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On the Reactivity Toward Ketones of New Methyl Amino Complexes of Rh(III) and Ag(I). Synthesis of Ortho-Rhodiated Acetophenone Methyl Imine Complexes†

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$MeNH_2$ reacts with silver salts AgX (2:1) to give $[Ag(NH_2Me)_2]X$ [X = TfO = CF_3SO_3 (**1·TfO**) and ClO_4 (**1·ClO$_4$**)]. Neutral mono(amino) Rh(III) complexes $[Rh(Cp^*)Cl_2(NH_2R)]$ [R = Me (**2a**), To = C_6H_4Me-4 (**2b**)] have been prepared by reacting $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ with RNH_2 (1:2). The following cationic methyl amino complexes have also been prepared: $[Rh(Cp^*)Cl(NH_2Me)(PPh_3)]TfO$ (**3·TfO**), from $[Rh(Cp^*)Cl_2(PPh_3)]$ and **1·TfO** (1:1); $[Rh(Cp^*)Cl(NH_2R)_2]X$, where R = Me, X = Cl, (**4a·Cl**), from $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ and $MeNH_2$ (1:4), or R = Me, X = ClO_4 (**4a·ClO$_4$**), from **4a·Cl** and $NaClO_4$ (1:4.8), or R = To, X = TfO (**4b·TfO**), from $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$, $ToNH_2$ and TlTfO (1:4:2); $[Rh(Cp^*)(NH_2Me)(^t\text{Bubpy})](TfO)_2$ (^{t}Bubpy = 4,4′-di-tert-butyl-2,2′-bipyridine, **5·TfO**), from **2a**, TlTfO and ^{t}Bubpy (1:2:1); $[Rh(Cp^*)(NH_2Me)_3](TfO)_2$ (**6·TfO**) from $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ and **1·TfO** (1:4). **2**–**6** constitute the first family of methyl amino complexes of rhodium. **1** and **4a·ClO$_4$** react with acetone to give, respectively, the methyl imino complexes $[Ag\{N(Me)=CMe_2\}_2]X$ [X = TfO (**7·TfO**), ClO_4 (**7·ClO$_4$**)], and $[Rh(Cp^*)Cl(Me\text{-}imam)]ClO_4$ [**8·ClO$_4$**, Me-imam = *N,N*′-N(Me)=C(Me)CH_2C$(Me)_2$NHMe]. **7·X** (X = TfO, ClO_4) are new members of the small family of methyl acetimino complexes of any metal whereas **8·ClO$_4$** results after a double acetone condensation to give the corresponding bis(methyl acetimino) complex and an aldol-like condensation of the two imino ligands. The acetimino complex $[Ag(NH=CMe_2)_2]ClO_4$ reacts with $[Rh(Cp^*)Cl(imam)]ClO_4$ [1:1, imam = *N,N*′-NH=C(Me)CH_2C$(Me)_2NH_2$] to give $[Rh(Cp^*)(imam)(NH=CMe_2)](ClO_4)_2$ (**9a·ClO$_4$**). **8·ClO$_4$** reacts with $AgClO_4$ (1:1) in MeCN to give $[Rh(Cp^*)(Me\text{-}imam)(NCMe)](ClO_4)_2$ (**9b·ClO$_4$**), which in turn reacts with XyNC (Xy = $C_6H_3Me_2$-2,6) or with $MeNH_2$ (1:1) to give $[Rh(Cp^*)(Me\text{-}imam)L](ClO_4)_2$ [L = XyNC (**9c·ClO$_4$**), $MeNH_2$ (**9d·ClO$_4$**)]. **6·TfO** reacts with acetophenone to give $[Rh(Cp^*)\{C,N\text{-}C_6H_4C(Me)=N(Me)\text{-}2\}(NH_2Me)]TfO$ (**10a·TfO**), the first complex resulting from such a condensation and cyclometalation reaction. In turn, **10a·TfO** reacts with isocyanides RNC (1:1) at room temperature to give $[Rh(Cp^*)\{C,N\text{-}C_6H_4C(Me)=NMe\text{-}2\}(CNR)]TfO$ [R = ^{t}Bu (**10b·TfO**), Xy (**10c·TfO**)], or 1:12 at 60 °C to give $[Rh(Cp^*)\{C,N\text{-}C(=NXy)C_6H_4C(Me)=N(Me)\text{-}2\}(CNXy)]TfO$ (**11·TfO**). The crystal structures of **9a·ClO$_4$·**acetone-d_6, **9c·ClO$_4$**, and **10a·TfO** have been determined.

Introduction

The synthesis of imino metal complexes is interesting because some of these ligands are very unstable, and its coordination offers an opportunity to study their properties.[1] Thus, in spite of the instability of acetimine, which decomposes after short periods of storage to give acetonine (2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine),[2] we have prepared a family of acetimino complexes of Au(I), Au(III),[3,4]

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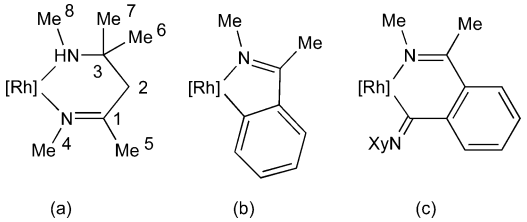
Ag(I),[5] Rh(I),[5] Rh(III),[6,7] Pt(II), and Pt(IV),[8] using in some cases $[Ag(NH{=}CMe_2)_2]^+$ or $[Au(NH{=}CMe_2)(PPh_3)]^+$ as efficient transmetalating agents. These complexes have offered us the possibility of preparing the first heteronuclear μ-acetimino complex of any metal, resulting from the substitution of the NH proton in an acetimino complex of platinum by the isolobal $AuPPh_3$ fragment[8] and also to observe, for the first time, the metal-assisted aldol-type condensation of two acetimino ligands to give a 4-imino-2-methylpentan-2-amino (imam) Rh(III) complex.[6]

To know more about the limits of such an aldol condensation reaction, we decided to study the synthesis and reactivity of methyl acetimino Rh(III) complexes $[Rh]N(Me){=}CMe_2$ and related species. However, methanimines RR′C═NMe (R, R′ = H, Me) are very difficult to prepare; they require, for example, pyrolysis of alkyl azides,[9,10] reactions of ketones with silazanes and silyl amines at 165 °C in the presence of a catalyst,[11] photolysis of azides in nitrogen at 12 K,[12] vacuum gas−solid dehydrochlorination of *N*-chloroalkylamines or dehydrocyanation of alpha-aminonitriles,[13] etc. In addition, they tend to polymerize.[9] For these reasons, the methods for the synthesis of their few reported metal complexes do not use the free imines. Thus, the unstable methyl imino chromium complex $[Cr(CO)_4\{N(Me){=}CHMe\}(PPh_3)]$ was serendipitously obtained by irradiation of the carbene complex $[Cr(CO)_4\{C(Me)NHMe\}(PPh_3)]$,[14] and the methyl acetimino complexes $[Pt(L)\{N(Me){=}CMe_2\}]TfO$ [LH = 1,3-bis(piperidylmethyl)benzene, TfO = CF_3SO_3],[15] or $[Au\{N(Me){=}CMe_2\}(PPh_3)]TfO$[3] were prepared by reacting the corresponding [PtCl(L)] with AgTfO and $MeNH_2$ in acetone or $[Au(NH_2Me)(PPh_3)]TfO$ with acetone, respectively. The usually named η^2-*N*,*C*-imino complexes, $[M](\eta^2$-*N*,*C*-$CH_2NMe)$, obtained by deprotonation of a dimethyl amido ligand, Me_2N-, do not actually contain the imine $H_2C{=}NMe$ but the ligand $(H_2C{-}NMe)^{2-}$.[16] In this article, we report the synthesis of a new member of this small family, $[Ag\{N(Me){=}CMe_2\}_2]^+$ and its use, along with that of our complex $[Au\{N(Me){=}CMe_2\}PPh_3]TfO$, to prepare methyl acetimino Rh(III) complexes. With the same objective, we describe reactions of methyl amino Rh(III) complexes with acetone. Among the many complexes of Rh(III) with primary amine ligands described so far, those with $MeNH_2$ are rather scarce.[17]

Chart 1. The New Ligands Present in the Reported Rh(III) Complexes and an Atom Numbering Scheme for the Me-imam Ligand



In this article, we also report the synthesis of new [Rh(III)]Cp* complexes containing the ligands (a) *N*,*N*′-MeN═C(Me)CH_2CMe_2NHMe (Me-imam), (b) *C*,*N*-$C_6H_4\{C(Me){=}N(Me)\}$-2, or (c) *C*,*N*-$C(=NXy)C_6H_4\{C(Me){=}N(Me)\}$-2 (Chart 1). As far as we are aware, no complex of any of these ligands has been reported so far for any metal.

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 a ca. 5×10^{-4} mol·L^{-1} acetone solution with a Crison Micro CM2200 conductimeter. IR spectra were recorded on a PerkinElmer 16F PC FTIR 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). When needed, NMR assignments were performed with the help of APT, HMBC, and HMQC experiments. The assignment in **8·ClO₄** and **9·ClO₄** was made according to the numbering shown in Chart 1. $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$[18] and $[Rh(Cp^*)Cl_2(PPh_3)]$[19] were prepared according to literature methods. The complex $[Rh(Cp^*)Cl(^tBubpy)]TfO$ (^{t}Bubpy = 4,4′-di-tert-butyl-2,2′-bipyridine) was prepared from $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$, TlTfO, and ^{t}Bubpy (1:2:2, 2 h, in CH_2Cl_2).[20] Its homologous BF_4 salt was mentioned in a previous article,[21] but no synthetic procedure or any other data were reported. TlTfO was obtained from CF_3SO_3H and Tl_2CO_3 (Fluka). XyNC, ^{t}BuNC, PPh_3 (Fluka), $ToNH_2$ (Merck), $MeNH_2$ (33% 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 $[Ag(NH_2Me)_2]X$ [X = TfO (1·TfO), ClO_4 (1·ClO_4)]. AgX (X = TfO, 500 mg, 1.95 mmol, X = ClO_4, 500 mg, 2.4 mmol) was reacted with $MeNH_2$ (**1·TfO**: 485 μL, 3.89 mmol;

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(20) ^{1}H NMR (200 MHz, acetone-d_6): δ 1.46 (s, 18 H, Me, ^{t}Bu), 1.78 (s, 15 H, Me, Cp*), 7.92 (dd, 2 H, H5, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 8.69 (d, 2 H, H3, $^4J_{HH}$ = 2 Hz), 9.00 (d, 2 H, H6, $^3J_{HH}$ = 6 Hz.
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1·ClO$_4$: 600.5 μL, 4.8 mmol) in Et_2O (15 mL). The resulting supension was stirred for 15 min, filtered, and the white solid collected was washed with Et_2O (3 × 5 mL) and suction dried.

1·TfO. Yield: 584 mg, 94%, mp (dec): 147 °C. ^{1}H NMR (400 MHz, dmso-d_6): δ 2.40 (s, 3 H, Me), 3.40 (br, 2 H, NH_2). ^{13}C-{^{1}H} APT NMR (50 MHz, dmso-d_6): δ 30.9 (Me). IR (cm^{-1}): $\nu_{NH,}$ 3326, 3282, 3178. Λ_M (Ω^{-1} cm^2 mol^{-1}): 173. Anal. Calcd for $C_3H_{10}AgF_3N_2O_3S$: C, 11.29; H, 3.16; N, 8.78; S, 10.05. Found: C, 11.40; H, 3.10; N, 8.40; S, 10.00.

