Inorg. Chem. **2003**, *42*, 7644–7651

Synthesis of $[Ag(NH{=}CMe_2)_2]ClO_4$ and Its Use as a Source of Acetimine. 1. Synthesis of the First Acetimine Rhodium Complexes and the First Crystal Structure of a Diacetonamine Complex

José Vicente,*,† María-Teresa Chicote,*,† Rita Guerrero,† Inmaculada Vicente-Hernández,† and Peter G. Jones‡

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Aptdo. 4021, Murcia, 30071 Spain, and Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38106 Braunschweig, Germany

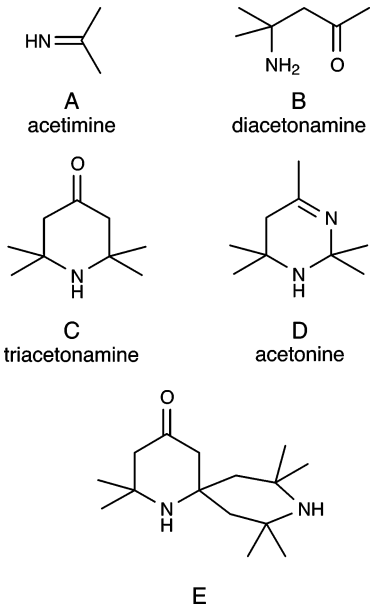
Received August 25, 2003

The reaction of $AgClO_4$ and NH_3 in acetone gave $[Ag(NH{=}CMe_2)_2]ClO_4$ (**1**). The reactions of **1** with $[RhCl(diolefin)]_2$ or $[RhCl(CO)_2]_2$ (2:1) gave the bis(acetimine) complexes $[Rh(diolefin)(NH{=}CMe_2)_2]ClO_4$ [diolefin = 1,5 cyclooctadiene = cod (**2**), norbornadiene = nbd (**3**)] or $[Rh(CO)_2(NH{=}CMe_2)_2]ClO_4$ (**4**), respectively. Mono(acetimine) complexes $[Rh(diolefin)(NH{=}CMe_2)(PPh_3)]ClO_4$ [diolefin = cod (**5**), nbd (**6**)] or $[RhCl(diolefin)(NH{=}CMe_2)]$ [diolefin = cod (**7**), nbd (**8**)] were obtained by reacting **2** or **3** with PPh_3 (1:1) or with Me_4NCl (1:1.1), respectively. The reaction of **4** with PR_3 (R = Ph, To, molar ratio 1:2) led to $[Rh(CO)(NH{=}CMe_2)(PR_3)_2]ClO_4$ [R = Ph (**9**), C_6H_4Me-4 = To (**10**)] while *cis*-$[Rh(CO)(NH{=}CMe_2)_2(PPh_3)]ClO_4$ (**11**) was isolated from the reaction of **1** with $[RhCl(CO)(PPh_3)]_2$ (1:1). The crystal structures of **5** and $[Ag\{H_2NC(Me)_2CH_2C(O)Me\}(PTo_3)]ClO_4$ (**A**), a product obtained in a reaction between NH_3, $AgClO_4$, and PTo_3, have been determined.

Introduction

The participation of imines in functional group transformations, carbon−carbon bond formation, and ring construction processes[1] makes them important intermediates in synthesis. Unlike N-substituted imines, which are generally stable and serve as ligands in many metal complexes,[2] the NH aldimines or ketimines are, with the exception of diarylketimines, unstable compounds that need to be trapped with various reagents.[1] In particular, $NH{=}CMe_2$ (acetimine) is a reactive compound that decomposes after short periods of storage, even at 0 °C, to give 2,2,4,4,6-pentamethyl-2,3,4,5-tetrahydropyrimidine (acetonine, see Chart 1) with NH_3 loss.[3] Acetimine has been prepared from α-aminonitriles and dicyclohexylcarbodiimide[3] and also from acetone and ammonia in high temperature and pressure processes[4]

Chart 1. Condensation Products of NH_3 and Acetone



† Grupo de Química Organometálica. E-mail: jvs@um.es (J.V.); mch@um.es (M.T.C); rgs@um.es (R.G.); inmavh@um.es (I.V.-H.). Web address: http://www.um.es/gqo/.

‡ Institut für Anorganische und Analytische Chemie. E-mail: p.jones@tu-bs.de.

(1) Robertson, G. M. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 3.

(2) Mehrotra, R. C. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2.

(3) Findeisen, K.; Heitzer, H.; Dehnicke, K. *Synthesis* **1981**, 702.

10.1021/ic035002+ CCC: $25.00
Published on Web 10/24/2003

catalyzed by NH_4Cl[5] or HZSM-5 zeolite. However, it has long been known that the reactions of acetone and ammonia, using different stoichiometric ratios and reaction conditions, lead to mixtures of a variety of condensation products (see Chart 1), including acetimine (A), $MeC(O)CH_2C(Me)_2NH_2$ (diacetonamine, B),[6] 2,2,6,6-tetramethyl-4-piperidone (triacetonamine, C),[6,7] acetonine (D),[7] and 1,9-diaza-2,2,8,8,10-hexamethylspiro[5.5]-undecan-4-one (E).[7] Many patents have been devoted to the study of such reactions since some of these condensation products have found application as intermediates for the synthesis of nitroxides, oxoammonium salts, pharmaceutical products, pesticides, and photostabilizers for polymers.[8−13]

The mentioned difficulties in the preparation and handling of acetimine account for the scarcity of complexes with this ligand. In fact, acetimine itself has not been used in the various syntheses of metal−acetimino complexes reported so far,[14−29] namely (i) the reaction of acetone with ammine complexes of Cr^0, Mo^0, W^0, Fe^{II}, Mn^I,[14] Au^I,[15,16] Os^{II};[17] (ii) the reactions in acetone between ammonium salts and complexes containing acetylacetonato ligands (Au^I),[16] or hydrido ligands (Ru^{II});[18] (iii) the reactions of carbene- or THF-carbonyl complexes of Cr^0,[19] or W^0,[20] with dimethylketoxime; (iv) the reactions in acetone between Pd^{II} complexes and NH_3(aq);[21] (v) the redox conversion into acetimine of 2,3-dimethyl-2,3-diaminobutane[22] or isopropylamine[23] ligands in Ru^{II} complexes or acetonitrile in one W^0 complex;[24] (vi) the redox transmetalation of imine from an acetimine Cr^0 complex and $CuBr_2$ to give an acetimino Cu^I complex;[14] (vii) the hydrogen transfer reaction in an alkenyl/azavinylidene Os^{IV} complex to give a vinylidene/acetimine Os^{II} complex;[25] (viii) the thermal decomposition of aminosiliceniotrichloroaluminates ($R_2SiNCMe_3 \cdot AlCl_3$);[26] (ix) the reaction of a Ni^0 dinitrogen complex with *N*-allyldimethyliminium tetraphenylborate to give a Ni^{II} acetimine complex;[27] (x) the reactions of $Na_2[M_2(CO)_{10}]$ (M = Cr, W) with 2-Br-2-nitrosopropane;[28] or (xi) the reaction of $[Bu_4N][Pt(C_6F_5)_3(azaH)]$ (aza =7-azaindole) with Ag_2CO_3 and NH_3(aq) in acetone to give $[Bu_4N][(C_6F_5)_3Pt(\mu\text{-aza})Ag(NH{=}CMe_2)]$.[29] In conclusion, although nearly as many different synthetic methods as acetimine complexes have been described, none of them have proven to be of general applicability.

A different type of NH-imines, R(R′O)C=NH, R(R′NH)C=NH, and R{R′C(O)(Ph_3P=)C}C=NH, also unstable in the free state, have been obtained by nucleophilic additions to metal-bound nitriles.[30−34]

In this paper, we report the synthesis of $[Ag(NH{=}CMe_2)_2]ClO_4$ which could provide (i) a general method for preparing [M]−acetimine complexes by reacting it with the appropriate [M]−X (X = Cl, Br, I, AcO, etc.) derivatives and (ii) a source of the free ligand. In an attempt to explore the application of this complex in synthesis of acetimine complexes, we have used it to prepare the first Rh^I−acetimine complexes.

