding of the quaternary Cp* carbon nuclei from 85.6 to 94.2 ppm, which can be attributed to the change of a π-donor by a π-acceptor ligand. The high δ values (94.8−97.4 ppm) found in complexes bearing a RNC ligand, show that isocyanides act mainly as σ-donor ligands.

The NMR spectra of complex **8** shows the above-mentioned four =CH (3.59, 3.66, 3.78, 3.80 (^{1}H), 65.9, 66.6, 67.2, 67.7 (^{13}C) ppm) and CH_2 (two extended multiplets 1.48−1.83 and 2.19−2.43 (^{1}H), 30.7, 31.0, 31.1, 31.2 (^{13}C) ppm) resonances and duplicated C*Me*$_2$ and N*Me* resonances, which requires the existence ot two isomers in solution. This behavior is not observed in complex **7** because the smaller nitrogen substituent (H vs Me) allows the free rotation of the imino ligand around the Ir−N bond.

The *C*≡N resonance is not observed in any of the isocyanide complexes here described, as is also the case in other isocyanide complexes previously reported.[30]

Complexes of rhodium homologues of **1**−**7**, **9**, **12**, **13**, **16**−**19**, and **21**−**24** have been previously reported by us.[8,13,15] When their NMR spetra are compared, it becomes apparent that the resonances due to carbon or phosphorus nuclei directly bonded to the metal are considerably shielded in the iridium complexes compared to the rhodium ones likely because of the stronger Ir−C or Ir−P bonds. In fact, the quaternary C_5Me_5 (**1**−**6**, **12**−**24**), CO (**9**), CH=CH (**7**, **8**, **10**, **11**), or C_{aryl} (**4**−**6**) ^{13}C NMR resonances or the ^{31}P resonance in **13** appear at 84.8−97.4, 171.5, 57.2−70.0, 154.6−164.7 or 8.9 ppm, respectively, the mean shielding with respect to their Rh homologues being of 7, 12, 15, 17, or 27 ppm, respectively. Similar chemical shift differences can be found in previously reported Rh/Ir couples of homologous complexes with Cp*-,[31,32] CO-,[33] cyclooctadiene,[34] aryl-,[32] or P-donor[35] ligands although, as far as we are aware, this observation has not been accounted for. This effect has also been observed when comparing the ^{31}P NMR spectra of homologous Pd and Pt complexes[36] and has been attributed to stronger Pt−P than Pd−P bonds.

The IR spectrum of the carbonyl complex **9** (C_{2v}) shows two ν(CO) bands at 2078 and 2009 cm^{-1}, shifted by some 20 cm^{-1} toward lower energy with respect to those in the homologous Rh complex (at 2092 and 2026 cm^{-1}),[8] which must be due to a slightly greater π-donor character of Ir. A strong absorption is observed in the spectra of the isocyanide complexes in the 2132−2206 cm^{-1} assignable to the ν(C≡N) stretching mode. Only one such band is observed for the two diastereoisomers of **24**, as it occurs in its Rh homologue.[15] None of the two expected ν(C≡N) bands is observed in the acetonitrilo complex **22** in spite of the fact that its rhodium homologue shows two weak absorptions at 2136 and 2288 cm^{-1}. Bands due to the counteranion are observed in the spectra of cationic complexes at around 1100 and 620 (ClO_4^-) cm^{-1} or in the 1150−1370 cm^{-1} (OTf) region.

Conclusion

We have prepared the first family of Ir(III) methylamino complexes including a neutral and the first mono- and dicationic species with the purpose of reacting them with ketones to prepare the first iridium methylimino complexes. The reactions of the neutral complex with acetone did not take place but, after refluxing an acetone solution of the monocationic complex $[Ir(Cp^*)Cl(NH_2Me)_2]^+$ an (imino)amino (Me-imam) complex was obtained. This contrasts with the behavior of its Rh homologue, which converts into the corresponding Me-imam derivative at room temperature. The Me-imam Ir complex must be the result of an aldol-like condensation reaction from the nonisolated methylimino complex $[Ir(Cp^*)Cl\{N(Me)=CMe_2\}_2]^+$. The dicationic methylamino complex $[Ir(Cp^*)(NH_2Me)_3]^{2+}$ reacts with acetone to give an unidentified mixture of products but with acetophenone one of the few orthometallated complexes of the corresponding imine was obtained. Transmetalation reactions using acetimino or methyl acetimino Ag(I) or Au(I) complexes and chloro Ir(I) or Ir(III) complexes have allowed us to prepare the first imino complexes $[Ir]\{N(R)=CMe_2\}$ (R = H, Me), except for $[Ir(III)]\{N(Me)=CMe_2\}$, which attempted syntheses always afforded mixtures of products or Me-imam complexes. This is a difference with respect to the chemistry of methylimino complexes of Rh(III). A family of H-imam Ir(III) complexes has been prepared from the

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corresponding bis- or tris-acetimino complexes or by reacting these products with various ligands.

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Supporting Information Available: Crystallographic files in CIF format for compounds **15** and **16c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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