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The First Acetimino Complexes of Rh(III). 4-Imino-2-methylpentan-2-amino–Rh(III) Complexes through Metal-Assisted Intramolecular Aldol-Type Condensation of Two Acetimino Ligands

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$[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ (Cp^* = pentamethylcyclopentadienyl) reacts (i) with $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$ (1:2) to give $[Rh(Cp^*)(\mu\text{-}Cl)(NH{=}CMe_2)]_2(ClO_4)_2$ (**1**), which in turn reacts with PPh_3 (1:2) to give $[Rh(Cp^*)Cl(NH{=}CMe_2)(PPh_3)]ClO_4$ (**2**), and (ii) with $[Ag(NH{=}CMe_2)_2]ClO_4$ (1:2 or 1:4) to give $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (**3**) or $[Rh(Cp^*)(NH{=}CMe_2)_3](ClO_4)_2{\cdot}H_2O$ (**4**·H_2O), respectively. Complex **3** reacts (i) with XyNC (1:1, Xy = 2,6-dimethylphenyl) to give $[Rh(Cp^*)Cl(NH{=}CMe_2)(CNXy)]ClO_4$ (**5**), (ii) with Tl(acac) (1:1, acacH = acetylacetone) or with $[Au(acac)(PPh_3)]$ (1:1) to give $[Rh(Cp^*)(acac)(NH{=}CMe_2)]ClO_4$ (**6**), (iii) with $[Ag(NH{=}CMe_2)_2]ClO_4$ (1:1) to give **4**, and (iv) with (PPN)Cl (1:1, PPN = $Ph_3P{=}N{=}PPh_3$) to give $[Rh(Cp^*)Cl(imam)]Cl$ (**7**·Cl), which contains the imam ligand (*N,N*-$NH{=}C(Me)CH_2C(Me)_2NH_2$ = 4-imino-2-methylpentan-2-amino) that results from the intramolecular aldol-type condensation of the two acetimino ligands. The homologous perchlorate salt (**7**·ClO_4) can be prepared from **7**·Cl and $AgClO_4$ (1:1), by treating **3** with a catalytic amount of $Ph_2C{=}NH$, in an atmosphere of CO, or by reacting **4** with (PPN)Cl (1:1). The reactions of **7**·ClO_4 with $AgClO_4$ and PTo_3 (1:1:1, To = C_6H_4Me-4) or XyNC (1:1:1) give $[Rh(Cp^*)(imam)(PTo_3)](ClO_4)_2{\cdot}H_2O$ (**8**) or $[Rh(Cp^*)(imam)(CNXy)](ClO_4)_2$ (**9**), respectively. The crystal structures of **3** and **7**·Cl have been determined.

Introduction

Acetimine, one of the condensation products of acetone and ammonia,[1] is an unstable compound that decomposes after short periods of storage to give acetonine (2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine).[2] The difficulties associated with the preparation and handling of acetimine[3] may account for the scarcity of complexes with this ligand. In fact, acetimine itself has never been used in the various syntheses of the metal−acetimino complexes reported so far.[4−8] The synthesis by us of $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$ [6] and $[Ag(NH{=}CMe_2)_2]ClO_4$ [8] prompted us to check if they could transmetalate the acetimine ligand(s) to different metal complexes, thus providing a general method for preparing acetimino complexes. In fact, using $[Ag(NH{=}CMe_2)_2]ClO_4$,

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we have recently synthesized the first family of acetimino−Rh(I) complexes.[8]

On the other hand, complexes with the ligand 4-imino-2-methylpentan-2-amine (imam) are very scarce, and only nine of them (including the Br^-, NO_3^-, and ClO_4^- salts of the $[Ni(imam)_2]^{2+}$ cation) have been fully characterized by their X-ray crystal structures.[9] They were obtained by reacting some ammino complexes of Co(III)[10] or Ni(II) with acetone,[11] by treating $Cu(NO_3)_2$[12,13] or some Pd(II) complexes[7] with ammonia in acetone, or by reacting some Ru(III) complexes[14] with ammonium thiobenzoate and acetone or with ammonia and mesityl oxide. It was suggested that the imam ligand forms by the condensation of two NH_3 ligands and two Me_2CO molecules or one of mesityl oxide in a template-type reaction.[10,12,14] Surprisingly, the formation of the Pd(imam) complexes was explained[7] on the assumption that the imam ligand forms in equilibrium with other species in ammonia/acetone mixtures. However, no experimental or bibliographic evidence is provided in support of the existence of this ligand in such mixtures.

We have preliminarily reported the synthesis and some structural features of $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (**3**) and of the product from the aldol-type condensation of the two acetimino ligands in **3**, namely $[Rh(Cp^*)Cl(imam)]Cl$ (**7**·Cl) (imam = 4-imino-2-methylpentan-2-amino).[5] In this paper, we report (i) new types of Rh(III) complexes with one ($[Rh(Cp^*)Cl(NH{=}CMe_2)(L)]ClO_4$ (L = PPh_3, XyNC) and $[Rh(Cp^*)(acac)(NH{=}CMe_2)]ClO_4$), two ($[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$), or three ($[Rh(Cp^*)(NH{=}CMe_2)_3](ClO_4)_2$) acetimino ligands, (ii) a new example of aldol-type condensation of two acetimino ligands from $[Rh(Cp^*)(NH{=}CMe_2)_3](ClO_4)_2$, (iii) a new type of imam complexes ($[Rh(Cp^*)(imam)(L)](ClO_4)_2$ (L = PPh_3, XyNC)), and (iv) full details of the crystal structures of **3** and **7**·Cl.

Experimental Section

IR spectroscopy, elemental analyses, and melting point determinations were carried out as described elsewhere.[6] Molar conductivities were measured on ca. 5×10^{-4} M acetone solutions with a Crison Micro CM2200 conductimeter. The NMR spectra were recorded on Bruker Avance 200, 300, or 400 MHz spectrometers. Chemical shifts are referred to TMS (^1H and $^{13}C\{^1H\}$) and H_3PO_4 ($^{31}P\{^1H\}$). Unless otherwise stated, all reactions were carried out at room temperature without special precautions against moisture. CH_2Cl_2, acetone, and Et_2O were distilled before use from CaH_2, $KMnO_4$, and Na/benzophenone, respectively. THF was distilled under nitrogen from Na/benzophenone. Other solvents (*n*-pentane (Baker) and *n*-hexane (Scharlau)) and reagents ($AgClO_4$ (Aldrich), PPh_3, PTo_3, XyNC (Fluka), and (PPN)Cl (Lancaster)) were obtained from commercial sources and used as received. The complexes $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$,[15] $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$,[6] $[Ag(NH{=}CMe_2)_2]ClO_4$,[8] and Tl(acac)[16] were prepared according to literature methods.