Experimental Section

IR spectroscopy, elemental analyses, and melting point determinations were carried out as described elsewhere.[16] Molar conductivities were measured on ca. 5×10^{-4} M acetone solutions with a Crison Micro CM2200 conductimeter. The NMR spectra were recorded on Varian Unity 300 MHz, Bruker Avance 200 MHz, or Bruker Avance 400 MHz spectrometers. Chemical shifts are referred to TMS (^{1}H and ^{13}C{^{1}H}) and H_3PO_4 (^{31}P{^{1}H}). Unless otherwise stated, all reactions were carried out at room temperature and 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. Other solvents [*n*-pentane (Baker) and *n*-hexane (Scharlau)] and reagents [$AgClO_4$ (Riedel-de Häen), anhydrous NH_3 (Carburos Metálicos), NaH (60%, dispersion in mineral oil), PPh_3, PTo_3 (C_6H_4Me-4 = To), Me_4NCl, cod, nbd (Fluka)] were obtained from commercial sources and used as received. The complexes $[RhCl(nbd)]_2$,[35] $[RhCl(CO)_2]_2$,[36] $[RhCl(cod)]_2$,[37] $[RhCl(CO)(PPh_3)_2]$,[38] and $[RhCl(CO)(PPh_3)]_2$[39] were prepared according to literature methods.

(4) Xu, T.; Zhang, J.; Haw, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 3171.
(5) Verardo, G.; Giumanini, A. G.; Strazzolini, P.; Poiana, M. *Synth. Commun.* **1988**, *18*, 1501.
(6) Bradbury, R. B.; Hancox, N. C.; Hatt, H. H. *J. Chem. Soc.* **1947**, 1394.
(7) Murayama, K.; Morimura, S.; Amakasu, O.; Toda, T.; Yamao, E. *Nippon Kagaku Zasshi* **1969**, *90*, 296; *Chem. Abstr.* **1969**, *70*, 324.
(8) Sasaki, K.; Oikawa, M.; Myake, K. (Sumitomo Chemical Co.) Patent JP 07,291,931; *Chem. Abstr.* **1996**, *124*, 202290j.
(9) Fukuda, Y. (Kyowa Yuka Kk) Patent JP 05,117,242; *Chem. Abstr.* **1993**, *119*, 180817d.
(10) Inaba, M.; Inui, Y. (Mitsubishi Petrochemical Co., Ltd.) Patent JP 01,233,271; *Chem. Abstr.* **1990**, *112*, 55627w.
(11) Kinishi, R.; Kasagi, M. (Yoshitomi Pharmaceutical Industries, Ltd.) Patent JP 62,132,859; *Chem. Abstr.* **1987**, *107*, 198104f.
(12) Sakanashi, K.; Azaki, Y. (Yoshitomi Pharmaceutical Industries, Ltd.) Patent JP 62,167,763; *Chem. Abstr.* **1988**, *108*, 150314t.
(13) Ma, Z.; Huang, Q.; Bobbit, J. M. *J. Org. Chem.* **1993**, *58*, 4837.
(14) Sellmann, D.; Thallmair, E. *J. Organomet. Chem.* **1979**, *164*, 337.
(15) Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D.; Guerrero, R.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1203.
(16) Vicente, J.; Chicote, M.-T.; Guerrero, R.; Saura-Llamas, I. M.; Jones, P. G.; Ramírez de Arellano, M. C. *Chem. Eur. J.* **2001**, *7*, 638.
(17) Harman, W. D.; Taube, H. *Inorg. Chem.* **1988**, *27*, 3261.
(18) Rappert, T.; Yamamoto, A. *Chem. Lett.* **1994**, 2211.
(19) Fischer, E. O.; Knauss, L. *Chem. Ber.* **1970**, *103*, 1262.
(20) Czarkie, D.; Shvo, Y. *J. Organomet. Chem.* **1985**, *280*, 123.
(21) Ruiz, J.; Rodríguez, V.; Cutillas, N.; López, G. *Organometallics* **2002**, *21*, 4912.
(22) Wong, K.-Y.; Che, C.-M.; Li, C.-K.; Chiu, C.-K.; Zhou, Z.-Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, 754.
(23) Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336.
(24) Yeh, W. Y.; Ting, C. S.; Peng, S. M.; Lee, G. H. *Organometallics* **1995**, *14*, 1417.
(25) Castarlenas, R.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2000**, *19*, 5454.
(26) Klingebiel, U.; Noltemeyer, M.; Schmidt, H.-G.; Schmidt-Bäse, D. *Chem. Ber.* **1997**, *130*, 753.
(27) Aresta, M.; Quaranta, E.; Dibenedetto, A.; Giannoccaro, P.; Tommasi, I.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1997**, *16*, 834.
(28) King, R. B.; Douglas, W. M. *Inorg. Chem.* **1974**, *13*, 1339.
(29) Forniés, J.; Casas, J. M.; Martín, A.; Rueda, A. J. *Organometallics* **2002**, *21*, 4560.
(30) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771.
(31) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299.
(32) Bokach, N. A.; Kukushkin, V. Y.; Haukka, M.; Dasilva, J.; Pombeiro, A. J. L. *Inorg. Chem.* **2003**, *42*, 3602.
(33) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *Inorg. Chem.* **1995**, *34*, 5441.
(34) Vicente, J.; Chicote, M. T.; Beswick, M. A.; Ramírez de Arellano, M. C. *Inorg. Chem.* **1996**, *35*, 6592.
(35) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3178.
(36) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.
(37) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.
(38) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 214.
(39) Maisonnat, A.; Kalck, P.; Poilblanc, R. *Inorg. Chem.* **1974**, *13*, 661.

Warning! Perchlorate salts of organic cations may be explosive. Preparations on a larger scale than that reported herein should be avoided. **Danger!** Ammonia solutions of silver salts produce explosive compounds (silver fulminate and fulminating silver) upon storing more than 2 h.

[Ag(NH=CMe$_2$)$_2$]ClO$_4$ (1). AgClO$_4$ (512 mg, 2.47 mmol) was dissolved in acetone (70 mL) and anhydrous NH$_3$ bubbled through the solution for 2 min. The reaction mixture was stirred for 30 min, the solution was concentrated to 2 mL, and Et$_2$O (25 mL) was added to give a colorless solid which was filtered off. The product was recrystalized from CH$_2$Cl$_2$/Et$_2$O (2:30 mL). The resulting mixture (729 mg) was placed in a flask with HNa (134 mg, 3.35 mmol) under a nitrogen atmosphere. Dry CH$_2$Cl$_2$ (120 mL) was added, and the reaction stirred for 75 min under a nitrogen atmosphere. The mixture was filtered in the air through Celite and concentrated to 2 mL. Upon adding Et$_2$O (40 mL), a colorless solid precipitated, which was filtered and air-dried to give **1**. Yield: 559 mg, 1.74 mmol (70%). Mp 103 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 2.27 (s, 12 H, Me), 9.03 (s, br, 2 H, NH). ^{1}H NMR (400 MHz, acetone-d_6, 20 °C): δ = 2.30 (s, 12 H, Me), 9.56 (s, br, 2 H, NH).^{1}H NMR (400 MHz, acetone-d_6, −60 °C): δ = 2.25 (s, 6 H, Me), 2.28 (s, 6 H, Me), 9.78 (br, 2 H, NH). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ = 28.47 (s, Me), 29.91 (s, Me), 188.20 (s, C=N). IR (Nujol): ν = 3294 (s) (NH), 1662 (s) (C=N) cm^{-1}. Λ_M: 156 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for C$_6$H$_{14}$AgClN$_2$O$_4$: C, 22.41; H, 4.39; N, 8.71. Found: C, 21.94; H, 4.52; N, 8.71.