1·ClO$_4$. Yield: 602 mg, 93%, mp (dec): 140 °C. ^{1}H NMR (400 MHz, dmso-d_6): δ 2.39 (s, 3 H, Me), 3.51 (br, 2 H, NH_2). ^{13}C-{^{1}H} NMR (75 MHz, dmso-d_6): δ 31.02 (Me). IR (cm^{-1}): ν_{NH} 3332, 3294, 3164. Λ_M (Ω^{-1} cm^2 mol^{-1}): 140. Anal. Calcd for $C_2H_{10}AgClN_2O_4$: C, 8.92; H, 3.74; N, 10.40. Found: C, 8.91; H, 3.78; N, 10.16.

Synthesis of [Rh(Cp*)Cl$_2$(NH$_2$R)] [R = Me (2a), To (2b)]. To a solution of [Rh(Cp*)Cl(μ-Cl)]$_2$ (**2a**: 250 mg, 0.40 mmol; **2b**: 102.5 mg, 0.16 mmol) in CH_2Cl_2 (15 mL) was added NH_2R (**2a**: R = Me, 100.7 μL, 0.81 mmol; **2b**: R = To, 35.5 mg, 0.33 mmol). After 1 (**2a**) or 24 (**2b**) h of being stirred, the solution was concentrated under a vacuum (1 mL) and Et_2O (25 mL) was added. The resulting suspension was filtered and the solid washed with Et_2O (3 × 5 mL) and dried by suction (**2a**) or under a vacuum for 12 h (**2b**) to give an orange solid.

2a. Yield: 266 mg, 97%, mp (dec): 185 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.71 (s, 15 H, Me, Cp*), 2.64 (t, 3 H, Me, $^3J_{HH}$ = 6 Hz), 3.01 (br, 2 H, NH_2). ^{13}C{^{1}H} APT NMR (50 MHz, $CDCl_3$): δ 9.26 (Me, Cp*), 31.5 (Me), 93.3 (d, C, Cp*, $^1J_{CRh}$ = 9 Hz). IR (cm^{-1}): ν_{NH} 3318, 3202, 3126. Λ_M (Ω^{-1} cm^2 mol^{-1}): 2.5. Anal. Calcd for $C_{11}H_{20}Cl_2NRh$: C, 38.85; H, 5.93; N, 4.12. Found: C, 38.99; H, 6.15; N, 4.22.

2b. Yield: 130 mg, 94%, mp (dec): 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44 (s, 15 H, Me, Cp*), 2.31 (s, 3 H, Me, To), 4.70 (br, 2 H, NH_2), 7.09 (br, 4 H, CH, To). ^{13}C{^{1}H} APT NMR (50 MHz, $CDCl_3$): δ 8.8 (Me, Cp*), 20.8 (Me, To), 93.7 (d, C, Cp*, $^1J_{CRh}$ = 9 Hz), 120.2 (CH, To), 129.6 (CH, To), 139.6 (C). IR (cm^{-1}): ν_{NH} 3294, 3196, 3146, 3100. Λ_M (Ω^{-1} cm^2 mol^{-1}): 1. Anal. Calcd for $C_{17}H_{24}Cl_2NRh$: C, 49.06; H, 5.81; N, 3.37. Found: C, 49.53; H, 6.01; N, 3.24.

Synthesis of [Rh(Cp*)Cl(NH$_2$Me)(PPh$_3$)]TfO·H$_2$O (3·TfO). To a solution of [Rh(Cp*)Cl$_2$(PPh$_3$)][19] (200 mg, 0.35 mmol) in CH_2Cl_2 (25 mL) was added **1·TfO** (112 mg, 0.35 mmol). The resulting white suspension was stirred for 30 min and filtered through a short pad of Celite. The solution was concentrated under a vacuum (2 mL) and Et_2O (20 mL) was added. The suspension was filtered, and the solid was washed with Et_2O (3 × 5 mL) and suction dried to give **3·TfO** as an orange solid. Yield: 225 mg, 90%, mp (dec): 140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.49 (d, 15 H, Me, Cp*, $^4J_{HP}$ = 1 Hz), 1.71 (s, 2 H, H_2O), 2.44 (t, 3 H, Me, $^3J_{HH}$ = 6 Hz), 5.03 (br, 2 H, NH_2), 7.52−7.63 (m, 15 H, Ph). ^{13}C{^{1}H} APT NMR (75 MHz, $CDCl_3$): δ 8.9 (d, Me, Cp*, $^3J_{CP}$ = 1 Hz), 32.5 (Me), 100.4 (dd, C, Cp*, $^1J_{CRh}$ = 7 Hz, $^2J_{CP}$ = 3 Hz). 127.4 (*ipso*-C, $^1J_{CP}$ = 45 Hz), 129.1 (d, *ortho*- or *meta*-C, J_{CP} = 8 Hz), 131.6 (d, *para*-C, $^4J_{CP}$ = 2 Hz), 134.6 (m, *ortho*- or *meta*-C). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 34.55 (d, $^1J_{PRh}$ = 141 Hz). IR (cm^{-1}): ν_{NH} 3306, 3232, 3151. Λ_M (Ω^{-1} cm^2 mol^{-1}): 132. Anal. Calcd for $C_{30}H_{37}ClF_3NO_4PRhS$: C, 49.09; H, 5.08; N, 1.91; S, 4.37. Found: C, 48.94; H, 5.07; N, 1.99; S, 3.96.

Synthesis of [Rh(Cp*)Cl(NH$_2$Me)$_2$]Cl (4a·Cl). To a solution of [Rh(Cp*)Cl(μ-Cl)]$_2$ (400 mg, 0.65 mmol) in CH_2Cl_2 (15 mL) was added $MeNH_2$ (322.3 μL, 2.59 mmol). The resulting orange suspension was stirred for 1 h and then filtered. The solid was washed with Et_2O (3 × 5 mL) and suction dried to give **4a·Cl** as an orange solid. Yield: 496 mg, 97%. mp (dec): 170 °C. ^{1}H NMR (300 MHz, dmso-d_6): δ 1.63 (s, 15 H, Me, Cp*), 2.34 (t, 6 H, Me, $^3J_{HH}$ = 6.0 Hz), 4.10 (br, 2 H, NH_2), 4.25 (br, 2 H, NH_2). ^{13}C{^{1}H} APT NMR (75 MHz, dmso-d_6): δ 8.4 (Me, Cp*), 31.4 (Me), 93.5 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz). IR (cm^{-1}): ν_{NH} 3552, 3408, 3216, 3140. Anal. Calcd for $C_{12}H_{25}Cl_2N_2Rh$: C, 38.83; H, 6.79; N, 7.55. Found: C, 38.67; H, 6.96; N, 7.21.

Synthesis of [Rh(Cp*)Cl(NH$_2$Me)$_2$]ClO$_4$ (4a·ClO$_4$). To a suspension of **4a·Cl** (245 mg, 0.66 mmol) in THF (25 mL) was added $NaClO_4$·H_2O (443 mg, 3.15 mmol). The suspension was stirred for 30 min and then concentrated under a vacuum to dryness. The residue was stirred with CH_2Cl_2 (20 mL), and the suspension was filtered through a short pad of Celite. The solution was concentrated under a vacuum (5 mL) and Et_2O (25 mL) was added. The suspension was filtered, and the orange solid was washed with Et_2O (3 × 5 mL) and suction dried to give **4a·ClO$_4$**. Yield: 250 mg, 87%, mp (dec): 190 °C. ^{1}H NMR (400 MHz, dmso-d_6): δ 1.61 (s, 15 H, Me, Cp*), 2.35 (t, 6 H, Me, $^3J_{HH}$ = 6 Hz), 3.95 (br, 2 H, NH_2), 4.02 (br, 2 H, NH_2). ^{13}C{^{1}H} NMR (300 MHz, dmso-d_6): 8.3 (Me, Cp*), 31.3 (Me), 93.5 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz). IR (cm^{-1}): ν_{NH} 3280, 3242, 3164. Λ_M (Ω^{-1} cm^2 mol^{-1}): 160. Anal. Calcd for $C_{12}H_{25}Cl_2N_2O_4Rh$: C, 33.12; H, 5.79; N, 6.44. Found: C, 33.01; H, 6.03; N, 6.40.

Synthesis of [Rh(Cp*)Cl(NH$_2$To)$_2$]TfO (4b·TfO). To a solution of [Rh(Cp*)Cl(μ-Cl)]$_2$ (100 mg, 0.16 mmol) in CH_2Cl_2 (15 mL) was added $ToNH_2$ (69.4 mg, 0.65 mmol) and TlTfO (114.4 mg, 0.32 mmol). The resulting suspension was stirred for 1h and then filtered through a short pad of Celite. The solution was concentrated under a vacuum (1 mL), Et_2O (25 mL) was added, and the resulting suspension was filtered. The orange solid collected was washed with Et_2O (3 × 5 mL) and suction dried to give **4b·TfO**. Yield: 163 mg, 79%, mp (dec): 270 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (s, 15 H, Me, Cp*), 2.31 (s, 6 H, Me, To), 4.59 (br, 2 H, NH_2), 6.37 (br, 2 H, NH_2), 7.07 (m, 4 H, CH, To), 7.42 (m, 4 H, CH, To). ^{13}C{^{1}H} APT NMR (100 MHz, $CDCl_3$): δ 8.1 (Me, Cp*), 20.9 (Me, To), 95.1 (d, C, Cp*, $^1J_{CRh}$ = 9 Hz), 121.5 (CH, To), 129.6 (CH, To), 135.4 (C), 139.0 (C). IR (cm^{-1}): ν_{NH} 3214, 3188, 3126. Λ_M (Ω^{-1} cm^2 mol^{-1}): 127. Anal. Calcd for $C_{25}H_{33}ClF_3N_2O_3RhS$: C, 47.14; H, 5.22; N, 4.40: S, 5.03. Found C, 46.80; H, 5.33; N, 4.30; S, 4.68.

Synthesis of [Rh(Cp*)(NH$_2$Me)(^{t}Bubpy)](TfO)$_2$ (5·TfO). To a solution of [Rh(Cp*)Cl$_2$(NH$_2$Me)](**2a**)(100 mg, 0.29 mmol) in acetone (15 mL) was added TlTfO (208 mg, 0.59 mmol) and ^{t}Bubpy (80 mg, 0.29 mmol). After stirring the suspension for 7 h, it was filtered through a short pad of Celite. The solution was concentrated under a vacuum to dryness, and Et_2O (5 mL) was added. The suspension was filtered, and the solid was suction dried to give **5·TfO** as a yellow solid. Yield: 238 mg, 97%, mp (dec): 214 °C. ^{1}H NMR (400 MHz, acetone-d_6) δ 1.45 (s, 18 H, Me, ^{t}-Bu), 1.81 (s, 15 H, Me, Cp*), 1.94 (t, 3 H, Me, $^3J_{HH}$ = 6 Hz), 4.42 (br, 2 H, NH_2), 8.04 (dd, 2 H, H5, $^3J_{HH}$ = 5.93 Hz, $^4J_{HH}$ = 1.80 Hz), 8.81 (d, 2 H, H3, $^4J_{HH}$ = 1.80 Hz), 9.13 (d, 2 H, H6, $^3J_{HH}$ = 5.93 Hz). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): 8.5 (Me, Cp*), 3.36 (Me, ^{t}Bu), 30.67 (Me, NH_2Me), 36.5 (C, ^{t}Bu), 99.0 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz), 122.7 (C3), 126.9 (C5), 153.1 (C6), 156.1 (C2), 166.8 (C4). IR (cm^{-1}): ν_{NH} 3267, 3239, 3158. Λ_M (Ω^{-1} cm^2 mol^{-1}): 210. Anal. Calcd for $C_{31}H_{44}N_3O_6S_2F_6Rh$: C, 44.55; H, 5.31; N, 5.03; S, 7.67. Found: C, 44.60; H, 5.26; N, 4.74; S, 7.20.