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

Synthesis of $[Rh(Cp^*)(\mu\text{-}Cl)(NH{=}CMe_2)]_2(ClO_4)_2$ (1). To a suspension of $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ (226 mg, 0.366 mmol) in acetone (15 mL) was added $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$ (450 mg, 0.731 mmol). After 2 h of being stirred, the orange suspension was filtered, and the solid was washed with CH_2Cl_2 (3 × 5 mL) and air-dried to give **1** as an orange powder. Yield: 232 mg, 74%. Mp: 218 °C. ^1H NMR (200 MHz, DMSO-d_6): δ 1.64 (s, 15 H, Me, Cp*), 2.30 (s, 3 H, Me), 2.37 (s, 3 H, Me), 10.07 (br, 1 H, NH). ^{13}C NMR (50 MHz, DMSO-d_6): δ 8.76 (Me, Cp*), 27.14 (Me), 28.87 (d, Me, $^3J_{CRh}$ = 2.2 Hz), 100.39 (d, C, Cp*, $^1J_{CRh}$ = 7.3 Hz), 191.58 (C=N). IR (cm^{-1}): ν(NH) 3242, ν(C=N) 1662, 1644. Anal. Calcd for $C_{26}H_{44}Cl_4N_2O_8Rh_2$: C, 36.30; H, 5.16; N, 3.26. Found: C, 36.32; H, 5.14; N, 3.27.

Synthesis of $[Rh(Cp^*)Cl(NH{=}CMe_2)(PPh_3)]ClO_4$ (2). To a suspension of **1** (146.2 mg, 0.17 mmol) in acetone (20 mL) was added PPh_3 (92 mg, 0.35 mmol). After being stirred for 1 h, the resulting solution was filtered through a short pad of Celite, and the filtrate was concentrated under vacuum (to ca. 2 mL). Upon addition of Et_2O (25 mL), **2** precipitated as a yellow powder, which was filtered and air-dried. Yield: 232 mg, 99%. Mp: 179 °C dec. ^1H NMR (400 MHz, $CDCl_3$): δ 1.50 (d, 15 H, Me, Cp*, $^4J_{HP}$ = 3.53 Hz), 1.91 (d, 3 H, Me, $^4J_{HH}$ = 0.64 Hz), 2.22 (s, 3 H, Me), 7.55 (m, 15 H, Ph), 8.69 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.11 (Me, Cp*), 26.88 (Me), 30.17 (Me), 100.65 (dd, C, Cp*, $^1J_{CRh}$ = 6.65 Hz, $^2J_{CP}$ = 2.42 Hz), 128.16 (*ipso*-C), 128.69 (d, *o*-C, $^2J_{CP}$ = 10.3 Hz), 131.36 (*m*-C), 134.6 (d, *p*-C, $^4J_{CP}$ = 8.9 Hz), 191.27 (C=N). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 35.70 (d, $^1J_{PRh}$ = 135.7 Hz). IR (cm^{-1}): ν(NH) 3273, ν(C=N) 1644. Λ_M: 158 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{31}H_{37}Cl_2NO_4PRh$: C, 53.77; H, 5.39; N, 2.02. Found: C, 53.92; H, 5.42; N, 1.98.

Synthesis of $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (3). To a suspension of $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ (144 mg, 0.233 mmol) in acetone (30 mL) was added $[Ag(NH{=}CMe_2)_2]ClO_4$ (150 mg, 0.467 mmol). The reaction mixture was stirred for 30 min, and was filtered through a short pad of Celite. The filtrate was concentrated under vacuum (to ca. 1 mL), and Et_2O (25 mL) was added to precipitate a solid that was filtered, washed with Et_2O (5 mL), and air-dried to give **3** as an orange powder. Yield: 194 mg, 85%. Mp: 180 °C dec. ^1H NMR (300 MHz, $CDCl_3$): δ 1.65 (s, 15 H, Me, Cp*), 2.37 (s, 6 H, Me), 2.41 (d, 6 H, Me, $^4J_{HH}$ = 1.2 Hz), 9.53 (br, 2 H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.08 (Me, Cp*), 26.77 (Me), 30.29 (d, Me, $^3J_{CRh}$ = 1.2 Hz), 95.37 (d, C, Cp*, $^1J_{CRh}$ = 8 Hz), 190.67 (C=N). IR (cm^{-1}): ν(NH) 3250, ν(C=N) 1642. Λ_M: 139 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{16}H_{29}Cl_2N_2O_4Rh$: C, 39.44; H, 6.00; N, 5.75. Found: C, 39.16; H, 6.03; N, 5.62. Single crystals of **3** grew by the liquid diffusion method using CH_2Cl_2 and Et_2O.

Synthesis of $[Rh(Cp^*)(NH{=}CMe_2)_3](ClO_4)_2{\cdot}H_2O$ (4·H_2O). To a solution of **3** (100 mg, 0.21 mmol) in CH_2Cl_2 (20 mL) was added $[Ag(NH{=}CMe_2)_2]ClO_4$ (66 mg, 0.21 mmol). The resulting suspen-

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sion was stirred for 5 h, and was filtered through a short pad of Celite. When the filtrate was concentrated under vacuum (to ca. 5 mL), a yellow solid precipitated that was filtered and dried under nitrogen to give **4**·H_2O as a yellow powder. Yield: 70 mg, 54%. Mp: 228 °C dec. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.59 (s, 15 H, Me, Cp*), 1.78 (s, 9 H, Me), 2.30 (s, 9 H, Me), 3.31 (br, 2 H, H_2O), 10.06 (br, 3 H, NH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 8.37 (Me, Cp*), 25.63 (Me), 29.10 (Me), 97.11 (d, C, Cp*, $^1J_{CRh}$ = 7.5 Hz), 190.51 (C═N). IR (cm^{-1}): ν(OH) 3600, ν(NH) 3240, ν(C═N) 1651, 1634. Λ_M: 198 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{19}H_{38}Cl_2N_3O_9Rh$: C, 36.44; H, 6.12; N, 6.71. Found: C, 36.43; H, 5.83; N, 6.74.

Synthesis of [Rh(Cp*)Cl(NH═CMe$_2$)(CNXy)]ClO$_4$ (5). To a suspension of **3** (100 mg, 0.205 mmol) in dry THF under nitrogen was added XyNC (27 mg, 0.206 mmol). After being stirred for 1 h, the resulting suspension was filtered, and the collected solid was washed with Et_2O (3 × 5 mL) and air-dried to give **5** as a yellow powder. Yield: 72 mg, 62%. Mp: 103 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.87 (s, 15 H, Me, Cp*), 2.38 (s, 3 H, Me), 2.45 (d, 3 H, Me, $^4J_{HH}$ = 1.2 Hz), 2.48 (s, 6 H, Me, Xy), 7.20 (m, 3 H, Xy), 9.49 (br, 1 H, NH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 9.68 (Me, Cp*), 18.76 (Me, Xy), 27.35 (Me), 30.16 (d, Me, $^3J_{CRh}$ = 1.5 Hz), 101.55 (d, C, Cp*, $^1J_{CRh}$ = 7.5 Hz), 128.2 (*m*-C), 130.2 (*p*-C), 135.9 (*o*-C), 190.8 (C═N) IR (cm^{-1}): ν(NH) 3177, ν(C≡N) 2170, ν(C═N) 1664, 1645. Λ_M: 170 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{22}H_{31}Cl_2N_2O_4Rh$: C, 47.08; H, 5.57; N, 4.99. Found: C, 46.66; H, 5.72; N, 5.01.