[Ag{H$_2$NC(Me)$_2$CH$_2$C(O)Me}(PTo$_3$)]ClO$_4$ (A). Anhydrous NH$_3$ was bubbled for 2 min through an acetone (20 mL) solution of AgClO$_4$ (200 mg, 0.96 mmol). The solution was stirred for 5 min and evaporated and the residue dissolved in acetone (20 mL). MgSO$_4$ was added, and the suspension was stirred for 7 days and filtered and the filtrate concentrated to dryness. A colorless oil was obtained (141 mg) which was dissolved in acetone (10 mL). A solution of PTo$_3$ (133 mg, 0.44 mmol) was then added dropwise, the solution stirred for 10 min and concentrated to 1 mL, and Et$_2$O (20 mL) added to give a sticky solid (124 mg). Its analytical [Calcd (%) for C$_{27}$H$_{34}$AgClNO$_5$P: C, 51.73; H, 5.47; N, 2.23. Found: C, 53.35; H, 5.75; N, 2.33.] and spectroscopic data show it is **A** with some impurities. From this mixture, two crystals of the title compound grew by the liquid diffusion method (CH$_2$Cl$_2$/Et$_2$O). One was used to determine its crystal structure by X-ray diffraction methods, and the other was studied by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.36 (s, 6 H, Me), 2.14 (s, 3 H, Me), 2.39 (s, 9 H, Me), 2.75 (s, 2 H, CH$_2$), 3.86 (br, 2 H, NH$_2$), 7.24−7.36 (AA′BB′, 12 H, C$_6$H$_4$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ = 14.18 (dd, $J_{109Ag-P}$ = 724, $J_{107Ag-P}$ = 631 Hz).

[Rh(diolefin)(NH=CMe$_2$)$_2$]ClO$_4$ [Diolefin = cod (2), nbd (3)]. To a solution of [RhCl(diolefin)]$_2$ [diolefin = cod (92.5 mg, 0.19 mmol), nbd (113 mg, 0.25 mmol)] in CH$_2$Cl$_2$ (30 mL) was added complex **1** [121 mg, 0.38 mmol or 158 mg, 0.49 mmol, respectively]. AgCl immediately formed. The resulting suspension was stirred for 30 min and then filtered through a short pad of Celite. The yellow filtrate was then concentrated (1 mL), and Et$_2$O (30 mL) was added to precipitate a solid, which was stirred for 5 min, filtered, and air-dried to give **2** (lemon yellow) or **3** (yellow).

Compound 2. Yield: 133 mg, 81%. Dec point 170 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.87 (m, 4 H, CH$_2$), 2.14 (d, 6 H, Me, $^4J_{H-H}$ = 0.8 Hz), 2.45 (m, 4 H, CH$_2$), 2.52 (s, 6 H, Me), 4.00 (br, 4 H, CH), 8.92 (br, 2 H, NH). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 28.42 (s, Me), 28.57 (s, Me), 30.42 (s, CH$_2$), 82.52 (d, CH, $^1J_{C-Rh}$ = 1.65 Hz), 185.18 (s, C=N). IR (Nujol): ν = 3252 (s) (NH), 1660 (s) (C=N) cm^{-1}. Λ_M: 146 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for C$_{14}$H$_{26}$ClN$_2$O$_4$Rh: C, 39.59; H, 6.17; N, 6.60. Found: C, 39.54; H, 6.51; N, 6.62.

Compound 3. Yield: 175 mg, 87%. Dec point 124 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.28 (s, 2 H, CH$_2$), 2.12 (s, 6 H, Me), 2.40 (s, 6 H, Me), 3.89 (s, 2 H, CH), 4.10 (s, 4 H, CH=CH), 8.68 (br, 2 H, NH). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ = 27.93 (s, Me), 28.49 (s, Me), 51.21 (d, CH, $^2J_{C-Rh}$ = 2.56 Hz), 60.43 (d, CH=CH, $^1J_{C-Rh}$ = 9.87 Hz), 62.70 (d, CH$_2$, $^3J_{C-Rh}$ = 5.85 Hz), 184.81 (s, C=N). IR (Nujol): ν = 3254 (s) (NH), 1656 (m) (C=N) cm^{-1}. Λ_M: 154 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for C$_{13}$H$_{22}$ClN$_2$O$_4$Rh: C, 38.21; H, 5.43; N, 6.85. Found: C, 37.96; H, 5.69; N, 6.75.

***cis*-[Rh(CO)$_2$(NH=CMe$_2$)$_2$]ClO$_4$ (4).** [RhCl(CO)$_2$]$_2$ (60 mg, 0.16 mmol) was added to a solution of **1** (120 mg, 0.31 mmol) in CH$_2$Cl$_2$ (20 mL). AgCl immediately precipitated. The resulting suspension was stirred for 10 min, filtered through a short pad of Celite, and then concentrated (1 mL). When Et$_2$O was added (20 mL), a cloudy solid precipitated, which was filtered and air-dried to give **4** as a pale yellow solid. Yield: 93 mg, 80%. Dec point 131 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.33 (s, 3 H, Me), 2.43 (s, 3 H, Me), 9.14 (br, 1 H, NH). ^{13}C{^{1}H} NMR (300 MHz, CDCl$_3$): δ = 28.77 (s, Me), 29.63 (s, Me), 183.31 (d, CO, $^1J_{C-Rh}$ = 66.7 Hz), 190.94 (s, C=N). IR (Nujol): ν = 3262 (s) (NH), 2092 (s), 2026 (s) (C=O), 1666 (s) (C=N) cm^{-1}. Λ_M: 147 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for C$_8$H$_{14}$ClN$_2$O$_6$Rh: C, 25.79; H, 3.79; N, 7.52. Found: C, 25.85; H, 3.85; N, 7.52.

[Rh(cod)(NH=CMe$_2$)(PPh$_3$)]ClO$_4$ (5). A solution of PPh$_3$ (50 mg, 0.19 mmol) in CH$_2$Cl$_2$ (5 mL) was added dropwise to a yellow solution of **2** (80 mg, 0.19 mmol). The resulting orange-yellow solution was stirred for 3 h and then concentrated to 1 mL. Upon adding Et$_2$O (20 mL), a solid precipitated. The suspension was filtered and the solid washed with Et$_2$O (2 × 3 mL) and air-dried to give **5** as a bright yellow solid. Yield: 108 mg, 91%. Dec point 163 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.78 (s, 3 H, Me), 1.79 (s, 3 H, Me), 2.07 (m, 2 H, CH$_2$), 2.14 (m, 2 H, CH$_2$), 2.44 (m, 2 H, CH$_2$), 2.54 (m, 2 H, CH$_2$), 3.60 (s, 2 H, CH), 5.19 (s, 2 H, CH), 5.30 (s, 2 H, CH$_2$Cl$_2$), 7.48−7.65 (m, 15 H, Ph), 9.47 (br, 1 H, NH). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$): δ = 27.90 (d, Me, $^3J_{C-Rh}$ = 1.46 Hz), 28.25 (s, Me), 29.01 (d, CH$_2$, $^2J_{C-Rh}$ = 1.83 Hz), 31.69 (d, CH$_2$, $^2J_{C-Rh}$ = 2.56 Hz), 80.04 (d, CH, $^1J_{C-Rh}$ = 11.34 Hz), 102.70 (dd, CH, $^1J_{C-Rh}$ = 10.6 Hz, $^2J_{C-P}$ = 7.68 Hz), 128.88 (d, *p*-Ph, $^4J_{C-P}$ = 9.88 Hz), 129.68 (d, *ipso*-Ph, $^1J_{C-P}$ = 42.42 Hz), 130.75 (d, *m*-Ph, $^3J_{C-P}$ = 2.56 Hz), 133.88 (d, *o*-Ph, $^2J_{C-P}$ = 11.34 Hz), 184.81 (d, C=N, $^2J_{C-Rh}$ = 1.46 Hz). ^{31}P{^{1}H} (162 MHz, CDCl$_3$): δ = 25.96 (d, PPh$_3$, $^1J_{P-Rh}$ = 153 Hz). IR (Nujol): ν = 3242 (m) (NH), 1652 (m) (C=N) cm^{-1}. Λ_M: 147 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for C$_{29}$H$_{34}$ClNO$_4$PRh·CH$_2$Cl$_2$: C, 50.41; H, 5.08; N, 1.96. Found: C, 50.64; H, 5.44; N, 2.05.