Synthesis of [Rh(Cp*)(NH$_2$Me)$_3$](TfO)$_2$ (6·TfO). To a solution of [Rh(Cp*)Cl(μ-Cl)]$_2$ (250 mg, 0.40 mmol) in CH_2Cl_2 (25 mL) was added **1·TfO** (516 mg, 1.62 mmol). The resulting suspension was stirred for 30 min and then concentrated under a vacuum to dryness. The residue was stirred with acetone (15 mL), and the

suspension was filtered through a short pad of Celite. The solution was concentrated under a vacuum (2 mL), and Et_2O (25 mL) was added. The resulting suspension was filtered, and the yellow solid collected was washed with Et_2O (3 × 5 mL) and suction dried to give **6·TfO**. Yield: 479 mg, 94%, mp (dec): 198 °C. ^{1}H NMR (300 MHz, dmso-d_6): δ 1.62 (s, 15 H, Me, Cp*), 2.33 (t, 9 H, Me, $^3J_{HH}$ = 6 Hz), 4.00 (d, 6 H, NH_2, $^3J_{HH}$ = 6 Hz). ^{13}C{^{1}H} APT NMR (75 MHz, dmso-d_6): δ 8.0 (Me, Cp*), 31.1 (Me), 94.7 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz), 120.7 (q, C, TfO, $^1J_{CF}$ = 322 Hz). IR (cm^{-1}): ν_{NH} 3288, 3264, 3184. Λ_M (Ω^{-1} cm^2 mol^{-1}): 225. Anal. Calcd for $C_{15}H_{30}F_6N_3O_6RhS_2$: C, 28.62; H, 4.80; N, 6.68; S, 10.19. Found: C, 28.88; H, 5.08; N, 6.67; S, 10.19.

Synthesis of [Ag{N(Me)=CMe$_2$}$_2$]X [X = TfO (7·TfO), ClO$_4$ (7·ClO$_4$)]. 1·TfO or **1·ClO$_4$** (ca. 100 mg) was stirred in acetone (10 mL) for 1 h, in the dark. The solvent was removed under a vacuum to give an oily material, which was shown by ^{1}H NMR to contain only the title complex. Although the acetone solutions of **7·TfO** are stable for longer periods than those of **7·ClO$_4$**, we recommend in both cases to use them freshly prepared.

7·TfO. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.06 (q, not well resolved, 3 H, CMe trans to Ag, $^5J_{HH}$ = 0.4 Hz), 2.33 (q, 3 H, CMe trans to NMe, $^5J_{HH}$ = 1.2 Hz), 3.35 (m, 3 H, NMe). The nature of **7·TfO** was confirmed by reacting it with [AuCl(PPh_3)] and isolating [Au{N(Me)=CMe_2}(PPh_3)]TfO (82% yield).[3]

7·ClO$_4$. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.09 (q, not well resolved, 3 H, CMe trans to Ag, $^5J_{HH}$ = 0.4 Hz), 2.36 (q, 3 H, CMe trans to NMe, $^5J_{HH}$ = 1.2 Hz), 3.36 (m, 3 H, NMe). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6): δ 18.93 (Me), 32.44 (Me), 41.93 (Me), 178.01 (*C*Me$_2$).

Synthesis of [Rh(Cp*)Cl{*N,N*′-N(Me)=C(Me)CH$_2$C(Me)$_2$NHMe}]-ClO$_4$ (8·ClO$_4$). A solution of **4a·ClO$_4$** (145 mg, 0.33 mmol) in acetone (15 mL) was refluxed for 2 h and then filtered through a short pad of Celite. The solution was concentrated under a vacuum (2 mL) and, upon the addition of Et_2O (25 mL), a suspension formed, which was filtered, and the orange solid collected washed with Et_2O (3 × 5 mL) and suction dried to give **8·ClO$_4$**. Yield: 157 mg, 91%. mp (dec): 221 °C. ^{1}H NMR (300 MHz, $CDCl_3$): A/B molar ratio = 1:1. Isomer A: δ 0.82 (s, 3 H, Me6), 1.56 (s, 3 H, Me7), 1.71 (s, 15 H, Me, Cp*), 2.33 (s, 3 H, Me5), 2.66 (d, 3 H, Me8, $^3J_{HH}$ = 6 Hz), 2.71 (d, 1 H, CH_2, $^2J_{HH}$ = 14 Hz), 2.97 (d, 1 H, CH_2, $^2J_{HH}$ = 14 Hz), 3.62 (s, 3 H, Me4), 4.24 (br, 1 H, NH). Isomer B: δ 1.21 (s, 3 H, Me6), 1.36 (s, 3 H, Me7), 1.74 (s, 15 H, Me, Cp*), 2.42 (s, 3 H, Me5), 2.51 (m, 2 H, CH_2), 2.73 (d, 3 H, Me8, $^3J_{HH}$ = 6 Hz), 3.55 (s, 3 H, Me4). ^{13}C{^{1}H} APT NMR (75 MHz, $CDCl_3$): Isomer A: δ 8.9 (Me, Cp*), 19.8 (Me6), 26.0 (Me5), 27.0 (Me7), 36.0 (Me8), 46.6 (Me4), 54.2 (C2), 55.8 (C3), 96.0 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz), 182.9 (C1). Isomer B: δ 9.8 (Me, Cp*), 25.0 (Me5), 25.3 (Me7), 26.0 (Me6), 34.9 (Me8), 45.5 (Me4), 56.6 (C2), 57.1 (C3), 95.9 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz), 183.4 (C1). IR (cm^{-1}): ν_{NH} 3256, 3240; $\nu_{C=N}$ 1659, 1652. Λ_M (Ω^{-1} cm^2 mol^{-1}): 158. Anal. Calcd for $C_{18}H_{33}Cl_2N_2O_4Rh$: C, 41.96, H, 6.46; N, 5.44. Found: C, 41.71; H, 6.49; N, 5.33. MS (FAB$^+$): (*m*/*z*, %) 415 (M$^+$, 100) 380 (M$^+$ - Cl, 10).

Synthesis of [Rh(Cp*){*N,N*′-NH=C(Me)CH$_2$C(Me)$_2$NH$_2$}-(NH=CMe$_2$)] (ClO$_4$)$_2$·H$_2$O (9a·ClO$_4$). To a solution of [Rh(Cp*)-Cl{NH=C(Me)CH_2C(Me)$_2$$NH_2$}]$ClO_4$[7] (101 mg, 0.21 mmol) in CH_2Cl_2 (25 mL) was added [Ag(NH=CMe_2)$_2$]ClO_4 (67 mg, 0,21 mmol). A white suspension immediately formed that was stirred for 30 min and then filtered through a short pad of Celite. The solution was concentrated under a vacuum (1 mL), and Et_2O was added to precipitate a yellow solid that was filtered, washed with Et_2O (3 × 5 mL), and dried by suction and then in an oven at 60 °C for 8 h to give **9a·ClO$_4$·H$_2$O**. Yield: 121 mg, 96%. mp (dec): 187 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 1.19 (s, 3 H, Me), 1.45 (s, 3 H, Me), 1.81 (s, 15 H, Me, Cp*), 2.07 (d, 1 H, CH_2, $^2J_{HH}$ = 17 Hz), 2.28 (s, 3 H, Me), 2.41 (s, 3 H, Me), 2.45 (d, 3 H, Me, $^4J_{HH}$ = 2 Hz), 2.63 (d, 1 H, CH_2, $^2J_{HH}$ = 17 Hz), 2.83 (br, 2 H, H_2O), 4.04 (d, 1 H, NH_2, $^2J_{HH}$ = 12 Hz), 4.58 (d, 1 H, NH_2, $^2J_{HH}$ = 12 Hz), 9.68 (s, 1 H, NH), 10.76 (s, 1 H, NH). ^{13}C{^{1}H} APT, HMQC, NMR (50 MHz, acetone-d_6): δ 8.9 (Me, Cp*), 24.7 (Me6), 26.8 (N=CMe trans to Rh), 30.0 (N=CMe trans to H), 30.1 (Me7), 31.3 (d, Me5, $^3J_{CRh}$ = 1 Hz) 47.5 (C2), 49.7 (C3), 98.2 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz), 189.4 (d, *C*=N, $^2J_{CRh}$ = 1 Hz), 193.5 (*C*=N). IR (cm^{-1}): ν_{NH} 3281, 3251, 3161; $\nu_{C=N}$ 1653, 1651. Λ_M (Ω^{-1} cm^2 mol^{-1}): 213. Anal. Calcd for $C_{19}H_{38}Cl_2N_3O_9Rh$: C, 36.43; H, 6.11; N, 6.70. Found: C, 36.36; H, 5.97; N, 6.83. Crystals suitable for an X-ray diffraction study were obtained from acetone-d_6 and Et_2O by the liquid diffusion method.

Synthesis of [Rh(Cp*){*N,N*′-N(Me)=C(Me)CH$_2$C(Me)$_2$NHMe}-(NCMe)] (ClO$_4$)$_2$ (9b·ClO$_4$). To a solution of **8·ClO$_4$** (354 mg, 0.69 mmol) in MeCN (15 mL) was added $AgClO_4$ (142.4 mg, 0.69 mmol). A suspension immediately formed, which was stirred for 15 min and then concentrated under a vacuum to dryness. The residue was stirred with CH_2Cl_2 (20 mL), and the suspension was filtered through a short pad of Celite. The solution was concentrated under a vacuum (2 mL) and Et_2O (25 mL) was added. The resulting suspension was filtered, and the yellow solid collected was washed with Et_2O (3 × 5 mL) and suction dried to give **9b·ClO$_4$**. Yield: 374 mg, 88%. mp (dec): 170 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 0.88 (s, 3 H, Me6), 1.53 (s, 3 H, Me7), 1.84 (s, 15 H, Me, Cp*), 2.39 (d, 1 H, CH_2, $^2J_{HH}$ = 18 Hz), 2.46 (s, 3 H, Me5), 2.78 (d, 3 H, Me8, $^3J_{HH}$ = 5.7 Hz), 2.99 (d, 1 H, CH_2, $^2J_{HH}$ = 17.5 Hz), 3.81 (s, 3 H, Me4), 4.65 (br, 1 H, NH). ^{1}H NMR (400 MHz, acetone-d_6, −80 °C): A/B molar ratio = 1:3.6. Isomer A: δ 0.73 (s, 3 H, Me6), 1.41 (s, 3 H, Me7), 1.78 (s, 15 H, Me, Cp*), 2.40 (s, 3 H, Me5), 2.71 (s, 3 H, MeCN or Me7), 3.98 (s, 3 H, Me4), 5.20 (br, 1 H, NH). Isomer B: δ 0.77 (s, 3 H, Me6), 1.40 (s, 3 H, Me7), 1.85 (s, 15 H, Me, Cp*), 2.30 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 2.38 (s, 3 H, Me5), 2.72 (s, 3 H, MeCN or Me8), 2.98 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 3.77 (s, 3 H, Me4), 4.84 (br, 1 H, NH). ^{13}C-{^{1}H} APT NMR (100 MHz, acetone-d_6): δ 4.0 (*Me*CN), 9.1 (Me, Cp*), 19.8 (Me6), 26.2 (Me5), 26.6 (Me7), 37.3 (Me8), 47.2 (Me4), 54.7(C2), 56.7 (C3), 100.0 (br, C, Cp*), 186.9 (C1). IR (cm^{-1}): ν_{NH} 3248 (br); $\nu_{C\equiv N}$ 2316, 2288; $\nu_{C=N}$ 1708, 1658. Λ_M (Ω^{-1} cm^2 mol^{-1}): 210. Anal. Calcd for $C_{20}H_{36}Cl_2N_3O_8Rh$: C, 38.72, H, 5.85; N, 6.77. Found: C, 38.30; H, 6.05; N, 6.45. MS (FAB$^+$): (*m*/*z*, %) [M$^+$ - MeCN] 379.1, 100; [M$^+$ + H_2O] 219.2, 15.