Synthesis of [Rh(Cp*)(acac)(NH═CMe$_2$)]ClO$_4$ (6). To a solution of **3** (83 mg, 0.17 mmol) in acetone (20 mL) was added Tl(acac) (52 mg, 0.17 mmol). After 1 h of being stirred, the resulting suspension was filtered through a short pad of Celite. The yellow filtrate was concentrated under vacuum (to ca. 1 mL), and Et_2O (25 mL) was added to precipitate a solid that was filtered and dried under nitrogen to give **6** as a yellow powder. Yield: 74 mg, 88%. Mp: 193 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (s, 15 H, Me, Cp*), 1.95 (s, 6 H, Me), 2.21 (s, 3 H, Me), 2.34 (d, 3 H, Me, $^4J_{HH}$ = 0.65 Hz), 5.07 (s, 1 H, CH), 8.71 (br, 1 H, NH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 8.35 (Me, Cp*), 25.54 (Me), 28.08 (Me), 29.69 (d, Me, $^3J_{CRh}$ = 1.23 Hz), 93.66 (d, C, Cp*, $^1J_{CRh}$ = 8.8 Hz), 98.55 (d, CH, $^3J_{CRh}$ = 1.25 Hz), 187.31 (C═N), 188.57 (C═O). IR (cm^{-1}): ν(NH) 3247, ν(C═N) 1663, ν(C═O) 1580. Λ_M: 165 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{18}H_{29}ClNO_6Rh$: C, 43.78; H, 5.92; N, 2.84. Found: C, 43.89; H, 5.96; N, 3.10.

Synthesis of [Rh(Cp*)Cl(imam)]Cl [7·Cl, imam = NH═C(Me)CH$_2$C(Me)$_2$NH$_2$]. To a solution of **3** (120 mg, 0.25 mmol) in acetone (15 mL) was added (PPN)Cl (141 mg, 0.25 mmol). After being stirred for 4 h, the resulting suspension was filtered, and the collected solid was washed with Et_2O (3 × 5 mL) and air-dried to give **7**·Cl as an orange powder. Yield: 54 mg, 52%. Mp: 210 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (s, 3 H, Me), 1.63 (s, 3 H, Me), 1.93 (s, 15 H, Me, Cp*), 2.19, 2.45 (AB system, 2 H, CH_2, J_{AB} = 16.5 Hz), 2.53 (s, 3 H, Me), 2.95 (d, 1 H, NH_2, $^2J_{HH}$ = 11 Hz), 6.31 (d, 1 H, NH_2, $^2J_{HH}$ = 11 Hz), 11.39 (br, 1 H, NH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 10.13 (Me, Cp*), 23.95 (Me), 31.25 (Me), 32.08 (Me), 48.41 (CH_2), 96.50 (d, C, Cp*, $^1J_{CRh}$ = 7.8 Hz), 185.13 (C═N). IR (cm^{-1}): ν(NH) 3218, 3192, 3110, ν(C═N) 1654, δ(NH_2) 1600. MS (FAB$^+$) (*m*/*z*, %): [M$^+$] 386.94, 100, [M$^+$ − Cl] 350.97, 26. Anal. Calcd for $C_{16}H_{29}Cl_2N_2Rh$: C, 45.41; H, 6.91; N, 6.62. Found: C, 45.23; H, 6.65; N, 6.33. Single crystals of **7**·Cl were obtained by the liquid diffusion method using CH_2Cl_2 and Et_2O.

[Rh(Cp*)Cl(imam)]ClO$_4$ (7·ClO$_4$). To a suspension of **7**·Cl (167 mg, 0.39 mmol) in acetone (40 mL) was added $AgClO_4$ (82 mg, 0.40 mmol). After 30 min of being stirred, the resulting suspension was filtered through Celite. The yellow filtrate was concentrated under vacuum (to ca. 1 mL), and Et_2O (25 mL) was added to precipitate a solid that was filtered and air-dried to give **7**·ClO_4 as an orange powder. Yield: 183 mg, 95%. Mp: 215 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (s, 3 H, Me), 1.54 (s, 3 H, Me), 1.76 (s, 15 H, Me, Cp*), 2.34, 2.56 (AB system, 2 H, CH_2, J_{AB} = 16.7 Hz), 2.41 (d, 3 H, Me, $^4J_{HH}$ = 1.1 Hz), 3.31 (d, 1 H, NH_2, $^2J_{HH}$ = 11.2 Hz), 4.22 (d, 1 H, NH_2, $^2J_{HH}$ = 11.2 Hz), 9.58 (br, 1 H, NH). IR (cm^{-1}): ν(NH) 3291, 3272, 3256, 3241, ν(C═N) 1657, δ(NH_2) 1585. Λ_M: 160 Ω^{-1} cm^2 mol^{-1}. MS (FAB$^+$): (*m*/*z*, %): [M$^+$] 386.91, 100, [M$^+$ − Cl] 350.93, 52. Anal. Calcd for $C_{16}H_{29}Cl_2N_2O_4Rh$: C, 39.44; H, 6.00; N, 5.75. Found: C, 39.43; H, 6.00; N, 5.61.