[Rh(nbd)(NH=CMe$_2$)(PPh$_3$)]ClO$_4$ (6). Complex **3** (120 mg, 0.29 mmol) and PPh$_3$ (77 mg, 0.29 mmol) were placed in a flask under a nitrogen atmosphere. Acetone (20 mL) was added, and the resulting solution was stirred for 15 min under a nitrogen atmosphere and then concentrated to 1 mL. Upon the addition of Et$_2$O under a nitrogen atmosphere, a product precipitated which was stirred for 5 min, filtered, and air-dried to give **6** as a yellow-orange solid. Yield: 145 mg, 80%. Mp 153 °C. ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.46 (s, 2 H, CH$_2$), 1.88 (s, 6 H, Me), 3.65 (br, 2 H, CH=CH), 3.96 (s, 2 H, CH), 5.38 (br, 2 H, CH=CH), 7.47−7.54 (m, 15 H, Ph), 9.30 (br, 1 H, NH). ^{1}H NMR (400 MHz, CDCl$_3$, −60 °C): δ = 1.50 (s, 2 H, CH$_2$), 1.82 (s, 3 H, Me), 1.89 (s, 3 H, Me), 3.68 (s, 2 H, CH=CH), 4.02 (s, 2 H, CH), 5.38 (s, 2 H, CH=CH), 7.52 (m, 15 H, Ph), 9.14 (s, 1 H, NH). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 27.90 (s, Me), 28.37 (s, Me), 52.25 (s, CH), 62.44 (d, CH=CH, $^1J_{C-Rh}$ = 8.47 Hz), 65.68 (s, CH$_2$), 84.20

(s, CH=CH), 128.92 (d, *p*-Ph, $^4J_{C-P}$ = 10.07 Hz), 129.41 (d, *ipso*-Ph, $^1J_{C-P}$ = 42.37 Hz), 130.72 (d, *m*-Ph, $^3J_{C-P}$ = 2.12 Hz), 133.49 (d, *o*-Ph, $^2J_{C-P}$ = 12.18 Hz), 184.47 (s, C=N). $^{31}P\{^1H\}$ (81 MHz, $CDCl_3$): δ = 28.62 (d, PPh_3, $^1J_{P-Rh}$ = 168 Hz). IR (Nujol): ν = 3222 (m) (NH), 1662 (m) (C=N) cm^{-1}. Λ_M: 116 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{28}H_{30}ClNO_4PRh$: C, 54.78; H, 4.93; N, 2.28. Found: C, 54.81; H, 5.10; N, 2.50.

[RhCl(cod)(NH=CMe$_2$)] (7). Complex **2** (160 mg, 0.37 mmol) was added to a suspension of Me_4NCl (45 mg, 0.41 mmol) in acetone (80 mL) under a nitrogen atmosphere. The resulting mixture was stirred for 6 h and then evaporated to dryness. The residue was extracted with Et_2O (7 × 40 mL), the extractions were collected and filtered through a short pad of Celite, and the filtrate concentrated (2 mL). At this point, a solid precipitated, which was filtered and air-dried to give **7** as a yellow solid. Yield: 48 mg, 42%. Dec point 223 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.80 (m, 4 H, CH_2), 2.11 (s, 3 H, Me), 2.44 (m, 4 H, CH_2), 2.60 (s, 3 H, Me), 3.61 (br, 2 H, CH), 4.56 (br, 2 H, CH), 8.31 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 28.01 (s, Me), 29.47 (s, Me), 30.76 (br, CH_2), 56.11 (s, CH), 183.95 (s, C=N). IR (Nujol): ν = 3186 (m) (NH), 1660 (m) (C=N) cm^{-1}. Λ_M: 1 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{11}H_{19}ClNRh$: C, 43.51; H, 6.31; N, 4.61. Found: C, 43.15; H, 6.75; N, 4.75.

[RhCl(nbd)(NH=CMe$_2$)] (8). Complex **3** (132 mg, 0.32 mmol) was added to a suspension of Me_4NCl (39 mg, 0.36 mmol) in acetone (80 mL) under a nitrogen atmosphere. The resulting mixture was stirred for 6 h and then evaporated to dryness. The residue was extracted with CH_2Cl_2 (15 mL) and the suspension filtered through a short pad of Celite. The yellow filtrate was evaporated to dryness, Et_2O (3 mL) was added, and the suspension was filtered off. Recrystallization of the solid from CH_2Cl_2/Et_2O afforded **8** as a yellow solid. Yield: 79 mg, 84%. Dec point 115 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (s, 2 H, CH_2), 2.06 (s, 3 H, Me), 2.40 (s, 3 H, Me), 3.82 (s, 2 H, CH), 3.99 (s, 4 H, CH=CH), 8.27 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 27.14 (s, Me), 29.04 (s, Me), 50.08 (s, CH), 50.11 (s, CH), 61.32 (d, CH_2, $^3J_{C-Rh}$ = 6.36 Hz), 183.00 (s, C=N). IR (Nujol): ν = 3194 (m) (NH), 1652 (m) (C=N) cm^{-1}. Λ_M: 2 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{10}H_{15}ClNRh$: C, 41.76; H, 5.26; N, 4.87. Found: C, 41.48; H, 5.50; N, 4.94.

***trans*-[Rh(CO)(NH=CMe$_2$)(PR$_3$)$_2$]ClO$_4$ [R = Ph (9), To (10)].** A solution of complex **4** (50 mg, 0.13 mmol) in CH_2Cl_2 (10 mL) was added dropwise (about 15 min) to another containing PR_3 (R = Ph, 70 mg, 0.27 mmol; To, 82 mg, 0.27 mmol) in the same solvent (5 mL). The yellow solution turned to bright yellow. The reaction mixture was stirred for 1 h 45 min and filtered through Celite and the filtrate concentrated (1 mL). Upon adding Et_2O (20 mL), a yellow solid precipitated, which was stirred for 5 min, filtered, and air-dried to give **9** (R = Ph) or **10** (R = To) as bright yellow solids.

Compound 9. Yield: 89 mg, 81%. Dec point 178 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, Me), 1.26 (s, 3 H, Me), 7.49−7.67 (m, 30 H, Ph), 8.99 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 26.84 (s, Me), 28.88 (s, Me), 128.96 (vt, *p*-Ph, N = 10.2 Hz), 130.95 (vt, *ipso*-Ph, N = 37.6 Hz), 131.03 (s, *m*-Ph), 134.17 (vt, *o*-Ph, N = 13.3 Hz), 185.65 (s, C=N), 189.97 (dt, CO, $^1J_{C-Rh}$ = 65.63 Hz, $^2J_{C-P}$ = 16.53 Hz). $^{31}P\{^1H\}$ (162 MHz, $CDCl_3$): δ = 31.69 (d, PPh_3, $^1J_{P-Rh}$ = 129 Hz). IR (Nujol): ν = 3242 (m) (NH), 1994 (s) (C=O), 1662 (m) (C=N) cm^{-1}. Λ_M: 149 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{40}H_{37}ClNO_5P_2Rh$: C, 59.16; H, 4.59; N, 1.72. Found: C, 58.86; H, 4.85; N, 1.81.

Compound 10. Yield: 100 mg, 89%. Dec point 207 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.23 (s, 3 H, Me), 1.27 (s, 3 H, Me), 2.38 (s, 18 H, Me), 7.25−7.28 + 7.45−7.55 (AA′BB′, 24 H, To), 8.81 (br, 1 H, NH). $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6): δ = 21.29 (s, Me), 27.50 (s, Me), 29.22 (s, Me), 129.13 (vt, *ipso*-Ph, N = 48.3 Hz), 130.44 (vt, *m*-Ph, N = 10.6 Hz), 135.01 (vt, *o*-Ph, N = 13.5 Hz), 142.45 (s, *p*-Ph), 186.58 (t, C=N, $^3J_{C-P}$ = 2.7 Hz), 191.48 (dt, CO, $^1J_{C-Rh}$ = 65.89, $^2J_{C-P}$ = 16.0 Hz). $^{31}P\{^1H\}$ (200 MHz, $CDCl_3$): δ = 30.37 (d, PTo_3, $^1J_{P-Rh}$ = 127.78 Hz). IR (Nujol): ν = 3236 (m) (NH), 1994 (s) (C=O), 1660 (m) (C=N) cm^{-1}. Λ_M: 128 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{46}H_{49}ClNO_5P_2Rh\cdot H_2O$: C, 60.43; H, 5.62; N, 1.53. Found: C, 60.63; H, 5.83; N, 1.82.