Synthesis of [Rh(Cp*){*N,N*′-N(Me)=C(Me)CH$_2$C(Me)$_2$NHMe}-(CNXy)] (ClO$_4$)$_2$ (9c·ClO$_4$). To a solution of **9b·ClO$_4$** (100 mg, 0.16 mmol) in acetone (15 mL) was added XyNC (21.2 mg, 0.16 mmol). After 2 h of being stirred, the yellow solution was concentrated under a vacuum (1 mL) and, upon addition of Et_2O (25 mL), a suspension formed, which was filtered. The lemon-yellow solid collected was washed with Et_2O (3 × 5 mL) and air-dried to give **9c·ClO$_4$**. Yield: 106 mg, 92%. mp (dec): 185 °C. ^{1}H NMR (400 MHz, dmso-d_6): A/B molar ratio = 1:1. Isomer A: δ 0.81 (s, 3 H, Me6), 1.42 (s, 3 H, Me7), 1.85 (s, 15 H, Me, Cp*), 2.07 (d, 1 H, CH_2, $^2J_{HH}$ = 15 Hz), 2.38 (s, 3 H, Me5), 2.47 (s, 6 H, Me, Xy), 2.65 (d, 3 H, Me8, $^3J_{HH}$ = 6 Hz), 2.92 (d, 1 H, CH_2, $^2J_{HH}$ = 15 Hz), 3.64 (s, 3 H, Me4), 4.8 (br, 1 H, NH), 7.34−7.48 (various m, 3 H, CH, Xy). Isomer B: δ 1.21 (s, 3 H, Me6), 1.22 (s, 3 H, Me7), 1.85 (s, 15 H, Me, Cp*), 1.99 (d, 1 H, CH_2, $^2J_{HH}$ = 14 Hz), 2.35 (s, 3 H, Me5), 2.51 (s, 6 H, Me, Xy), 2.62 (d, 3 H, Me8, $^3J_{HH}$ = 6 Hz), 2.98 (d, 1 H, CH_2, $^2J_{HH}$ = 4 Hz), 3.56 (s, 3 H, Me4), 5.25 (br, 1 H, NH), 7.34−7.48 (various m, 3 H, CH, Xy). ^{13}C{^{1}H} APT NMR (50 MHz, dmso-d_6): δ 8.90 (Me, Cp*), 9.6 (Me), 18.7 (Me,

Xy), 25.5 (Me), 26.4 (Me), 39.4 (Me8), 49.7 (Me4), 53.3 (C3), 55.7 (C2), 103.3 (d, C, Cp*, $^1J_{CRh}$ = 7 Hz), 128.5 (*meta*-C), 130.9 (*para*-C), 136.1 (*orto*-C), 187.6 (C1). IR (cm^{-1}) Isomer A: ν_{NH} 3240; $\nu_{C\equiv N}$ 2166; $\nu_{C=N}$ 1656. Λ_M (Ω^{-1} cm^2 mol^{-1}): 227. Anal. Calcd for $C_{27}H_{42}Cl_2N_3O_8Rh$: C, 45.65; H, 5.96; N, 5.91. Found: C, 45.40; H, 6.05; N, 5.74. Crystals of **9c·ClO$_4$** suitable for an X-ray diffraction study were obtained from acetone and Et_2O by the liquid diffusion method.

Synthesis of [Rh(Cp*){N,N′-N(Me)=C(Me)CH$_2$C(Me)$_2$NHMe}-(NH$_2$Me)](ClO$_4$)$_2$ (9d·ClO$_4$). To a suspension of **9b·ClO$_4$** (242 mg, 0.39 mmol) in CH_2Cl_2 (15 mL) was added NH_2Me (48.5 μL, 0.39 mmol). After 1 h of stirring, the suspension was filtered and the solid collected was washed successively with CH_2Cl_2 (2 × 5 mL) and Et_2O (2 × 5 mL). It was dried by suction and then in an oven at 60 °C for 3 days to give **9d·ClO$_4$·H$_2$O** as a yellow solid. Yield: 230 mg, 97%. mp (dec): 168 °C. ^{1}H NMR (200 MHz, acetone-d_6): A/B molar ratio = 2.5:1. Isomer A: δ 1.02 (s, 3 H, Me), 1.56 (s, 3 H, Me), 1.81 (s, 15 H, Me, Cp*), 2.40 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz) 2.51 (s, 3 H, Me), 2.67−2.72 (m, 6 H, *Me*NH_2 + Me8), 3.02 (br, 2 H, H_2O), 3.14 (d, 1 H, CH_2, $^2J_{HH}$ = 16 Hz), 3.84 (s, 3 H, Me4), 3.98 (br, 2 H, NH_2), 4.67 (br, 1 H, NH). Isomer B: δ 1.41 (s, 3 H, Me), 1.48 (s, 3 H, Me), 1.82 (s, 15 H, Me, Cp*), 2.43 (d, 1 H, CH_2, $^2J_{HH}$ = 15 Hz), 2.47 (s, 3 H, Me5), 2.67−2.72 (m, 3 H, *Me*NH_2), 2.97 (d, 3 H, Me8, $^3J_{HH}$ = 4 Hz), 3.17 (d, 1 H, CH_2, $^2J_{HH}$ = 15 Hz), 3.56 (s, 3 H, Me4), 4.22 (br, 2 H, NH_2), the NH resonance is not observed. $^{13}C\{^1H\}$ APT NMR (75 MHz, acetone-d_6): Isomer A: δ 8.9 (Me, Cp*), 20.8 (Me6), 26.5 (Me5), 28.3 (Me7), 32.8 (NH_2*Me*), 35.8 (Me8), 47.2 (Me4), 56.1 (C2), 56.2 (C3), 98.2 (d, C, Cp*, $^1J_{CRh}$ = 7.8 Hz), 187.7 (C1). Isomer B: δ 9.6 (Me, Cp*), 25.7 (Me7), 25.8 (Me5), 26.0 (Me6), 32.9 (NH_2*Me*), 37.4 (Me8), 44.7 (Me4), 57.5 (C2), 58.8 (C3), 98.1 (d, C, Cp*, $^1J_{CRh}$ = 7.8 Hz), 187.8 (C1). IR (cm^{-1}): ν_{NH} 3302, 3270, 3177; $\nu_{C=N}$ 1652, 1604. Λ_M (Ω^{-1} cm^2 mol^{-1}): 245. Anal. Calcd for $C_{19}H_{40}Cl_2N_3O_9Rh$: C, 36.32; H, 6.42; N, 6.69. Found: C, 36.25; H, 6.53; N, 6.69.

Synthesis of [Rh(Cp*){*C,N*-C$_6$H$_4$C(Me)=N(Me)-2}(NH$_2$Me)]-TfO (10a·TfO). A suspension of **6·TfO**(234 mg, 0.37 mmol) in acetophenone (3 mL) was heated at 80 °C for 4 h. The resulting brownish suspension was filtered, and upon the addition of Et_2O (30 mL) to the filtrate, a suspension formed, which was filtered. The yellow solid collected was washed with Et_2O (3 × 10 mL) and suction dried to give **10a·TfO**. Yield: 191 mg, 93%. mp: 133 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.68 (s, 15 H, Me, Cp*), 2.03 (t, 3 H, Me, $^3J_{HH}$ = 6 Hz), 2.42 (s, 3 H, Me), 3.80 (s, 3 H, Me), 7.14 (t, 1 H, CH, $^3J_{HH}$ = 8 Hz), 7.28 (t, 1 H, CH, $^3J_{HH}$ = 8 Hz), 7.44 (d, 1 H, CH, $^3J_{HH}$ = 8 Hz), 7.72 (d, 1 H, CH, $^3J_{HH}$ = 8 Hz). $^{13}C\{^1H\}$ APT NMR (75 MHz, $CDCl_3$): δ 9.1 (Me, Cp*), 15.3 (C*Me*), 32.4 (Me, $MeNH_2$), 44.5 (N*Me*), 96.3 (d, C=C, Cp*, $^1J_{CRh}$ = 8 Hz), 123.7 (CH, Ph), 127.8 (CH, Ph), 131.3 (CH, Ph), 135.2 (CH, Ph), 147.3 (*ipso*-C, Ph), 181.0 (d, C−Rh, $^1J_{CRh}$ = 30 Hz), 181.8 (d, C=N, $^2J_{CRh}$ = 2 Hz). IR (cm^{-1}): ν_{NH} 3292, 3256; $\nu_{C=N}$ 1602. Λ_M (Ω^{-1} cm^2 mol^{-1}): 140. Anal. Calcd for $C_{21}H_{30}F_3N_2O_3RhS$: C, 45.82; H, 5.49; N, 5.09; S, 5.83. Found: C, 45.34; H, 5.64; N, 4.83; S, 6.04. MS (FAB$^+$): (*m*/*z*, %) [M$^+$] 401.2, 9.67; [M$^+$ - $MeNH_2$] 370, 100. Crystals of **10a·TfO** suitable for an X-ray diffraction study were obtained from CH_2Cl_2 and Et_2O by the liquid diffusion method.

Synthesis of [Rh(Cp*){*C,N*-C$_6$H$_4$C(Me)=NMe}-2](CNR)]-TfO [R = ^{t}Bu (10b·TfO), Xy (10c·TfO)]. To a solution of **10a·TfO** (150 mg, 0.27 mmol for **10b·TfO**; 300 mg, 0.55 mmol for **10c·TfO**) in $CHCl_3$ (**10b·TfO**: 20 mL) or CH_2Cl_2 (**10c·TfO**: 20 mL) was added the isocyanide RNC (**10b·TfO**: R = ^{t}Bu, 185 μL, 1.64 mmol; **10c·TfO**: R = Xy, 107 mg, 0.82 mmol). The reaction mixture was refluxed for 3 h (**10b·TfO**) or 3 days (**10c·TfO**) and then filtered through a short pad of Celite. In the case of **10b·TfO**, the solution was concentrated under a vacuum to dryness, and the residue was washed with *n*-pentane (3 × 5 mL) and suction dried to give a yellow solid. In the case of **10c·TfO**, the solution was concentrated to 1 mL, and Et_2O (30 mL) was added. The resulting suspension was filtered, and the yellow solid collected was washed with Et_2O (3 × 10 mL) and suction dried.

10b·TfO. Yield: 117 mg, 71%. mp (dec): 152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (s, 9 H, Me, ^{t}Bu), 1.78 (s, 15 H, Me, Cp*), 2.49 (s, 3 H, Me), 3.74 (s, 3 H, Me), 7.18 (td, 1 H, CH, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.28 (td, 1 H, CH, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.47−7.51 (m, 2 H, CH). $^{13}C\{^1H\}$ APT NMR (75 MHz, $CDCl_3$): δ 9.5 (Me, Cp*), 15.8 (d, C*Me*, $^3J_{CRh}$ = 2 Hz), 30.4 (Me, ^{t}Bu), 46.0 (Me, N*Me*), 58.9 (C, ^{t}Bu), 101.2 (d, C, Cp*, $^1J_{CRh}$ = 5 Hz), 124.3 (CH, Ph), 128.4 (CH, Ph), 131.4 (d, CH, Ph, $^2J_{CRh}$ = 1 Hz), 135.7 (CH, Ph), 146.73 (*ipso*-C, Ph), 174.0 (d, C−Rh, $^1J_{CRh}$ = 29 Hz), 182.0 (C=N). IR (cm^{-1}): $\nu_{C\equiv N}$ 2182; $\nu_{C=N}$ 1602. Λ_M (Ω^{-1} cm^2 mol^{-1}): 158. Anal. Calcd for $C_{25}H_{34}F_3N_2O_3RhS$: C, 49.84; H, 5.69; N, 5.65; S, 5.32. Found: C, 49.52; H, 5.86; N, 5.78; S, 5.15.