Synthesis of [Rh(Cp*)(imam)(PTo$_3$)](ClO$_4$)$_2$·H$_2$O (8). To a solution of **7**·ClO_4 (47 mg, 0.10 mmol) in acetone (20 mL) were successively added $AgClO_4$ (20 mg, 0.10 mmol) and PTo_3 (29 mg, 0.10 mmol) with an interval of 2 min. After 1 h of being stirred, the resulting suspension was concentrated to dryness under vacuum. The residue was stirred with CH_2Cl_2 (10 mL), and the suspension was filtered through a short pad of Celite. The yellow filtrate was concentrated under vacuum (to ca. 1 mL), and Et_2O (30 mL) was added to precipitate a solid that was filtered and air-dried to give **8** as a lemon yellow powder. Yield: 58 mg, 69%. Mp: 210 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.08 (d, 1 H, CH_2, $^2J_{HH}$ = 18 Hz), 1.08 (s, 3 H, Me), 1.25 (s, 3 H, Me), 1.60 (d, 15 H, Me, Cp*, $^4J_{HP}$ = 3 Hz), 1.77 (s, 2 H, H_2O), 1.90 (d, 1 H, CH_2, $^2J_{HH}$ = 18 Hz), 2.40 (s, 3 H, Me), 2.44 (s, 9 H, Me, To), 2.75 (d, 1 H, NH_2, $^2J_{HH}$ = 9 Hz), 5.21 (d, 1 H, NH_2, $^2J_{HH}$ = 12 Hz), 7.32−7.46 (m, 12 H, To), 10.29 (br, 1 H, NH). ^{13}C NMR (50 MHz, $CDCl_3$): δ 9.47 (d, Me, Cp*, $^2J_{CP}$ = 1.1 Hz), 21.45 (d, Me, To, $^5J_{CP}$ = 1.6 Hz), 25.2 (Me), 31.08 (Me), 31.71 (Me), 49.30 (CH_2), 102.76 (dd, C, Cp*, $^1J_{CRh}$ = 5.9 Hz, $^2J_{CP}$ = 1.6 Hz), 123.35 (d, *ipso*-*C*, $^1J_{CP}$ = 47.3 Hz), 130.65 (d, *o*-C, $^2J_{CP}$ = 10.7 Hz), 134.1 (d, *m*-C, $^3J_{CP}$ = 5.4 Hz), 143.6 (d, *p*-C, $^4J_{CP}$ = 2.7 Hz), 189.70 (C═N). ^{31}P NMR (121 MHz, $CDCl_3$): δ 34.1 (d, $^1J_{PRh}$ = 134.1 Hz). IR (cm^{-1}): ν(OH) 3604, ν(NH) 3289, 3241, ν(C═N) 1644, δ(NH_2) 1597, 1583. Λ_M: 210 Ω^{-1} cm^2 mol^{-1}. MS (FAB$^+$) (*m*/*z*, %): [M$^+$ − ClO_4^-], 754.84, 5, [M$^+$ − ClO_4^- − PTo_3] 450.96, 66, [M$^+$ − 2ClO_4^- − PTo_3] 350.98, 100. Anal. Calcd for $C_{37}H_{52}Cl_2N_2O_9PRh$: C, 50.87; H, 6.00; N, 3.21. Found: C, 51.12; H, 5.96; N, 3.37.

Synthesis of [Rh(Cp*)(imam)(CNXy)](ClO$_4$)$_2$ (9). Solid $AgClO_4$ (26 mg, 0.125 mmol), **3** (60 mg, 0.123 mmol), and XyNC (16 mg, 0.122 mmol) were placed in a flask under nitrogen. Acetone (20 mL) was added, and the resulting suspension was stirred for 2 h. The mixture was filtered through a short pad of Celite, and the yellow filtrate was concentrated under vacuum (to ca. 1 mL). Upon the addition of Et_2O (25 mL), a solid precipitated that was filtered and dried under nitrogen to give **9** as a lemon yellow powder. Yield: 79 mg, 95%. Mp: 155 °C dec. ^{1}H NMR (300 MHz, acetone-d_6): δ 1.36 (s, 3 H, Me), 1.41 (s, 3 H, Me), 2.05 (s, 15 H, Me, Cp*), 2.49 (s, 6 H, Me, Xy), 2.56 (d, 3 H, Me, $^4J_{HH}$ = 3 Hz), 2.71, 2.87 (AB system, 2 H, CH_2, J_{AB} = 16.5 Hz), 4.14 (d, 1 H, NH_2, $^2J_{HH}$ = 12 Hz), 5.32 (d, 1 H, NH_2, $^2J_{HH}$ = 12 Hz), 7.33 (m, 3 H, Xy), 10.55 (br, 1 H, NH). ^{13}C NMR (100 MHz, acetone-d_6): δ 9.50 (s, Me, Cp*), 18.97 (Me, Xy), 26.96 (Me), 28.25 (Me), 31.48 (Me), 48.74 (CNH_2), 50.77 (CH_2), 103.91 (d, C, Cp*, $^1J_{CRh}$ = 6.6 Hz), 129.15 (*m*-C) 131.51 (*p*-C), 137.21 (*o*-C), 191.05 (C═N). IR (cm^{-1}): ν(NH) 3243, 3161, ν(C≡N) 2169, ν(C═N) 1659, δ(NH_2) 1598. Λ_M: 180 Ω^{-1} cm^2 mol^{-1}. MS (FAB$^+$) (*m*/*z*, %): [M$^+$ − ClO_4^-] 581.99, 5, [M$^+$ − ClO_4^- − XyNC] 450.93, 52, [M$^+$ − 2

Table 1. Crystal Data for Compounds **3** and **7**·Cl

	3	**7**·Cl
formula	$C_{16}H_{29}Cl_2N_2O_4Rh$	$C_{16}H_{29}Cl_2N_2Rh$
cryst size (mm^3)	0.25 × 0.19 × 0.16	0.11 × 0.11 × 0.10
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$C2/c$
a (Å)	8.5542(3)	13.5331(6)
b (Å)	15.9110(6)	12.0370(4)
c (Å)	15.4317(6)	22.7027(8)
α (deg)	90	90
β (deg)	102.1380(10)	94.644(4)
γ (deg)	90	90
V ($Å^3$)	2053.39(13)	3686.1(2)
Z	4	8
ρ_{calcd} (mg m^{-3})	1.576	1.525
M_r	487.22	423.22
T (K)	100(2)	133(2)
F(000)	1000	1744
index ranges	$-10 \le h \le 10$	$-19 \le h \le 19$
	$-20 \le k \le 20$	$-17 \le k \le 17$
	$-19 \le l \le 19$	$-32 \le l \le 32$
μ (Mo Kα; mm^{-1})	1.21	1.11
θ range (deg)	1.35−27.10	1.80−30.50
abs corr	semiempirical from equiv	semiempirical from equiv
no. of reflns collected	23 574	42 399
no. of indep reflns	8876	5620
R_{int}	0.0150	0.0458
transm	0.8419/0.7682	0.8883/0.7774
data/restraints/params	8876/15/479	5620/0/210
R1 [$I > 2\sigma(I)$]	0.0198	0.0262
wR2 (all reflns)	0.0488	0.0607
largest difference peak and hole (e $Å^{-3}$)	0.482 and −0.408	0.765 and −0.366