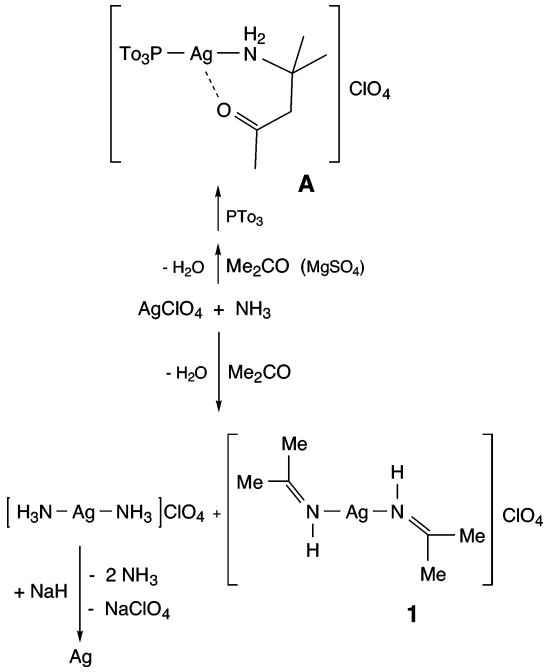
***cis*-[Rh(CO)(NH=CMe$_2$)$_2$(PPh$_3$)]ClO$_4$ (11).** $[RhCl(CO)(PPh_3)]_2$ (200 mg, 0.23 mmol) was added to a solution of **1** (150 mg, 0.47 mmol) in CH_2Cl_2 (20 mL). AgCl immediately formed. The suspension was stirred for 5 min and then filtered through a short pad of Celite. The yellow filtrate was then concentrated to 1 mL, and Et_2O (25 mL) was added to precipitate a pale yellow solid, which was stirred for 10 min, filtered, and air-dried to give **11** as a pale yellow solid. Yield: 260 mg, 93%. Mp 140 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.72 (s, 3 H, Me), 1.83 (s, 3 H, Me), 2.29 (d, 3 H, Me, $^4J_{H-H}$ = 1.1 Hz), 2.47 (s, 3 H, Me), 7.42−7.64 (m, 15 H, Ph), 8.60 (s, 1 H, NH), 9.49 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: too unstable to be recorded. $^{31}P\{^1H\}$ (162 MHz, $CDCl_3$): δ = 44.19 (d, PPh_3, $^1J_{P-Rh}$ = 152 Hz). IR (Nujol): ν = 3284 (s) (NH), 1988 (C=O) (vs), 1662 (C=N) (s) cm^{-1}. Λ_M: 148 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{25}H_{29}ClN_2O_5PRh$: C, 49.48; H, 4.82; N, 4.62. Found: C, 49.20; H, 5.15; N, 4.67.

Table 1. Crystal Data for Compounds **5** and **A**

	5	**A**
formula	$C_{29}H_{34}ClNO_4PtRh$	$C_{27}H_{34}AgClNO_5P$
crystal size (mm^3)	0.36 × 0.18 × 0.18	0.30 × 0.12 × 0.08
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	9.7384(8)	10.1821(8)
b (Å)	32.027(3)	12.2233(8)
c (Å)	17.5949(14)	12.4631(8)
α (deg)	90	100.159(4)
β (deg)	93.951(4)	108.292(4)
γ (deg)	90	96.667(4)
V (Å^3)	5474.6(8)	1425.07(17)
Z	8	2
ρ_{calcd} (Mg m^{-3})	1.528	1.462
M_r	629.90	626.84
T (K)	133(2)	133(2)
F(000)	2592	644
μ Mo Kα (mm^{-1})	0.816	0.893
θ range (deg)	1.27 to 30.03	1.72 to 30.03
abs corr	semiempirical from equivalents	semiempirical from equivalents
reflns collected	96871	29022
indep reflns	16011	8301
R_{int}	0.0495	0.0271
transm	0.928/0.828	0.949/0.836
data/restraints/params	16011/29/711	8301/1/339
R1 [$I > 2\sigma(I)$]	0.0334	0.0267
wR2 (all reflns)	0.0902	0.0649

X-ray Structure Determinations. The structures of **5** and **A** were solved (Table 1). Data were registered on a Bruker SMART 1000 CCD diffractometer at 133 K using Mo Kα radiation (λ = 0.71073 Å) to a maximum 2θ of 60°. Absorption corrections were applied using the program SADABS. Structures were solved by the heavy-atom method and refined anisotropically on F^2 (program system SHELXL, G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included as follows: NH and coordinated olefin CH freely refined but with distance restraints, rigid methyls, others riding.

Scheme 1



Compound 5. Crystal data: $C_{29}H_{34}ClNO_4PRh$ (629.90), monoclinic, $P2_1/c$, $a = 9.7384(8)$ Å, $b = 32.027(3)$ Å, $c = 17.5949(14)$ Å, $\beta = 93.951(4)°$, $V = 5474.6(8)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.528$ Mg/m^3, $\mu = 0.816$ mm^{-1}, $F(000) = 2592$,; $-13 \le h \le 13$, $-44 \le k \le 45$, $-24 \le l \le 24$; reflns collected, 96871; indep reflns, 16011 ($R_{int} = 0.0495$), data/restraints/params 16011/29/711, GOF on $F^2 = 1.012$, final R indices [$I > 2\sigma(I)$], R1 = 0.0334, wR2 = 0.0815, R indices (all data) R1 = 0.0557, wR2 = 0.0902; largest diff peak and hole 2.740 and -0.446 e Å^{-3}.

[Ag{H$_2$NC(Me)$_2$CH$_2$C(O)Me}(PTo$_3$)]ClO$_4$. Crystal data: $C_{27}H_{34}AgClNO_5P$ (626.84), triclinic, $P\bar{1}$, $a = 10.1821(8)$ Å, $b = 12.2233(8)$ Å, $c = 12.4631(8)$ Å, $\alpha = 100.159(4)°$, $\beta = 108.292(4)°$, $\gamma = 96.667(4)°$, $V = 1425.07(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.461$ Mg/m^3, $\mu = 0.893$ mm^{-1}, $F(000) = 644$; $-13 \le h \le 14$, $-17 \le k \le 17$, $-17 \le l \le 17$; reflns collected, 29022; indep reflns, 8301 ($R_{int} = 0.0271$), data/restraints/params 8301/1/339, GOF on $F^2 = 0.982$, final R indices [$I > 2\sigma(I)$], R1 = 0.0267, wR2 = 0.0618, R indices (all data) R1 = 0.0368, wR2 = 0.0649; largest diff peak and hole 0.635 and -0.299 e Å^{-3}.

Results and Discussion

Synthesis of [Ag(NH=CMe$_2$)$_2$]ClO$_4$ (1) and [Ag{H$_2$NC(Me)$_2$CH$_2$C(O)Me}(PTo$_3$)]ClO$_4$ (To = C$_6$H$_4$Me-4) (A). Complex **1** could be obtained by bubbling anhydrous NH_3(g) through an acetone solution of $AgClO_4$ for 2 min (Scheme 1) and stirring the solution for 30 min (step 1). At this point, the reaction was still not complete, since **1** was contaminated with some $[Ag(NH_3)_2]ClO_4$[40] (the IR spectrum shows a band at 3364 cm^{-1} due to $[Ag(NH_3)_2]ClO_4$). Although recrystallization from CH_2Cl_2/Et_2O removed most of the ammine complex, treatment of the recrystallized product in CH_2Cl_2 with NaH (step 2) was necessary in order to obtain pure **1**, since only $[Ag(NH_3)_2]ClO_4$ reacted to give metallic silver along with some unidentified soluble decomposition products that could easily be separated upon filtration and precipitation with Et_2O to give **1** in 70% yield. The reaction times are crucial because shorter periods of stirring in step 1 (5 or 20 min) lead to mixtures enriched in $[Ag(NH_3)_2]ClO_4$ while longer ones give diacetonamine complexes. On the other hand, acetone solutions of $AgClO_4$ with an excess of aqueous NH_3 resulted in mixtures containing **1** contaminated with variable amounts of $[Ag(NH_3)_2]ClO_4$, diacetonamine, and/or triacetonamine and/or acetonine species (see Chart 1) and/or other unidentified compounds, depending on the reaction conditions. We were unable to separate these mixtures.