10c·TfO. Yield: 281 mg, 79%. mp: 117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88 (s, 15 H, Me, Cp*), 2.04 (s, 6 H, Me, Xy), 2.53 (s, 3 H, Me), 3.82 (s, 3 H, Me), 7.04 (d, 2 H, CH, Xy, $^3J_{HH}$ = 7 Hz), 7.17 (t, 1 H, CH, Xy, $^3J_{HH}$ = 7 Hz), 7.22 (t, 1 H, CH, $^3J_{HH}$ = 7 Hz), 7.32 (t, 1 H, CH, $^3J_{HH}$ = 7 Hz), 7.54 (d, 1 H, CH, $^3J_{HH}$ = 7 Hz), 7.58 (d, 1 H, CH, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ APT NMR (75 MHz, $CDCl_3$): δ 9.7 (Me, Cp*), 16.0 (C*Me*), 18.2 (Me, Xy), 46.4 (Me, N*Me*), 102.2 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz), 124.7 (CH, Ph), 128.2 (*meta*-C, Xy), 128.7 (CH, Ph), 129.7 (*para*-C, Xy), 131.7 (CH, Ph), 134.9 (*orto*-C, Xy), 136.1 (CH, Ph), 146.9 (*ipso*-C, Ph), 173.2 (d, C−Rh, $^1J_{CRh}$ = 30 Hz), 182.6 (C=N). IR (cm^{-1}): $\nu_{C\equiv N}$ 2146; $\nu_{C=N}$ 1600. Λ_M (Ω^{-1} cm^2 mol^{-1}): 163. Anal. Calcd for $C_{29}H_{34}F_3N_2O_3SRh$: C, 53.54; H, 5.27; N, 4.31; S, 4.93. Found: C, 53.50; H, 5.52; N, 4.40; S, 4.86.

Synthesis of [Rh(Cp*){*C,N*-C(=NXy)C$_6$H$_4$}{C(Me)=NMe}-2}(CNXy)]TfO·2H$_2$O (11·TfO). A solution containing **10a·TfO** (60 mg, 0.11 mmol) and XyNC (172 mg, 1.30 mmol) in $CHCl_3$ (15 mL) was refluxed for 1 day and then filtered through a short pad of Celite. The solution was concentrated under a vacuum (1 mL), and Et_2O (30 mL) was added. The resulting suspension was filtered, and the orange solid collected was washed with Et_2O (3 × 10 mL) and suction dried to give **11·TfO**. Yield: 53 mg, 62%. mp: 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 3 H, Me, Xy), 1.60 (s, 19 H, Me, Cp*, H_2O), 2.34 (s, 3 H, Me, Xy), 2.36 (s, 6 H, Me, Xy), 2.79 (s, 3 H, Me), 3.95 (s, 3 H, Me), 6.54−7.85 (m, 10 H). $^{13}C\{^1H\}$ APT NMR (75 MHz, $CDCl_3$) δ 9.1 (Me, Cp*), 18.51 (Me, Xy), 18.8 (Me, Xy), 18.9 (Me, Xy), 20.5 (C*Me*), 52.2 (N*Me*), 102.8 (d, C, Cp*, $^1J_{CRh}$ = 5 Hz), 122.3 (CH), 122.7 (CH), 127.5 (CH), 127.8 (CH), 128.2 (CH), 128.6 (CH), 129.6 (CH), 130.1 (CH), 131.3 (CH), 131.1 (C), 135.3 (C), 150.0 (C). IR (cm^{-1}): $\nu_{C\equiv N}$ 2134; $\nu_{C=N}$ 1620. Λ_M (Ω^{-1} cm^2 mol^{-1}): 126. Anal. Calcd for $C_{38}H_{47}N_3F_3O_5RhS$: C, 55.81; H, 5.79; N, 5.14; S, 3.92. Found: C, 55.52; H, 5.30; N, 5.52; S, 3.79. MS (FAB$^+$): (*m*/*z*, %) [M$^+$] 632.2, 100; [M$^+$ - XyNC] 501.0, 37.55; [M$^+$ - 2 XyNC] 370, 54.95. From the CH_3Cl/Et_2O mother liquor from which **11·TfO** precipitated, orange crystals grew, which were submitted for an X-ray diffraction study (below).

X-ray Structure Determinations. 9a·ClO$_4$·acetone-d_6, 9c·ClO$_4$ 10a·TfO, and **11·TfO** were measured on a Bruker Smart APEX machine. Data were collected using monochromated Mo−Kα radiation in w scan mode. Crystal data and refinement details for **9a·ClO$_4$·acetone-d_6**, **9c·ClO$_4$**, and **10a·TfO** are presented in Table

Table 1. Crystal Data and Structure Refinement

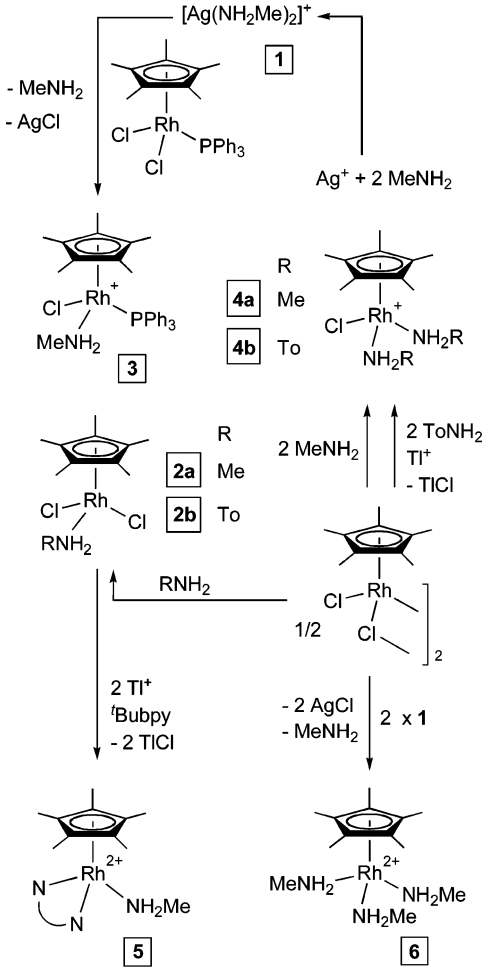
complex	**9a·ClO$_4$·**acetone-d_6	**9c·ClO$_4$**	**10a·TfO**
formula	$C_{22}H_{36}D_6Cl_2N_3O_9Rh$	$C_{27}H_{42}Cl_2N_3O_8Rh$	$C_{21}H_{30}F_3N_2O_3RhS$
fw	678.40	710.45	550.44
temperature (K)	293(2)	100(2)	100(2)
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	P 2(1)/n	P bca
a (Å)	10.3800(5)	11.3390(5)	12.1899(5)
b (Å)	11.1724(5)	15.8885(6)	14.9406(6)
c (Å)	13.4906(6)	17.0075(7)	24.7220(10)
α (deg)	68.798(2)	90	90
β (deg)	86.115(2)	96.140(2)	90
γ (deg)	82.602(2)	90	90
V (Å^3)	1446.08(11)	3046.5(2)	4502.5(3)
Z	2	4	8
ρ_{calcd} (Mg m^{-3})	1.558	1.549	1.624
μ (Mo K$_\alpha$)(mm^{-1})	0.827	0.788	0.901
F(000)	692	1472	2256
cryst size (mm^3)	0.32 × 0.22 × 0.12	0.30 × 0.12 × 0.05	0.15 × 0.10 × 0.05
θ range (deg)	1.97−26.73	1.76−26.37	1.65−28.27
no. of rflns coll	16 361	33 093	49 809
no. of indep rflns	6080	6225	5362
R_{int}	0.0167	0.0394	0.0580
max. and min. transmsn	0.9073 and 0.7779	0.9617 and 0.7979	0.9563 and 0.8766
restraints/params	0/359	22/432	1/296
GOF on F^2	1.080	1.088	1.080
R1 [$I > 2\sigma(I)$]	0.0291	0.0336	0.0367
wR2 (all reflns)	0.0719	0.0744	0.0744
largest diff. peak and hole (e.Å^{-3})	0.943 and −0.811	0.641 and 0.454	0.784 and −0.606

1. The structure of **9a·ClO$_4$** was solved by direct methods and **9c·ClO$_4$** and **10a·TfO** were solved by the heavy-atom method. All of the non-hydrogen atoms were refined anisotropically on F^2 (program *SHELX-97m*, G. M. Sheldrick, Univerity of Göttingen: Göttingen, Germany). Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. Hydrogen atoms were refined as free (NH) or using a rigid (Me) or a riding (all other hydrogens) model. *Special features:* In **9a·ClO$_4$**, the oxygen atoms of one of the perchlorate anions are disordered over two positions (ca. 80:20). In **9c·ClO$_4$**, the amino−imino ligand is disordered over two positions (ca. 70:30). The NH hydrogen of the minority part was not included in the refinement. The crystal structure of **11·TfO** was measured at −173 °C, but because it contains (1) eight unit formulas per asymmetric unit, (2) some solvent (Et_2O) of crystallization, (3) some phenyl rings and triflate anions disordered over two positions, and (4) a Rint = 0.1032, convergence was found to be very slow. Additionally, there was also some residual electron density as a solitary peak. All these reasons made it impossible to refine the structure properly. Different crystals were measured, trying to get better data, but all of them gave the same problems. The unit cell parameters are: monoclinic, a = 39.3716(19), b = 30.1642(15), c = 26.5919(13) Å, β = 98.868(2)°, V = 31203.36 (6) Å^3, T = 100(2) K, space group $P2(1)/c$, Z = 32, 198 853 reflections measured, 70 422 unique (R_{int} = 0.1032).

Results and Discussion

Synthesis of Ag$^+$ and Rh(III) Methyl Amino Complexes. The reaction of AgX with $MeNH_2$ (1:2, Et_2O) produces almost quantitative precipitation of $[Ag(NH_2Me)_2]X$ [X = TfO (**1·TfO**), ClO_4 (**1·ClO$_4$**); Scheme 1]. Two homologous complexes with $N(CF_3SO_2)_2^-$ [22] or $[Cr(NCS)_4(NH_2Ph)_2]^-$ [23] counterions have been reported, and other salts have been studied theoretically.[24]

Scheme 1



Neutral mono(amino) Rh(III) complexes $[Rh(Cp^*)Cl_2(NH_2R)]$ [R = Me (**2a**), To (**2b**)] were prepared by reacting

(22) Jing-Fang, H.; Huimin, H.; Sheng, D. *J. Electrochem. Soc.* **2006**, *153*, j9.

$[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ with the stoichiometric amount of RNH_2 (R = Me, To = C_6H_4Me-4, Scheme 1). The synthesis of **2b** was reported long ago,[19] although no NMR data were provided and it was said to be unstable in solution, which we cannot corroborate.

Monocationic mono(amino) complex $[Rh(Cp^*)Cl(NH_2Me)(PPh_3)]TfO\cdot H_2O$ (**3·TfO**) was obtained by reacting equimolar amounts of $[Rh(Cp^*)Cl_2(PPh_3)]$[19] and **1·TfO** in CH_2Cl_2 (Scheme 1). The reaction of the same rhodium complex with **1·TfO** (1:2, in CH_2Cl_2), intended to produce $[Rh(Cp^*)(NH_2Me)_2(PPh_3)](TfO)_2$, gave instead a mixture of the expected product[25] along with **3·TfO** and other species that we could not separate and were shown by ^{31}P NMR to contain some $[Ag^+]PPh_3$ species.