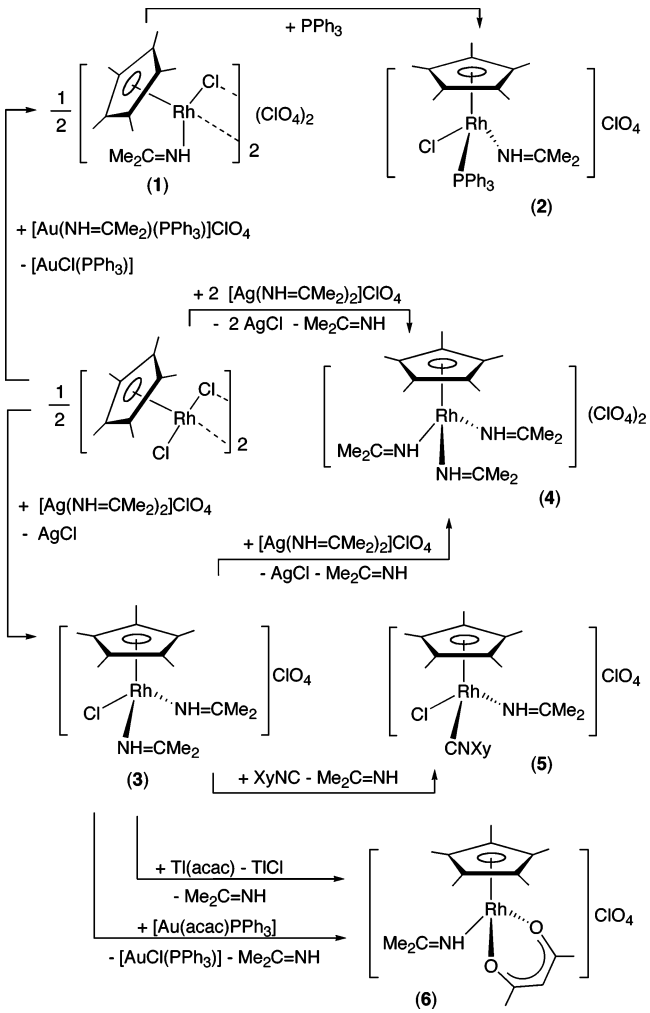
ClO_4^- − XyNC] 350.95, 100. Anal. Calcd for $C_{25}H_{38}Cl_2N_3O_8Rh$: C, 44.00; H, 5.61; N, 6.16. Found: C, 43.63; H, 5.63; N, 6.15.

X−ray Structure Determinations. The structures of **3** and **7**·Cl were determined (Table 1). Data were registered on Bruker SMART APEX at 100 K (**3**) and Bruker SMART 1000 at 133 K CCD diffractometers, respectively, using Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using the program SADABS. Structures were refined anisotropically on F^2 using program system SHELXL.[17] Hydrogen atoms were included as follows: NH free, rigid methyls, others riding.

Results and Discussion

Synthesis of Acetimino Complexes of Rh(III). The imine transfer reaction between $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$ and $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ (2:1, in acetone, Scheme 1) produced the dinuclear complex $[Rh(Cp^*)(\mu\text{-}Cl)(NH{=}CMe_2)]_2(ClO_4)_2$ (**1**) in good yield, which could easily be separated from the byproduct $[AuCl(PPh_3)]$ because of the insolubility of **1** in acetone and CH_2Cl_2. The use of gold(I) complexes as transmetallating agents[6,18,19] is increasing. We have used this method for the synthesis of other gold complexes.[6,19] The addition of 2 equiv of PPh_3 to an acetone suspension of **1** produced a solution from which $[Rh(Cp^*)Cl(NH{=}CMe_2)(PPh_3)]ClO_4$ (**2**) was obtained in almost quantitative yield. However, the reactions of **1** with chloride (Me_4NCl (1:4) or PPNCl (1:2), both in acetone), expected to produce bridge splitting with formation of $[Rh(Cp^*)Cl_2(NH{=}CMe_2)]$, instead gave mixtures of compounds (by ^1H NMR) that we could not separate.

Scheme 1



The mononuclear bis(acetimino)−Rh(III) complex $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (**3**) formed along with AgCl from the reaction of $[Ag(NH{=}CMe_2)_2]ClO_4$ with $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ (2:1, in acetone or CH_2Cl_2), and could be isolated in good yield.

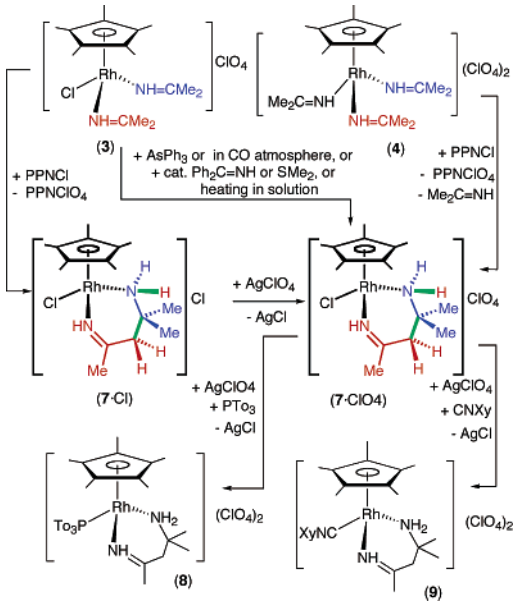
The reaction of **3** with $[Ag(NH{=}CMe_2)_2]ClO_4$ (1:1, in CH_2Cl_2) produced the tris(acetimino) complex $[Rh(Cp^*)(NH{=}CMe_2)_3](ClO_4)_2{\cdot}H_2O$ (**4**·H_2O), which could also be obtained directly from $[Rh(Cp^*)Cl(\mu\text{-}Cl)]_2$ and 4 equiv of $[Ag(NH{=}CMe_2)_2]ClO_4$. **4** is rather hygroscopic, and was isolated as a monohydrate even though it was filtered and dried under nitrogen. The yield was only moderate, but we

(17) Sheldrick, G. M. *SHELXL*; University of Göttingen: Göttingen, Germany.

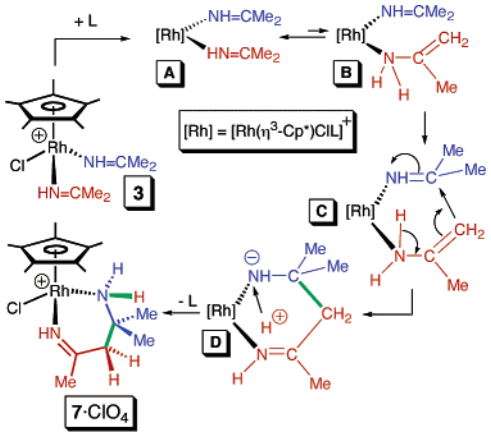
(18) Singh, A.; Sharp, P. R. *J. Chem. Soc., Dalton Trans.* **2005**, 2080. Bruce, M. I.; Humphrey, P. A.; Melino, G.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Inorg. Chim. Acta* **2005**, *358*, 1453. Contel, M.; Stol, M.; Casado, M. A.; van Klink, G. P. M.; Ellis, D. D.; Spek, A. L.; van Koten, G. *Organometallics* **2002**, *21*, 4556. Ferrer, M.; Rodríguez, L.; Rossell, O.; Lima, J. C.; Gómez-Sal, P.; Martín, A. *Organometallics* **2004**, *23*, 5096. Gregory, J.; Ingold, C. K. *J. Chem. Soc. B* **1969**, 276. Bennett, M. A.; Bhargava, S. K.; Griffiths, K. D.; Robertson, G. B.; Wickramasinghe, W. A.; Willis, A. C. *Angew. Chem., Int. Ed.* **1987**, *26*, 258.

(19) Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Jones, P. G. *Organometallics* **1997**, *16*, 5628. Vicente, J.; Chicote, M. T.; Abrisqueta, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 497. Vicente, J.; Chicote, M. T.; Abrisqueta, M. D.; Alvarez-Falcón, M. M. *J. Organomet. Chem.* **2002**, *663*, 40. Vicente, J.; Chicote, M. T.; Jones, P. G. *Inorg. Chem.* **1993**, *32*, 4960.