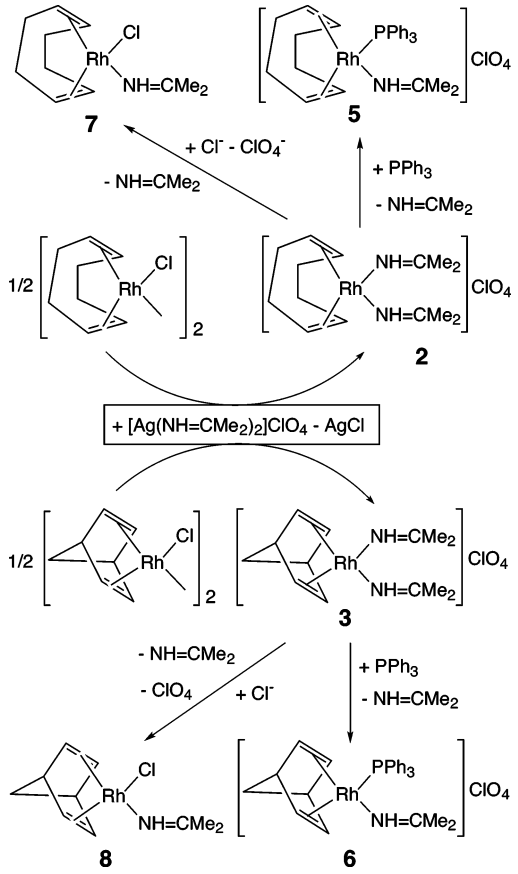
The gold complexes $[Au(NH{=}CMe_2)_2]X$ (X = ClO_4, CF_3SO_3), homologous to **1**, were prepared in good yields by stirring $[Au(NH_3)_2]X$ in acetone for 5 days or by reacting $PPN[Au(acac)_2]$ with NH_4X in acetone, in a shorter time (3 h).[16] However, we could not obtain pure **1** from $[Ag(NH_3)_2]ClO_4$[40] and acetone, nor from NH_4ClO_4 and Ag_2CO_3 or AgOAc. After 24 h of stirring, the reaction of $[Ag(NH_3)_2]ClO_4$ and acetone produces a mixture of the starting silver complex and a small amount of **1**. When the stirring was prolonged over 4 days, the mentioned mixture was contaminated with diacetonamine (B in Chart 1) or some "Ag(diacetonamine)" species (by ^{1}H NMR). After many experiments in which drying agents [anhydrous $MgSO_4$ or $CaCl_2$, or $Me_2C(OMe)_2$] were added to the same reaction mixture, with the intention of facilitating the condensation process, we concluded that their use not only did not increase the production of **1** but also, in some cases ($CaCl_2$), produced additionally triacetonamine (C in Chart 1) or some "Ag(triacetonamine)" complex (by ^{1}H NMR). The reactions of NH_4ClO_4 with Ag_2CO_3 or AgOAc also failed to give **1** since a complex mixture, which we could not separate, was obtained in the case of Ag_2CO_3, and no reaction was observed with AgOAc. Experiments in refluxing acetone did not give any better results.

In the mixture of products obtained after bubbling NH_3(g) through an acetone solution of $AgClO_4$ (2 min), removing the excess under vacuum, adding fresh acetone and anhydrous $MgSO_4$, and stirring the suspension for 7 days, we observed that a diacetonamine species was the major product, contaminated with only small amounts of different impurities. The compound precipitated as a very sticky oily product that, even after many attempts, we could not convert into a solid. By reacting it with PTo_3 (To = C_6H_4Me-4, in CH_2Cl_2, $AgClO_4/PTo_3$ = 1:1), a new mixture of products resulted, from which, by the liquid diffusion method using CH_2Cl_2 and Et_2O, single crystals grew of $[Ag\{H_2NC(Me)_2CH_2C(O)Me\}(PTo_3)]ClO_4$ (**A**, Scheme 1), the crystal structure of which was determined by X-ray diffraction methods. A search of the Cambridge Crystallographic Data Center (CCDC) reveals that this is the first crystal structure of a diacetonamine complex of any metal.

Synthesis of Acetimine Complexes of Rhodium(I). $[Rh(diolefin)(NH{=}CMe_2)_2]ClO_4$ [diolefin = 1,5-cyclooctadiene = cod (**2**), norbornadiene = nbd (**3**)] and *cis*-$[Rh(CO)_2(NH{=}CMe_2)_2]ClO_4$ (**4**) were obtained in good yield (80−87%) by reacting **1** in CH_2Cl_2 with the appropriate $[RhCl(diolefin)]_2$ or $[RhCl(CO)_2]_2$ complexes in 2:1 molar

(40) Miles, M. G.; Patterson, J. H.; Hobbs, C. W.; Hopper, M. J.; Overend, J.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 1721.

Scheme 2

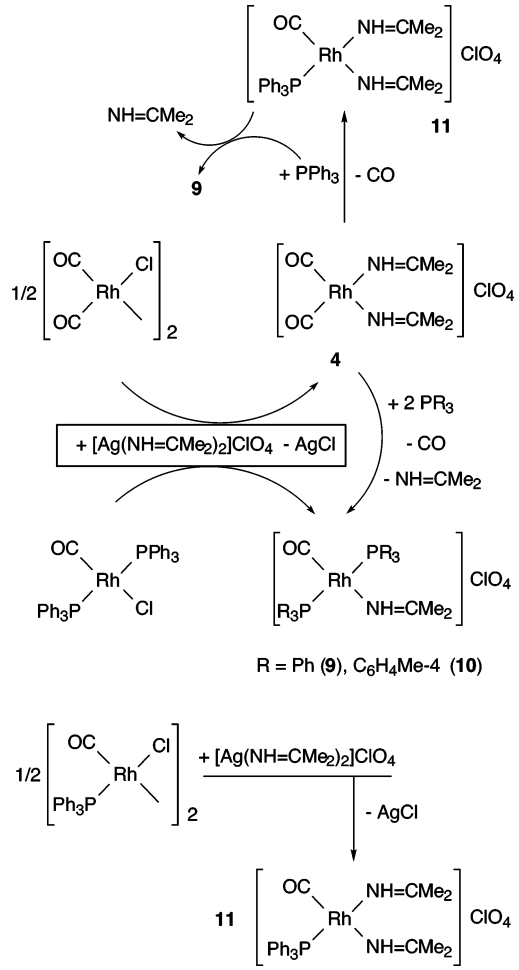


ratio (Scheme 2). The only byproduct, AgCl, was removed by filtration.

Complexes **2** or **3** reacted in CH_2Cl_2 with the equimolar amount of PPh_3, to give the cationic complex [Rh(diolefin)(NH=CMe_2)(PPh_3)]ClO_4 [diolefin = cod (**5**), nbd (**6**)] (Scheme 2). Whereas complex **5** was obtained pure, complex **6** was contaminated with Ph_3PO [$^{31}P\{^1H\}$ NMR]. The isolation of pure **6** required working in a dry nitrogen atmosphere and using acetone as solvent. Similarly, the neutral complexes [RhCl(diolefin)(NH=CMe_2)] [diolefin = cod (**7**), nbd (**8**)] were obtained by reacting **2** or **3**, respectively, with Me_4NCl (1:1.1, in acetone, under nitrogen). The byproduct Me_4NClO_4, and the excess of Me_4NCl, were separated by extracting the complex with Et_2O (**7**) or CH_2Cl_2 (**8**). When other ammonium salts (PPNCl, Bu_4NCl) were used instead of Me_4NCl, the resulting perchlorate salt could not be separated from the corresponding complex even after repeated recrystallizations.