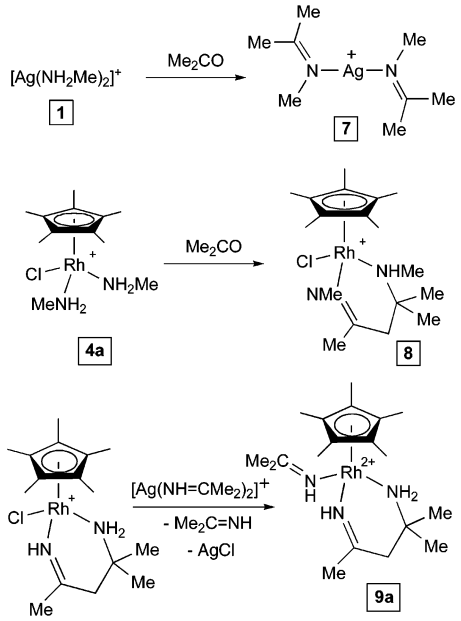
The monocationic bis(amino) complexes $[Rh(Cp^*)Cl(NH_2R)_2]X$ [R = Me, X = Cl (**4a·Cl**), ClO_4 (**4a·ClO₄**), R = C_6H_4Me-4 (To), X = CF_3SO_3 (TfO) (**4b·TfO**)] were prepared, respectively, by reacting $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ with $MeNH_2$ (1:4) in CH_2Cl_2, from **4a·Cl** and $NaClO_4\cdot H_2O$ (1:4.8) in THF, or by the one-pot reaction of $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$, $ToNH_2$ (To = C_6H_4Me-4), and TlTfO (1:4:2) in CH_2Cl_2. **4a·Cl** is insoluble in CH_2Cl_2 and was isolated in almost quantitative yield by filtration of the reaction mixture.

Dicationic mono(amino) complex $[Rh(Cp^*)(NH_2Me)(^t\text{Bubpy})](TfO)_2$ (**5·TfO**) was prepared by reacting **2a** with TlTfO and ^{t}Bubpy (1:2:1), and the dicationic tris(amino) $[Rh(Cp^*)(NH_2Me)_3](TfO)_2$ (**6·TfO**) was obtained, in almost quantitative yield, by reacting $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ with **1·TfO** (1:4). The reaction to prepare **6·TfO** from $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$, $MeNH_2$, and XTfO (X = Ag, Tl) (1:6:4, in CH_2Cl_2) is not convenient because in this way it forms along with **4a·TfO**. Additionally, massive decomposition took place when AgTfO was used.

As mentioned in the Introduction, in spite of the many known Rh(III) complexes with primary amine ligands, those with $MeNH_2$ are scarce, and only one organometallic compound has been reported, without experimental details. **2**−**6** constitute the first family of methyl amino complexes of rhodium. It includes neutral, mono-, and dicationic complexes with 1 to 3 $MeNH_2$ ligands. Silver complex **1** is a key reagent in the synthesis of dicationic complex **6** and could have application for the synthesis of other metal complexes.

Reactivity of Methyl Amino Complexes Toward Acetone. Synthesis of $[Ag\{N(Me)=CMe_2\}_2]^+$ and Me-imam Rh(III) Complexes. Complexes **1** react with acetone (1 h, at room temperature) to give solutions from which oily materials are obtained. Their ^1H NMR spectra show only the three resonances expected for complexes $[Ag\{N(Me)=CMe_2\}_2]X$ [X = TfO (**7·TfO**), ClO_4 (**7·ClO₄**)] (Scheme 2). In both complexes, the two Me groups bonded to carbon give one quartet each. That at a lower δ value is not well resolved, and we assign it to the Me group cis to the NMe group, whereas the other, displaying a $^5J_{HH}$ coupling constant of 1.2 Hz, is assigned to the CMe protons trans to NMe. The expected quartet of quartets for NMe protons is observed as a multiplet. The solutions of **7·TfO** are more stable in acetone than in $CHCl_3$, and both are more stable than those of **7·ClO₄**. We have always used them freshly prepared. The reaction of **7·TfO** with $[AuCl(PPh_3)]$ (1:1, in acetone) produced the previously reported complex $[Au\{N(Me)=CMe_2\}(PPh_3)]TfO$[3] in 82% yield which, along with the ^1H NMR spectra, offer sufficient evidence about the nature of these oily compounds.

Scheme 2



From the Rh(III) methyl amino complexes, we have unfruitfully attempted the synthesis of the corresponding imino complexes by reacting them with acetone under different reaction conditions, as evidenced by the lack of the resonance around 3.3−3.7 ppm expected for the C=NMe protons in the reaction products. When reactions with acetone at room temperature were attempted, the monoamino complexes **2a** (3 days), **3·TfO** (2h), and **5·TfO** (7h or 24 h refluxing) were recovered unchanged irrespective their charge, and **4a·Cl** (3 days) or **6·TfO** (5 h) gave mixtures of species containing **2a** or $[Rh(Cp^*)(Me\text{-}imam)(NH_2Me)](TfO)_2$ (**9d·ClO₄**, below), respectively. Refluxing **2a** (1 day) or **3·TfO** (2h) in acetone or by reacting $[Rh(Cp^*)Cl_2(PPh_3)]$ with TlTfO and $MeNH_2$ (1:2:2, 24 h) in acetone under N_2, afforded $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ in the first case, or a complex mixture, in the others.

Upon stirring an acetone solution of **4a·ClO₄** at room temperature for 1 day or refluxing it for 2 h, the complex $[Rh(Cp^*)Cl(Me\text{-}imam)]ClO_4$ (**8·ClO₄**) formed in 91% yield (Scheme 2). The reaction is likely to occur through the intermediate bis(imino) complex $[Rh(Cp^*)Cl\{N(Me)=CMe_2\}_2]ClO_4$ that would be unstable toward the intramo-

(23) Mathur, P. K.; Srivastara, L. N. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2112.
(24) El Aribi, H.; Rodríguez, C. F.; Shoeib, T.; Y., L.; Hopkinson, A. C.; Michel Siu, K. W. *J. Phys. Chem. A* **2002**, *106*, 8798. Widmer-Cooper, A. N.; Lindoy, L. F.; Feimers, J. R. *J. Phys. Chem. A* **2001**, *105*, 6567.
(25) ^1H NMR (400 MHz, dmso-d_6): δ 1.62 (d, 15 H, Me, Cp*, $^4J_{HP}$ = 2 Hz), 2.33 (t, 6 H, Me, $^3J_{HH}$ = 6 Hz), 3.97 (br, 4 H, NH_2), 7.37−7.59 (m, Ph, 30 H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): 33.53 (d, $^1J_{P-Rh}$ = 142.8 Hz).

lecular 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 $[Rh(Cp^*)Cl\{NH{=}CMe_2\}_2]ClO_4$[6,7] that could be isolated and is stable in acetone solution for 24 h at room temperature, although it also converts into the imino−amino ("imam") condensed product when it is refluxed in acetone or treated with CO or with chloride or with catalytic amounts of $Ph_2C{=}NH$ or SMe_2 or with $AsPh_3$ (1:1).

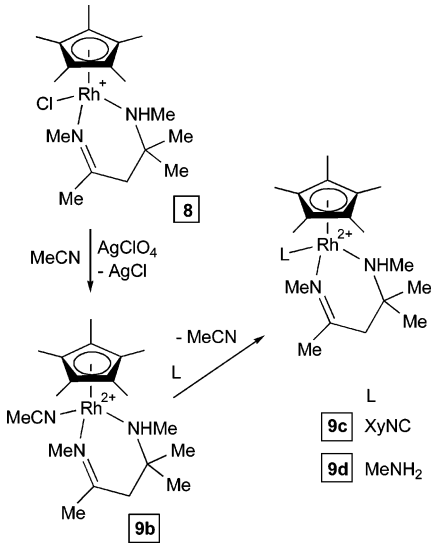
In conclusion, the reactions of neutral, mono, or dicationic $[Rh(III)]NH_2Me$ complexes with acetone did not allow us to isolate any $[Rh(III)]N(Me){=}CMe_2$ species. It seems that the expected complexes are unstable and either decompose to give unidentified species or hydrolyze back to the amino starting complexes or undergo an aldol-like condensation process to give "Me-imam" derivatives.

Attempts to Prepare Methyl Acetimino Complexes through Transmetalation Reactions. We have prepared different imino complexes through transmetalation reactions.[3,7] However, the analogous reactions of $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$, (1) with $[Au\{N(Me){=}CMe_2\}(PPh_3)]TfO$ (1:2, in dry acetone, under N_2 or in the air) led to mixtures containing $[AuCl(PPh_3)]$ and, among other species, **8·TfO** (reaction under N_2) or **2a** (reaction in the air), (2) with **7·TfO** (1:4, in dry acetone, N_2) gave a mixture of both diastereoisomers of $[Rh(Cp^*)(Me\text{-}imam)(NH_2Me)](TfO)_2$ (**9d·TfO**, below) plus a small amount of **8·TfO**, or (3) with $[Rh(Cp^*)Cl(^t Bubpy)]$-TfO with **7·TfO** (1:1, in dry acetone, N_2), afforded a 1:1 mixture (by ^1H NMR) of the desired complex $[Rh(Cp^*)\{N(Me){=}CMe_2\}(^t Bubpy)](TfO)_2$[26] and **5·TfO**, which converted into pure **5·TfO** after recrystallization from acetone/Et_2O. Again, all these reactions strongly suggest that the $[Rh(Cp^*)]$-$NMe{=}CMe_2$ complexes are unstable and decompose through aldol-like condensation or hydrolysis.

We have also unfruitfully attempted to prepare complexes containing a mixed-imam ligand resulting from the aldol condensation of $HN{=}CMe_2$ and $MeN{=}CMe_2$ by reacting in acetone, under N_2 (1) $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$[6] with **7·ClO₄** (1:1, 2 h), (2) $[Rh(Cp^*)(\mu\text{-}Cl)(NH{=}CMe_2)]_2(ClO_4)_2$[6] with $MeNH_2$ (1:1, 5 h), (3) **3·TfO** and $[Ag(NH{=}CMe_2)_2]ClO_4$ (1:1, 1 h), and (4) **2a** with $[Ag(NH{=}CMe_2)_2]ClO_4$ (1:1, 1 h). The latter reaction gave a mixture of **4a·ClO₄** and $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (by NMR), which converted into $[Rh(Cp^*)Cl(Me\text{-}imam)]ClO_4$ (**8·ClO₄**) and $[Rh(Cp^*)Cl(imam)]ClO_4$ when the stirring was prolonged for 3 days.

Reactivity of Rh(III) imam and Me-imam Complexes. **8·ClO₄** reacts with $AgClO_4$ (1:1) in acetonitrile to give the dicationic complex $[Rh(Cp^*)(Me\text{-}imam)(NCMe)](ClO_4)_2$ (**9b·ClO₄**) in 92% yield (Scheme 3). The reaction of **9b·ClO₄** with XyNC or with $MeNH_2$ (1:1, in acetone for 2 h or CH_2Cl_2 for 1 h, respectively; Xy = $C_6H_3Me_2$-1,6) produces the replacement of the labile MeCN ligand to give $[Rh(Cp^*)$-

Scheme 3



$(Me\text{-}imam)L](ClO_4)_2$ [L = XyNC (**9c·ClO₄**), NH_2Me (**9d·ClO₄**)]. One of the diastereoisomers of **9c·ClO₄** is insoluble in acetone, whereas the other is partially soluble, which allowed us to isolate the first one in 58% yield by washing the mixture with a small volume of acetone. The ^1H NMR spectrum of **9d·ClO₄** in acetone-d_6 (300 MHz) shows the presence of two diastereoisomers in a 3:1 molar ratio.

We have also failed to prepare complex $[Rh(Cp^*)(Me\text{-}imam)\{N(Me){=}CMe_2\}](ClO_4)_2$ by reacting **9d·ClO₄** with NH_2Me in dry acetone (15 h, under nitrogen). We have attempted to isolate the free Me-imam ligand by displacing it from **8·ClO₄**, but it does not react with $NH_2(CH_2)_2NH_2$ or with $Ph_2P(CH_2)_2PPh_2$ under different reaction conditions.