Scheme 2



Scheme 3



could not improve it by adding Et_2O to complete the precipitation because, in this case, **4**·H_2O precipitated along with an unidentified impurity.

Complex **3** reacted with XyNC (1:1, THF, under nitrogen) to give [Rh(Cp*)Cl(NH═CMe_2)(CNXy)]ClO_4 (**5**), which could not be obtained directly from **1** and XyNC (1:2, THF), although it was identified by ^{1}NMR in the resulting mixture.

The reaction between equimolar amounts of **3** and [Au(acac)(PPh_3)] in acetone, which we carried out in an attempt to replace the NH hydrogen atom of one of the acetimino ligands by the isolatable $AuPPh_3$ group, instead gave the complex [Rh(Cp*)(acac)(NH═CMe_2)]ClO_4 (**6**), which was isolated in good yield. It could also be obtained by using Tl(acac) instead of [Au(acac)(PPh_3)]. Complex **6** is rather hygroscopic, and was isolated under nitrogen.

Synthesis of 4-Imino-2-methylpentan-2-amino Complexes of Rh(III). When we reacted **3** with PPNCl (1:1, acetone, 4 h) in an attempt to prepare the neutral monoacetimino derivative [Rh(Cp*)Cl_2(NH═CMe_2)], which we could not obtain from **1** and PPNCl, an orange suspension of [Rh(Cp*)Cl(imam)]Cl (**7**·Cl; imam = κ^2-*N*,*N*-4-imino-2-methylpentan-2-amino) formed, in which the unexpected imam ligand results from the aldol-like condensation of two acetimino ligands (Scheme 2).

The homologous perchlorate salt [Rh(Cp*)Cl(imam)]ClO_4 (**7**·ClO_4) was obtained in almost quantitative yield by reacting **7**·Cl with $AgClO_4$ (1:1, acetone, 30 min) or **4** with PPNCl (1:1, acetone, 7 h). Notice that the reaction of **4** with PPNCl does not produce the substitution of acetimino by chloro to give complex **3**. In fact, **3** was not even detected in the reaction mixture. Although **3** remains unchanged after being stirred in acetone at room temperature for 24 h, we have found that, surprisingly, it converts quantitatively into **7**·ClO_4 when the same acetone solution is stirred for 24 h under a CO atmosphere of 1.8 bar, or is treated with a catalytic amount of Ph_2C═NH (1:0.1, 24 h). Complex **7**·ClO_4 also forms as the major product when **3** is reacted with an equimolar amount of $AsPh_3$ (acetone, 24 h) or a catalytic amount of SMe_2 (1:0.1, acetone, 24 h), or when it is heated at 70 °C in solution (CH_2Cl_2 or acetone, in a Carius tube) for 24 h. However, in all these cases, a small amount of another product was detected by ^{1}H NMR.

As we have mentioned in the Introduction, all the previous data on imam metal complexes suggest that this ligand forms from the condensation of acetone or mesityl oxide with ammonia in a template reaction assisted by a base.[12,20] The formation of complexes **7**·Cl and **7**·ClO_4 shows for the first time that the imam ligand can form by an intramolecular aldol-type self-condensation of two acetimino ligands, promoted by gentle heating or by the addition of various ligands. An intermolecular process involving the attack of a free acetimine molecule (generated by a replacement or dissociation process) to an acetimino ligand can be ruled out, as the reactions of **3** with PPh_3, XyNC, or [Ag(NH═CMe_2)$_2$]ClO_4 (1:1) gave the corresponding mono- (**2**, **5**) or triacetimino (**4**) products (by NMR), respectively, whereas no imam complex could be detected despite the presence of free acetimine in such reaction mixtures.

On the assumption that the same mechanism applies to all the reactions of **3** with L to give **7**·ClO_4, the ability of CO to promote the condensation process allows us to conclude that the role of the added ligand is not that of the base usually required as the catalyst in aldol condensations. However, it is evident that the coordination of L can modify both the electronic properties of the metal (changing the coordination mode of Cp* from η^5 to η^3 (**A** in Scheme 3), among other effects) and/or the geometry of the complex (change in the coordination number or relative disposition of the ligands, particularly the two acetimino ligands). The latter seems to be the most important effect because (i) condensation also occurs in the absence of added L upon gentle heating of **3** and (ii) the nature of the ligands capable of effecting condensation ranges from σ and π donor (Cl^-, SMe_2) to π acceptor/weak σ donor (CO). Similarly, the observed transformation of **4** into **7**·ClO_4 upon addition of PPNCl could take place by coordination of chloride, condensation of two acetimino ligands into the chelating imam, and displacement of the most labile acetimino ligand.

(20) Curtis, N. F.; Powell, H. K. J.; Puschmann, H.; Rickard, C. E. F.; Waters, J. M. *Inorg. Chim. Acta* **2003**, *355*, 25.

Scheme 3 shows a reasonable proposal for this rearrangement involving the imine−enamine tautomerization of one of the ligands (**A** → **B**). This, along with the modified geometrical and/or electronic properties of the complex, could help the C−C coupling (**C**) that gives the imino−imido intermediate (**D**) and a proton that would migrate to the negatively charged imido nitrogen, the final step being the dissociation of L to give **7**·ClO_4.

Note that (i) the condensation involves the formation of a new C−C bond and the transfer of one proton between two nitrogen atoms without the need for an external base, (ii) the added ligands responsible for the condensation act catalytically, (iii) the changes necessary to effect condensation in **3** can be achieved by gentle heating, and (iv) any ligand capable of replacing one of the acetimino ligands in **1**·ClO_4, such as PPh_3 or XyNC, precludes the synthesis of **7**.

At present, we are studying the possibility of obtaining complexes with the terdentate imino−bis(amino) ligand $NH{=}C(Me)CH_2C(NH_2)C(Me)CH_2C(Me_2)NH_2$ that would result from the further reaction between the imino moiety of a $NH{=}C(Me)CH_2C(NH_2)Me_2$ ligand and an acetimino ligand. With this intention, we attempted the synthesis of $[Rh(Cp^*)(NH{=}CMe_2)\{NH{=}C(Me)CH_2C(NH_2)Me_2\}](ClO_4)_2$ by reacting **7**·ClO_4 with equimolar amounts of $[Ag(NH{=}CMe_2)_2]ClO_4$ (CH_2Cl_2) or $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$ (acetone). However, although the complex $[Rh(Cp^*)(NH{=}CMe_2)\{NH{=}C(Me)CH_2C(NH_2)Me_2\}](ClO_4)_2$ is the major product in both reactions (by ^{1}H NMR (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, $^2J_{HH}$ = 17.4 Hz), 2.28 (s, 3 H, Me), 2.41 (d, 3 H, Me, $^4J_{HH}$ = 0.9 Hz), 2.45 (d, 3 H, Me, $^4J_{HH}$ = 1.5 Hz), 2.63 (d, 1 H, CH_2, $^2J_{HH}$ = 17.4 Hz), 4.03 (d, 1 H, NH_2, $^2J_{HH}$ = 11.5 Hz), 4.58 (d, 1 H, NH_2, $^2J_{HH}$ = 11.5 Hz) 9.68 (s, br, 1 H, NH), 10.76 (s, br, 1 H, NH)), it is contaminated with small amounts of **7**·ClO_4, which so far we have not been able to separate.