High yields of pure *trans*-[Rh(CO)(NH=CMe_2)(PR_3)$_2$]ClO_4 [R = Ph (**9**), C_6H_4Me-4 (To) (**10**)] were obtained by reacting **4** with 2 equiv of the appropriate phosphine (Scheme 3). Complex **9** was also obtained, though in lower yield (52%), by reacting **1** with [RhCl(CO)(PPh_3)$_2$] (1:1, 45 min, in acetone). However, the dropwise addition of 1 equiv of PPh_3 to **4** in CH_2Cl_2, intended to produce a monosubstituted product ([Rh(CO)(NH=CMe_2)$_2$(PPh_3)]ClO_4 or [Rh(CO)$_2$(NH=CMe_2)(PPh_3)]ClO_4), gave instead a mixture of compounds that we could not separate. Its ^1H and $^{31}P\{^1H\}$ NMR spectra showed the presence of a small amount of complex

Scheme 3



9, while the remaining ^1H and $^{31}P\{^1H\}$ NMR resonances suggest the main component of the mixture to be one of the expected complexes *cis*-[Rh(CO)(NH=CMe_2)$_2$(PPh_3)]ClO_4 (**11**) (Scheme 3). A 10:1 (**11**:**9**) molar ratio was deduced from the $^{31}P\{^1H\}$ NMR spectrum of the mixture. Following the reaction course by ^1H and $^{31}P\{^1H\}$ NMR, both in the air or in CO atmosphere, showed the disubstitution product **9** to be present in the first measured spectra. The solid IR spectrum of the mixture reveals the presence of a small amount of **4**, the ^1H NMR resonances of which were obscured by those of the other complexes. Pure **11** could be obtained in very good yield by reacting **1** with [RhCl(CO)(PPh_3)]$_2$ (1:2) in CH_2Cl_2 (Scheme 3)

Although the exclusive formation of **11** would suggest a greater trans effect of acetimine with respect to CO, its formation can be better understood in terms of the destabilizing effect of two mutually trans π-acidic ligands on Rh^I complexes.[41] In fact, a search of the CCDC for mononuclear square planar Rh^I complexes reveals the great tendency of CO to avoid CO or PPh_3 ligands in trans position since, apart from $[Rh(CO)_4]^+$ [42] and two $[Rh(CO)_2(PR_3)_2]^+$ complexes with very bulky phosphine ligands,[43,44] *trans*-$[Rh(CO)_2Cl_2]^-$ [45]

(41) Cavallo, L.; Solà, M. *J. Am. Chem. Soc.* **2001**, *123*, 12294.
(42) Lupinetti, A. J.; Havighurst, M. D.; Miller, S. M.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1999**, *121*, 11920.
(43) Dunbar, K. R.; Haefner, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 9540.

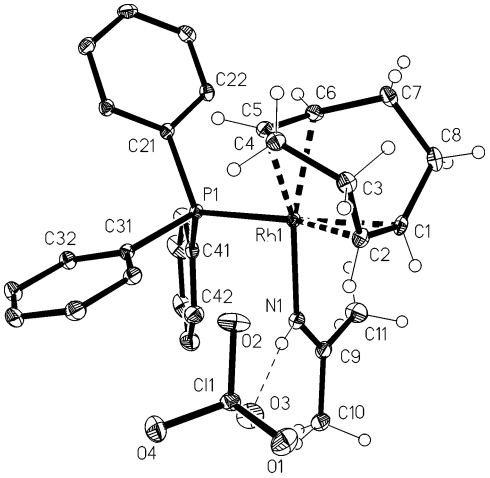


Figure 1. Crystal structure of complex **5** showing the atom numbering. Ellipsoids correspond to 30% probability levels. Selected bond lengths [Å] and angles [deg]: Rh(1)−N(1) 2.070(2), Rh(1′)−N(1′) 2.093(2), Rh(1)−C(5) 2.153(2), Rh(1′)−C(5′) 2.124(3), Rh(1)−C(6) 2.168(2), Rh(1′)−C(6′) 2.155(3), Rh(1)−C(1) 2.210(2), Rh(1′)−C(1′) 2.215(3), Rh(1)−C(2) 2.215(2), Rh(1′)−C(2′) 2.245(2), Rh(1)−P(1) 2.3371(6), Rh(1′)−P(1′) 2.3003(6), N(1)−C(9) 1.279(3), N(1′)−C(9′) 1.276(3), C(1)−C(2) 1.375(3), C(1′)−C(2′) 1.369(4), C(5)−C(6) 1.396(3), C(5′)−C(6′) 1.387(4); N(1)−Rh(1)−C(1) 88.85(9), N(1′)−Rh(1′)−C(1′) 90.33(9), N(1)−Rh(1)−C(2) 89.16(9), N(1′)−Rh(1′)−C(2′) 89.26(9), N(1)−Rh(1)−P(1) 90.01(6), N(1′)−Rh(1′)−P(1′) 89.42(6), C(5)−Rh(1)−P(1) 89.45(7), C(5′)−Rh(1′)−P(1′) 92.76(8), C(6)−Rh(1)−P(1) 98.32(7), C(6′)−Rh(1′)−P(1′) 95.57(7).

is the only example of a *trans*-$(CO)_2Rh^I$ complex, while $[Rh(CO)(PPh_3)_3]^+$ [46] is the only complex with CO trans to PPh_3. Accordingly, complexes **9**−**11** would be the thermodynamic results of the corresponding reactions.

Crystal Structure of [Rh(cod)(NH═CMe$_2$)(PPh$_3$)]ClO$_4$ (5). The crystal structure of **5** (Figure 1) involves two independent formula units; the $[Rh(cod)(NH{=}CMe_2)(PPh_3)]^+$ cations display only small differences in bond distances and angles. The cations show the rhodium atoms in slightly distorted square-planar environments, the coordinating double bonds being defined in terms of their midpoints. The Rh−C(5), Rh−C(5′) and Rh−C(6), Rh−C(6′) distances are longer than Rh−C(1), Rh−C(1′) and Rh−C(2), Rh−C(2′), in agreement with the greater trans influence of PPh_3 with respect to the imine. The C═N bond distances [1.279(3), 1.276(3) Å] are in the range found for the few other acetimine complexes structurally characterized [1.259(4)−1.290(10) Å].[16,21,22,24−26] The acetimine ligand is almost coplanar with the trans olefinic group from cod (interplanar angles 13.6° and 7.8°). Classical hydrogen bonds N−H···O are formed between the perchlorate anions and the NH groups of the acetimine ligands (Table 2). A further eight interactions C−H···O, with H···O < 2.6 Å and angles > 120°, may be regarded as weak hydrogen bonds. Most of them are involved in forming broad layers of cations and anions parallel to the *xz* plane.

Crystal Structure of [Ag{H$_2$NC(Me)$_2$CH$_2$C(O)Me}(PTo$_3$)]ClO$_4$. The crystal structure of the title compound

Table 2. Hydrogen Bonds [Å and deg] for **5**[a]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N(1)−H(01)···O(3)	0.79(2)	2.32(2)	3.110(3)	172(3)
N(1′)−H(01′)···O(8)	0.80(2)	2.31(2)	3.092(3)	169(3)
C(25)−H(25)···O(1)#1	0.95	2.40	3.261(3)	150.9
C(22)−H(22)···O(7)#2	0.95	2.47	3.421(3)	175.3
C(8)−H(8A)···O(5)#2	0.99	2.52	3.503(3)	170.8
C(35)−H(35)···O(4)	0.95	2.54	3.309(4)	137.8
C(10)−H(10B)···O(8)#3	0.98	2.54	3.482(4)	161.1
C(44)−H(44)···O(8)#4	0.95	2.55	3.182(4)	124.3
C(1′)−H(1′)···O(6)	0.962(16)	2.54(2)	3.348(4)	141(2)
C(33′)−H(33′)···O(6)#5	0.95	2.56	3.510(3)	177.4

[a] Symmetry transformations used to generate equivalent atoms: #1, *x* − 1, −*y* + 1/2, *z* − 1/2; #2, −*x* + 1, −*y*, −*z* + 1; #3, *x* + 1, *y*, *z* + 1; #4, *x*, *y*, *z* + 1; #5, *x* + 1, *y*, *z*.