Synthesis of Acetophenone Methyl Imino Complexes. When suspensions of **2a** or **4a·Cl** in MeC(O)Ph were stirred at room temperature or refluxed, formation of $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ was observed. When **6·TfO** was stirred at room temperature with MeC(O)Ph (1:6) in THF or in net acetophenone for 2 or 24 h, respectively, it was recovered unchanged. However, when a solution of **6·TfO** was heated in a small volume of MeC(O)Ph at 80 °C for 4 h, the orthometalated complex $[Rh(Cp^*)\{C,N\text{-}C_6H_4\{C(Me){=}N(Me)\}\text{-}2\}(NH_2Me)]TfO$ (**10a·TfO**) formed along with $[MeNH_3]TfO$ (Scheme 4). No complex of any metal with this 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.[27]

The result of the reaction of **10a·TfO** with $^t BuNC$ or XyNC in refluxing $CHCl_3$ depends on the isocyanide. Thus, in the case of $^t BuNC$ complex $[Rh(Cp^*)\{C,N\text{-}C_6H_4\{C(Me){=}N(Me)\}\text{-}2\}(CN^t Bu)]TfO$ (**10b·TfO**) was the only species isolated, even if a large excess of isocyanide was used and the refluxing was prolonged for several days. However, in

(26) ^1H NMR (300 MHz, acetone-d_6): δ 1.44 (s, 18 H, Me, $^t Bu$), 1.80 (s, 15 H, Me, Cp*), 2.16 (s, Me), 2.38 (m, Me), 3.35 (s, N-Me), 8.10 (dd, 2 H, H5, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 8.73 (d, 2 H, H3, $^4J_{HH}$ = 2 Hz), 9.37 (d, 2 H, H6, $^3J_{HH}$ = 6 Hz).

(27) Cambridge Structural Database, version 5.27, Cambridge Crystallographic Data Center: Cambridge, U.K., August, 2006.

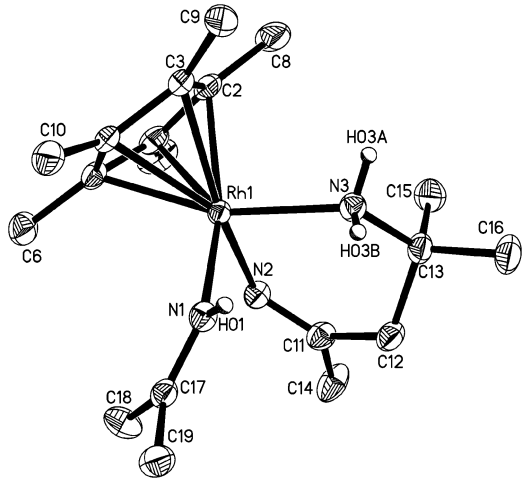
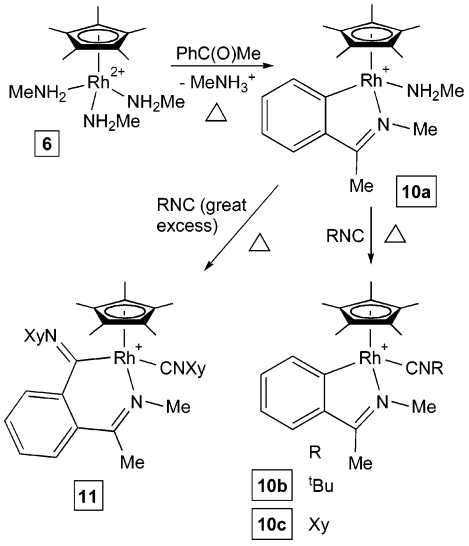


Figure 1. Ellipsoid representation of the cation of **9a·ClO$_4$** (50% probability). Selected bond lengths (Å) and angles (°): Rh(1)−N(2) = 2.0771(19), Rh(1)−N(1) = 2.1082(18), Rh(1)−N(3) = 2.1571(19), Rh(1)−C(1) = 2.170(2), Rh(1)−C(2) = 2.160(2), Rh(1)−C(3) = 2.174(2), Rh(1)−C(4) = 2.177(2), Rh(1)−C(5) = 2.155(2), N(1)−C(17) = 1.279(3), N(2)−C(11) = 1.278(3), N(3)−C(13) = 1.496(3), N(2)−Rh(1)−N(1) = 90.73(7), N(2)−Rh(1)−N(3) = 88.06(7), N(1)−Rh(1)−N(3) = 85.06(7), C(17)−N(1)−Rh(1) = 136.25(16), C(11)−N(2)−Rh(1) = 130.99(16), C(13)−N(3)−Rh(1) = 121.91(14).

Scheme 4



the case of XyNC, the reaction produced the homologous complex [Rh(Cp*){*C*,*N*-C$_6$H$_4${C(Me)═N(Me)}-2}(CNXy)] (**10c·TfO**) when a 1:1.5 molar ratio of the reagents was used and the reaction mixture was refluxed for 3 days, but when a larger excess of XyNC (1:12) was used, complex [Rh(Cp*){*C*,*N*-C(═NXy)C$_6$H$_4${C(Me)═N(Me)}-2}(CNXy)]-TfO (**11·TfO**) formed after 1 day of heating. Thus, XyNC, apart from replacing the MeNH$_2$ ligand, is also capable of inserting into the Rh−C bond to give an iminoacyl fragment and, consequently, an imino(iminoacyl) complex. As far as we are aware, only one previous insertion of isocyanide into a Rh(III)−C$_{aryl}$ bond has been reported.[28]

X-ray Crystal Structures. The crystal structures of **9a·ClO$_4$**·acetone-d_6 (Figure 1), **9c·ClO$_4$** (Figure 2), and **10a·TfO** (Figure 3) have been determined. Numerical details are presented in Table 1. In all cases, the cations exhibit a pseudo-octahedral three-leged piano-stool geometry, with the Cp* group occupying three fac coordination sites. The Rh−N(amino) [**9a·ClO$_4$**: 2.1571(19), **9c·ClO$_4$**: 2.07(3), **10a·TfO**: 2.139(2) Å], Rh−N(imino) [**9a·ClO$_4$**: 2.077(1), 2.1082(18), **9c·ClO$_4$**: 2.110(11), **10a·TfO**: 2.026(2) Å] and C═N [**9a·ClO$_4$**: 1.279(3), 1.278(3), **9c·ClO$_4$**: 1.275(10), **10a·TfO**: 1.294(3) Å] bond distances are in the ranges found for other Cp*−Rh(III) complexes (2.016−2.214, 2.067−2.182, and 1.148−1.384 Å, respectively).[27] The C−Rh−N [**9c·ClO$_4$**: 91.3(4), 92.5(2), **10a·TfO**: 78.26(9), 87.11(9)°] and N−Rh−N [**9a·ClO$_4$**: 90.73(7), 85.06(7), 88.06(7), **9c·ClO$_4$**: 89.8(3), **10a·TfO**: 91.48(8)°] angles are all close to

(28) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 686.

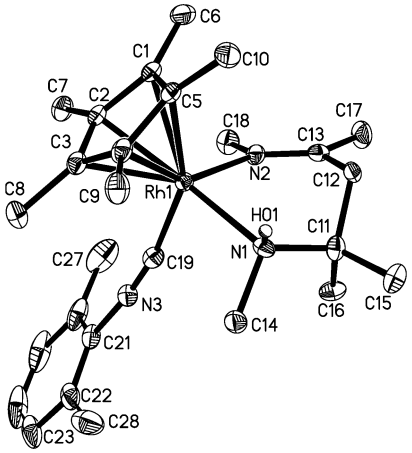


Figure 2. Ellipsoid representation of the cation of **9c·ClO$_4$** (50% probability). Selected bond lengths (Å) and angles (°): Rh(1)−N(1) = 2.191(8), Rh(1)−N(2) = 2.110(11), Rh(1)−C(1) = 2.211(2), Rh(1)−C(2) = 2.165(2), Rh(1)−C(3) = 2.180(2), Rh(1)−C(4) = 2.203(2), Rh(1)−C(5) = 2.195(2), Rh(1)−C(19) = 1.992(3), N(1)−C(11) = 1.498(9), N(1)−C(14) = 1.510(8), N(2)−C(13) = 1.275(10), N(2)−C(18) = 1.451(10), N(3)−C(19) = 1.152(3), C(19)−Rh(1)−N(2) = 91.3(4), N(2)−Rh(1)−N(1) = 89.8(3), N(1)−C(11)−C(12) = 106.2(4), N(2)−C(13)−C(12) = 120.9(6), N(3)−C(19)−Rh(1) = 170.3(2).

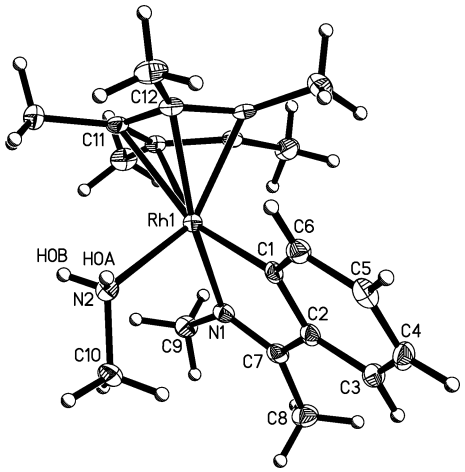


Figure 3. Ellipsoid representation of the cation of **10a·TfO** (50% probability). Selected bond lengths (Å) and angles (°): Rh(1)−C(1) = 2.026(2), Rh(1)−N(1) = 2.086(2), Rh(1)−N(2) = 2.139(2), Rh(1)−C(11) = 2.252(2), Rh(1)−C(12) = 2.153(2), Rh(1)−C(13) = 2.177(2), Rh(1)−C(14) = 2.165(2), Rh(1)−C(15) = 2.263(2), N(1)−C(7) = 1.294(3), N(2)−C(10) = 1.477(3), C(1)−Rh(1)−N(1) = 78.26(9), C(1)−Rh(1)−N(2) = 87.11(9), N(1)−Rh(1)−N(2) = 91.48(8), C(7)−N(1)−C(9) = 122.4(2), C(7)−N(1)−Rh(1) = 117.35(17), C(9)−N(1)−Rh(1) = 120.25(16), C(10)−N(2)−Rh(1) = 119.38(16).

Table 2. Hydrogen Bonds [Angstroms and Degrees] in **9a·ClO$_4$**·acetone-d_6, **9c·ClO$_4$**, and **10a·TfO**[a]

D−H···A	d(D−H)	d(H...A)	d(D...A)	<(DHA)
9a·ClO$_4$·acetone-d_6		**10a·TfO**		
N(1)−H(01)···Cl(2)#1	0.82(3)	2.98(3)	3.7721(19)	165(2)
N(3)−H(03B)···Cl(2)#1	0.87(3)	2.90(3)	3.726(2)	160(2)
N(2)−H(02)···O(3)#2	0.81(3)	2.25(3)	3.003(3)	155(3)
C(7)−H(7B)···O(3)#2	0.96	2.55	3.462(4)	157.9
C(19)−H(19C)···O(2)#3	0.96	2.58	3.365(3)	139.4
C(8)−H(8C)···O(4)	0.96	2.46	3.296(3)	145.5
C(99)−H(99B)···O(2)	0.96	2.42	3.366(3)	167.7
		9c·ClO$_4$		
C(25)−H(25)···O(8)#1	0.95	2.53	3.375(4)	147.5
C(7)−H(7A)···O(1)#2	0.98	2.57	3.452(3)	149.2
		10a·TfO		
N(2)−H(0A)···O(3)#1	0.85(2)	2.25(2)	3.055(3)	159(3)
N(2)−H(0B)···O(1)#2	0.84(2)	2.26(2)	3.058(3)	157(3)
C(9)−H(9B)···O(3)#2	0.98	2.50	3.452(3)	163.9
C(20)−H(20B)···O(1)#3	0.98	2.57	3.467(3)	151.4

[a] Symmetry transformations used to generate equivalent atoms: **9a·ClO$_4$**·acetone-d_6: #1 $x, y-1, z$ #2 $x+1, y, z$ #3 $-x+1, -y+1, -z$. **9c·ClO$_4$**:#1 $-x, -y, -z+1$ #2 $-x+{}^1/_2, y-{}^1/_2, -z+{}^3/_2$. **10a·TfO**: #1 $-x+{}^3/_2, y-{}^1/_2, z$ #2 $-x+1, y-{}^1/_2, -z+{}^3/_2$ #3 $-x+{}^1/_2, y-{}^1/_2, z$.