Crystal Structures of $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]ClO_4$ (3) and $[Rh(Cp^*)Cl\{NH{=}C(Me)CH_2C(NMe_2)NH_2\}]Cl$ (7·Cl). The structure of **3** involves two independent $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]^+$ cations displaying only small differences in bond distances and angles (one of them is represented in Figure 1). Both cations, $[Rh(Cp^*)Cl(NH{=}CMe_2)_2]^+$ and $[Rh(Cp^*)Cl(imam)]^+$ (Figure 2), exhibit a pseudo-octahedral "three-legged piano stool" geometry, with the Cp* group occupying three *fac* coordination sites.

The Rh−Cl (**3**: 2.4069(7), 2.4114(7) Å; **7**: 2.4074(5) Å), Rh−N(amine) (**7**: 2.1539(16) Å), Rh−N(imine) (**3**: 2.092(2)-2.105(2) Å; **7**: 2.0851(16) Å), and C=N (**3**: 1.267(3)−1.283(3) Å; **7**: 1.274(2) Å) bond distances are in the ranges found for other Cp*−Rh(III) complexes (2.335−2.474, 2.016−2.214, 2.067−2.182, and 1.148−1.384 Å, respectively, for Rh−Cl, Rh−N(amine), Rh−N(imine), and C=N).[9] The N−Rh−Cl (**3**: 92.15(6), 88.82(6), 92.38(6), 89.69(6)°; **7**: 85.76(4), 86.11(5)°) and N−Rh−N (**3**: 83.96(8), 84.09(9)°; **7**: 88.34(6)°) angles are close to those expected for an octahedral disposition. The Cp*−Rh moieties do not display special features.

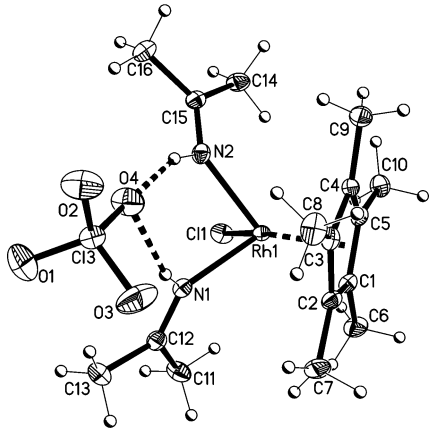


Figure 1. Ellipsoid representation of the cation in complex **3** (50% probability level). Selected bond lengths (Å) and angles (deg): Rh(1)−N(1) 2.096(2), Rh(1)−N(2) 2.104(2), Rh(1)−C(1) 2.160(2), Rh(1)−C(2) 2.163(3), Rh(1)−C(3) 2.128(3), Rh(1)−C(4) 2.172(2), Rh(1)−C(5) 2.171(2), Rh(1)−Cl(1) 2.4069(7), N(1)−C(12) 1.276(3), N(2)−C(15) 1.272(4); N(1)−Rh(1)−N(2) 83.96(8), N(1)−Rh(1)−Cl(1) 92.15(6), N(2)−Rh(1)−Cl(1) 88.82(6), C(12)−N(1)−Rh(1) 134.66(18), C(15)−N(2)−Rh(1) 133.64(19).

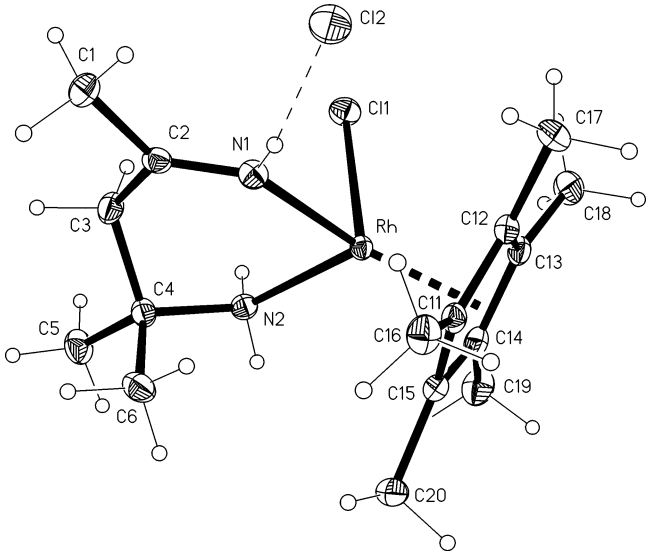


Figure 2. Ellipsoid representation of complex **7**·Cl (50% probability level). Selected bond lengths (Å) and angles (deg): Rh−N(1) 2.0851(16), Rh−N(2) 2.1539(16), Rh−C(11) 2.1588(17), Rh−C(12) 2.1595(18), Rh−C(13) 2.1804(18), Rh−C(14) 2.1614(18), Rh−C(15) 2.1654(18), Rh−Cl(1) 2.4074(5), N(1)−C(2) 1.274(2), N(2)−C(4) 1.493(2); N(1)−Rh−N(2) 88.34(6), N(1)−Rh−Cl(1) 85.76(4), N(2)−Rh−Cl(1) 86.11(5), C(2)−N(1)−Rh 130.92(14), C(4)−N(2)−Rh 118.77(11), N(1)−C(2)−C(3) 121.19(17), C(2)−C(3)−C(4) 115.95(15), N(2)−C(4)−C(3) 108.02(15).

The cations of **3** aggregate into dimers (Figure 3 and the Supporting Information) because of the formation of C−H···Cl hydrogen bonds. Additionally, each dimer is hydrogen-bonded to two others via two perchlorate anions, giving rise to a ribbon structure.

In complex **7**·Cl, the six-membered Rh−N(1)−C(2)−C(3)−C(4)−N(2) chelate ring adopts a screw-boat conformation with the C(3) and the C(4) atoms lying 0.27 Å below and 0.57 Å above the plane, respectively, of the other four atoms. The cations of **7**·Cl aggregate into dimers (Figure 4 and the Supporting Information) because of the formation of N−H···Cl hydrogen bonds between the coordinated chlorine atom in one molecule and one of the NH_2 hydrogen

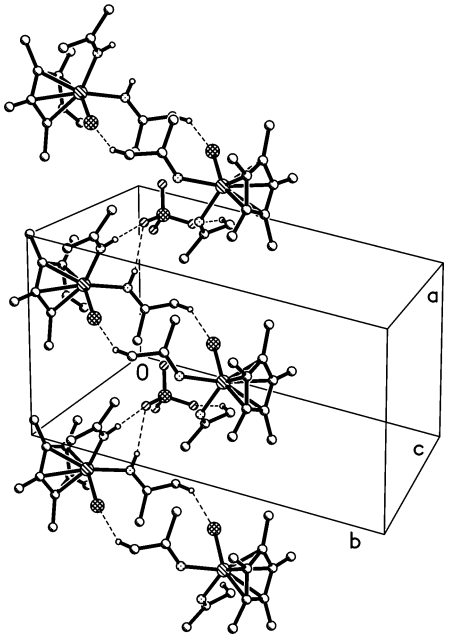


Figure 3. Hydrogen bonds for **3**.

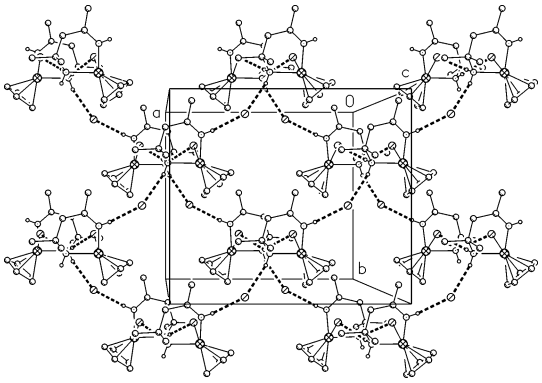


Figure 4. Hydrogen bonds for **7**·Cl.

atoms in another molecule. Additionally, each of these dimers is conected with four others through N−H···Cl hydrogen bonds in which both the NH and NH_2 groups are involved.

NMR Spectra. The rhodium atom in complexes **2**, **5**, and **7**−**9** is chiral. However, in the absence of another chiral center, only one resonance for each type of active nucleus is observed. The ^{1}H NMR spectra of complexes **1**−**9** show the resonance due to the methyl protons of the Cp* group in the 1.50−2.05 ppm range as a singlet (**1**, **3**−**7**, **9**) or as a doublet (**2**, **8)** due to coupling with ^{31}P. Both the acetimino and the 4-imino-2-methylpentan-2-amino complexes show the NH imino proton as a broad resonance in the 8.69−11.39 ppm interval.

The ^{1}H NMR spectra of acetimino complexes **1**−**6** show two separate resonances for the methyl protons, indicating inequivalence caused by restricted rotation around the C═N bond at room temperature. In the spectra of complexes **1** and **4**, measured in DMSO-d_6, both resonances are singlets; for complexes **2**, **3**, **5**, and **6,** one of them splits into a doublet, likely due to coupling with the *trans*-NH proton ($^4J_{HH}$, 0.6−1.2 Hz), as we have previously observed in some acetimino−gold(I)[6] and −Rh(I)[8] complexes.

The ^{1}H NMR spectra of 4-imino-2-methylpentan-2-amino complexes **7**−**9** show three resonances for the inequivalent methyl groups in the ranges 1.08−1.36, 1.25−1.63, and 2.40−2.56 ppm. In complexes **7**·Cl and **8**, the groups are all singlets, whereas in complexes **7**·ClO_4 and **9**, one of the methyl groups (at 2.41 and 2.56 ppm, respectively) splits into a doublet ($^4J_{HH}$ = 1.1 and 3 Hz, respectively), likely due to coupling with the NH proton. The spectra also show the NH_2 and methylene protons to be inequivalent. The former give rise to two doublets in the ranges 2.75−4.14 and 4.22−6.31 ppm with $^2J_{HH}$ values around 12 Hz, whereas the latter are shown as an AB system (**7**·Cl, **7**·ClO_4, **9**) in the 2.19−2.87 ppm range or as two doublets (**8**, −0.08 and 1.90 ppm**)** with $^2J_{HH}$ values of 16−18 Hz. These assignments have been confirmed by means of a ^{1}H/^{13}C HMQC experiment carried out on complex **8**, which proves the resonances at −0.08 and 1.90 ppm in the ^{1}H NMR spectrum are related to that at 49.30 ppm in the ^{13}C NMR spectrum (see below), which is assigned to the CH_2 carbon. The ^{31}P NMR spectra of phosphino compounds **2** and **8** show two doublets at 35.25 and 34.1 ppm, respectively, arising from coupling with ^{103}Rh.

In the ^{13}C{^{1}H} NMR spectra of complexes **1**−**9**, the Cp* methyl carbon atoms are shown in the 8.35−10.13 ppm interval as a singlet resonance or as a doublet due to coupling with ^{31}P (**8**, $^2J_{CRh}$ = 1.1 Hz), whereas the Cp* ring carbon atoms appear in the 93.66−103.91 ppm interval as a doublet due to coupling with ^{103}Rh ($^1J_{CRh}$ = 5.9−8.8 Hz) or as a doublet of doublets due to the additional coupling with ^{31}P (**2**, $^2J_{CP}$ = 2.4 Hz; **8**, $^2J_{CP}$ = 1.6 Hz). In complexes **1**−**9**, the C═N carbon gives a singlet resonance in the 185−192 ppm range. In the acetimino complexes, the inequivalent Me carbon atoms give two separate resonances. However, although one of the methyl carbon atoms in complexes **1**, **3**, **5**, and **6** is shown as a doublet that we attribute to coupling with the trans ^{103}Rh nucleus ($^3J_{CRh}$ in the range of 1.2−2.2 Hz), this coupling is observed neither in the remaining acetimino complexes (**2**, **4**) nor in the amino−imino derivatives **7**−**9**.

IR Spectra. Complexes **1**−**9** show ν(N−H) and ν(C═N) bands in the ranges 3161−3294 and 1644−1664 cm^{-1}, respectively. Additionally, the amino−imino complexes **7**−**9** show sharp $\delta(NH_2)$ bands in the range 1583−1600 cm^{-1}. The isocyanide complexes **5** and **9** show the ν(C≡N) band at 2170 and 2169 cm^{-1}, respectively, and the acac complex **6** shows the expected ν(C═O) band at 1580 cm^{-1}.[21]

Conclusions

The transmetalation reactions between $[Ag(NH{=}CMe_2)_2]$-ClO_4 or $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$ and Rh(III)−pentamethylcyclopentadienylchloro complexes have allowed the synthesis of mono-, bis-, and trisacetimino complexes, which are the first Rh(III) derivatives with such a ligand. The aldol-like condensation of two acetimino ligands into the imam chelating ligand takes place in bis- or tris(acetimino)Rh(III) complexes under mild experimental conditions, i.e., upon the

(21) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986.

addition of labile ligands in excess (CO), stoichiometric (Cl^-, $AsPh_3$), or even catalytic amounts ($Ph_2C{=}NH$), or just upon being stirred in solution at 70 °C, to give the first Rh complexes with this ligand. This is the first report of the synthesis of imam complexes of any metal from acetimino complexes. We have proposed a reasonable reaction pathway for the aldol-like condensation of two acetimino ligands that supports the previous proposal of a template-type reaction for the synthesis of the reported imam complexes.

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Supporting Information Available: Tables of X-ray data for the complexes in CIF format, hydrogen bond data. This material is available free of charge via the Internet at http://pubs.acs.org.

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