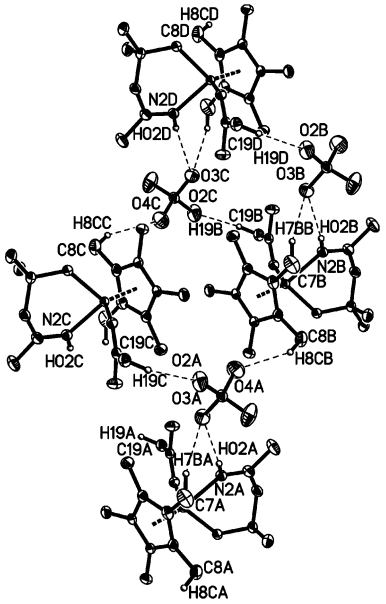


Figure 4. View of some of the hydrogen bonds in **9a·ClO$_4$**.

those expected for an octahedral disposition, with the exception of the C(1)−Rh(1)−N(1) angle in **10a·TfO**, which is narrow [78.26(9)°], likely imposed by the five-membered metallacycle of which they form a part. The Cp*−Rh moieties do not display special features.

The three crystal structures display various hydrogen bonds, for which distances and angles are shown in Table 2. In **9a·ClO$_4$**·acetone-d_6, the N−H···Cl, N−H···O, and C−H···O hydrogen bonds involve NH (acetimine), CH (Me, from Cp* or from the acetone molecule), and ClO_4 groups. One perchlorate is linked to three different cations through four hydrogen bonds (Figure 4). With two of them (C8−H8C···O4 and C19−H19C···O2), two cations and two anions generate macrocycles, which are extended with the other hydrogen bonds to form a 3D network. In **9c·ClO$_4$**, two C−H bonds, one from a Cp*−Me and the other

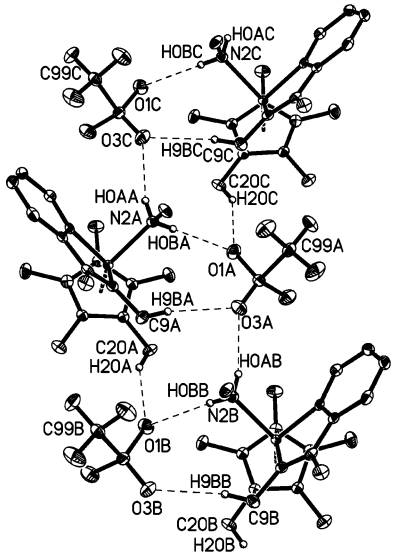


Figure 5. Hydrogen bonds in **10a·TfO**.

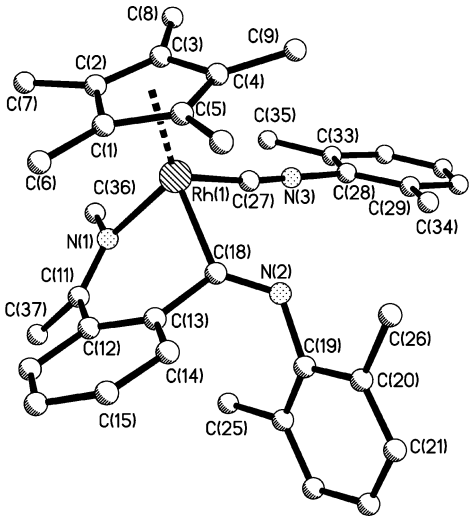


Figure 6. The cation of **11·TfO** showing the connectivity pattern.

from a Xy−Me group, participate in CH···O hydrogen bonds to two different ClO_4 anions. In **10a·TfO** (Figure 5), the cations and the triflate anions are associated through two hydrogen bonds (C9−H9B···O1 and N2−H0B···O1). Additionally, the N2−H0A···O3 and C20−H20B···O1 hydrogen bonds link these aggregates, forming ribbons parallel to the *a* axis.

As stated above, the structure of **11·TfO** could not be refined because of the data quality, but the connectivity of the cation could be established unambiguously (Figure 6).

NMR Spectra. The NMR spectra of all of the complexes have been measured. **11·TfO** decomposes slowly in solution and, although its ^{1}H NMR spectrum is that of the pure compound, the ^{13}C shows some decomposition impurities, making the assignment of some resonances difficult. In all of the cases, the Cp* resonances appear in the 1.13−1.88 (Me protons), 8.0−9.5 (Me carbons), and 93.3−103.3 (quaternary carbons) ppm ranges. The later resonance is usually a doublet with J_{CRh} values of 5 to 9 Hz, although in **3·TfO**, it appears as a doublet of doublets because of additional coupling to ^{31}P ($^2J_{CP}$ = 3 Hz), whereas in

9b·ClO$_4$, it is a broad singlet. In complexes with $MeNH_2$ ligands (**1**−**6** and **10a·TfO)**, the Me protons give a singlet (**1**) or a triplet in the 2.03−2.64 ppm region, with $^3J_{HH}$ values of some 6 Hz; the NH_2 protons give a broad resonance between 3.01 and 4.70 ppm except in **10a·TfO** (two singlets), and the Me carbons appear in the 30.9−32.5 ppm range.

Me-imam complexes **8** and **9b**−**d** bear two chiral centers. Their NMR spectra show, at room temperature for **8·ClO$_4$**, **9c·ClO$_4$**, and **9d·ClO$_4$**, or at −80 °C for **9b·ClO$_4$**, the resonances of the two expected diastereoisomers, suggesting that in the later, a fast interconversion process takes place at room temperature, probably through dissociation of MeCN. In complex **8·ClO$_4$**, we have observed that the relative proportion of both diastereoisomers depends on the solvent. Thus, in $CDCl_3$, they are in a 1:1 molar ratio, whereas in acetone-d_6 and in dmso-d_6, one of them transforms into the other, the difference of concentration being greater in dmso-d_6 (3:1) than in acetone (1.25:1). It is reasonable to assume that this isomerization is catalyzed by the solvent through the formation of the dicationic intermediate [Rh(Cp*)(Me-imam)(S)]Cl(ClO_4) (S = acetone, dmso). The resonances of the Me-imam ligand in **8** and **9** have been fully assigned by means of HMQC and HMBC correlation experiments (Experimental Section and Chart 1). All of these complexes show (1) the Me protons and carbon nuclei on the iminic nitrogen less shielded (Me4: 3.5−3.98 and 45.5−49.7 ppm, respectively) than those on the aminic nitrogen (Me8: 2.65−2.73 and 34.9−37.3 ppm, respectively); (2) the N=C carbon nuclei (C1:182.9−187.6 ppm) less shielded than the NH−C ones (C3: 53.3−57.1 ppm); (3) the inequivalent methylene protons as two doublets in the 1.99−2.70 and 2.92−2.98 ppm regions with the exception of one isomer of **8·ClO$_4$** that unexpectedly shows this resonance as a singlet at 2.51 ppm; and (4) the NH proton in the 4.2−5.3 ppm region.

In the NMR spectra of **10·TfO**, the resonances due to the NMe groups are deshielded (^{1}H: 3.74−3.82, ^{13}C: 44.5−46.4 ppm) with respect to the CMe ones (^{1}H: 2.42−2.53, ^{13}C: 15.3−16.0 ppm). The XyNC ligand in **10c·TfO** is free to rotate about the Rh−C or Xy−N bond, giving rise to a single resonance for both Me groups (^{1}H: 2.04; ^{13}C: 18.2 ppm). In the ^{1}H NMR spectrum of **11·TfO**, the same trends are observed for the NMe, CMe (at 3.95 and 2.79 ppm, respectively), and Me protons of the XyNC ligand. However, one of the Xy groups shows two inequivalent Me groups due to its prevented rotation around the Xy−N bond, owing to its proximity to the Cp* ligand, if it is that of the XyNC ligand, or to the aryl group, if it is that of the iminoacyl group. We have also observed this behavior in some Xy iminoacyl palladium(II) complexes.[29]

IR Spectra. In the 3100−3326 cm^{-1} region, the IR show one (**9c·ClO$_4$**), two (**8·ClO$_4$**, **10a·TfO**), three (**1, 5·TfO**, **3**, **4a·ClO$_4$**, **4b·TfO**, **9a·ClO$_4$, 9d·ClO$_4$**), or four (**4a·Cl**) ν_{NH} bands. **9b·ClO$_4$** displays a very broad absorption that we assume to include two ν_{NH} bands. For complexes **8·ClO$_4$** and **9b·ClO$_4$**, the ν_{NH} bands along with two $\nu_{C=N}$ bands (Me-imam ligand: 1650−1708 cm^{-1}) and additionally, in **9b·ClO$_4$**, two $\nu_{C\equiv N}$ bands due to the MeCN ligand at 2136 and 2288 cm^{-1}, suggest the presence or both possible diastereoisomers of these complexes in the solid state. Correspondingly, the isolated isomer of its homologous **9c·ClO$_4$** shows only one band of each type in its spectrum.

Conclusion

We have isolated and characterized the first family of methyl amino complexes of rhodium, which includes neutral, mono-, and dicationic complexes with 1 to 3 $MeNH_2$ ligands, and the silver complex $[Ag(NH_2Me)_2]^+$, which is a key reagent in the synthesis of the dicationic complex [Rh(Cp*)-$(NH_2Me)_3$]$(TfO)_2$. We report the synthesis of [Ag{N(Me)=CMe_2}$_2$]ClO_4 and its use to prepare [Au{N(Me)=CMe_2}-(PPh_3)]ClO_4. Both are some of the few known methyl acetimino metal complexes. However, many attempts to prepare complexes [Rh(III)]N(Me)=CMe_2 by condensation of acetone with complexes [Rh(III)]NH_2Me or by transmetalatation using [Au{N(Me)=CMe_2}(PPh_3)]ClO_4 or [Ag-{N(Me)=CMe_2}$_2$]ClO_4 and different Rh(III) complexes gave instead complexes [Rh(III)]NH_2Me or [Rh(III)](Me-imam) (Me-imam = *N*,*N*′-N(Me)=C(Me)CH_2C(Me)$_2$NHMe. The latter are the result of the aldol condensation of the non-isolated [Rh(III)]{N(Me)=CMe_2}$_2$ complexes. The only [Rh-(III)](Me-imam) complex isolated and characterized from these reactions has been [Rh(Cp*)Cl(Me-imam)]ClO_4, from which dicationic [Rh(Cp*)(Me-imam)L]$(ClO_4)_2$ have been prepared. Acetophenone reacts with [Rh(Cp*)$(NH_2Me)_3$]-$(TfO)_2$ to give [Rh(Cp*){*C*,*N*-C_6H_4{C(Me)=N(Me)}-2}-(NH_2Me)]TfO, which is the first product of such a condensation and cyclometalation reaction, from which an adduct and an insertion product with XyNC have been prepared.

Acknowledgment. We thank Dirección General de Investigación, Ministerio de Educación y Ciencia, and FEDER for financial support (Grant CTQ2004-05396) and for a contract to I.V.H.

Supporting Information Available: CIF files for **9a·ClO$_4$**·acetone-d_6, **9c·ClO$_4$**, and **10a·TfO**. This material is available free of charge via the Internet at http://pubs.acs.org.

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