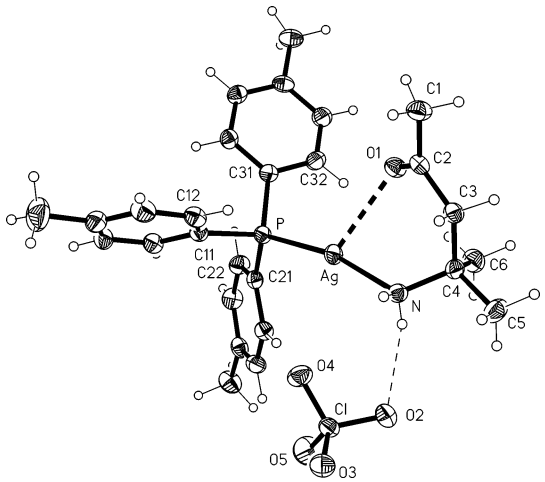


Figure 2. Crystal structure of complex **A** showing the atom numbering. Ellipsoids correspond to 50% probability levels. Selected bond lengths [Å] and angles [deg]: Ag−N 2.1677(14), Ag−P 2.3385(4), Ag−O(1) 2.6568(11), N−Ag−P 167.08(4), N−Ag−O(1) 81.16(5), P−Ag−O(1) 111.62(3).

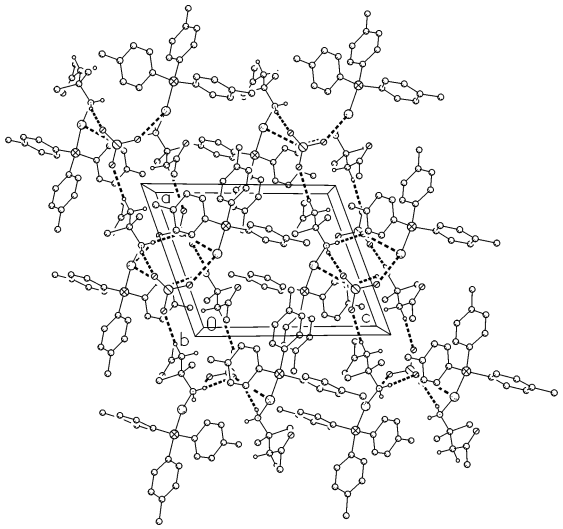


Figure 3. Packing diagram of **A** viewed parallel to the *y* axis. Secondary contacts (see text) are drawn as dashed bonds.

(Figures 2 and 3) consists of perchlorate anions and $[Ag\{H_2NC(Me)_2CH_2C(O)Me\}(PTo_3)]^+$ cations in which the silver atom is surrounded by the atoms P, N, and (at the greater distance of 2.6568(11) Å) O(2) to give an essentially planar but distorted T-shaped environment [P−Ag−N 167.08(4)°, N−Ag−O(1) 81.16(5)°, P−Ag−O(1) 111.62(3)°]. There is only one reported crystal structure of a silver complex

(44) Numberg, O.; Werner, H. *J. Organomet. Chem.* **1993**, *460*, 163.
(45) Matsubayashi, G.; Yokoyama, K.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1988**, 253.
(46) Clark, H. C. S.; Coleman, K. S.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Langer, J.; Smith, I. M. *J. Fluorine Chem.* **1998**, *91*, 207.

Table 3. Hydrogen Bonds [Å and deg] for **A**[a]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
N−H(01)···O(2)	0.833(15)	2.339(16)	3.1327(19)	159.4(18)
N−H(02)···O(4)#1	0.818(15)	2.280(15)	3.089(2)	170.3(18)
C(27)−H(27B)···O(2)#2	0.98	2.61	3.580(2)	169.7
C(12)−H(12)···O(3)#1	0.95	2.58	3.520(2)	169.5
C(26)−H(26)···O(4)	0.95	2.60	3.545(2)	172.4
C(3)−H(3B)···O(5)#3	0.99	2.46	3.449(2)	172.9

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x+1, -y+1, -z$; #2, $-x+2, -y+1, -z+1$; #3, $x-1, y, z$.

containing a primary amine and a phosphine (PMe_3).[47] Its Ag−P (2.373 Å) and Ag−N (2.367 Å) distances are greater than those in our complex [2.3385(4) and 2.1677(14) Å, respectively]. There is also only one reported crystal structure of a silver complex containing an intramolecular Ag···O=CR_2 contact through five bonds,[48] with a Ag···O distance (2.601 Å) slightly shorter than in our complex [2.6568(11) Å]. The perchlorate oxygens act as acceptors for a variety of secondary interactions; classical hydrogen bonds N−H···O, weak hydrogen bonds C−H···O (Table 3), and contacts Ag···O [Ag···O(4) 3.17 Å, Ag···O(3) ($1-x$, $1-y$, $-z$) 3.15 Å]. The classical hydrogen bonds, Ag···O contacts, and the shortest C−H···O combine to link the residues into chains parallel to the *x* axis (Figure 3).

NMR Spectra. The CD_3CN ^{1}H NMR spectrum of NH=CMe_2[3] shows one singlet ($\delta = 1.93$ ppm) for both Me groups while the NH resonance is not observed. The ^{1}H NMR spectra of complexes **1**−**10** show the NH resonance as a broad signal in the 8.27−9.30 ppm range.

At room temperature, the ^{1}H NMR spectrum of complex **2** shows two resonances [δ 2.14 (d, $^4J_{H-H} = 0.8$ Hz), 2.52 (s)] indicating the restricted rotation around the C=N bond at room temperature whereas in complexes **3**−**5** and **7**−**10** two singlets are observed. In those reported complexes giving only one doublet in their ^{1}H NMR spectra,[14,16−18,20,24,25,27] therefore corresponding to the Me trans to the NH proton, this resonance is at lower frequency than the other one appearing as a singlet. This allows the same assignment for the doublet at 2.14 ppm in **2** and for the singlet at lower frequency in all the other complexes. In the room-temperature spectra of complexes **1** and **6**, only one singlet resonance is observed for both Me groups, suggesting the free rotation of the C=N bond, as previously observed in the spectrum of [Au(NH=CMe_2)(PPh_3)]ClO_4 at 60 °C.[16] However, the acetone-d_6 spectrum of **1** between −60 and −90 °C shows two singlets (2.25, 2.28 ppm). In the cod and nbd complexes **5**−**8**, the signals corresponding to the olefinic protons were assigned by comparison with those of the free ligand and the bis(imine) complexes **2** and **3**. In all cases, the resonances from the CH=CH moieties are high field shifted with respect to those in the free ligands.

The ^{31}P{^{1}H} NMR spectra of the phosphino complexes **5**, **6**, **9**, and **10** show, in all cases, one doublet arising from coupling with ^{103}Rh, thus requiring the bis(phosphino) complexes **9** and **10** to be of trans geometry and the reactions leading to them to be stereoselective. Comparison of the $^1J_{P-Rh}$ coupling constants in **5** and **6** (around 160 Hz), with those in **9** and **10**, (around 128 Hz) suggests the trans influence of triarylphosphines to be greater than that of olefins.

IR Spectra. The vibrational spectra of NH=CMe_2 show two weak ν(NH) bands (Raman, 3326 and 3260 cm^{-1}) and two ν(C=N) bands (IR, 1658, 1670 sh cm^{-1}).[3] In the IR spectra of complexes **1**−**10**, a medium to strong broad ν(NH) band is observed in the 3186−3294 cm^{-1} region. Only one absorption is observed in the 1652−1666 cm^{-1} range from the ν(C=N) stretching mode, both for the mono- and bis-(imine) derivatives although the related complex [Au(NH=CMe_2)$_2$]ClO_4 shows two bands in the same region (1660, 1643 cm^{-1}). The IR spectrum of **4** shows two ν(CO) bands (2092, 2026 cm^{-1}) supporting its cis (C_{2v}) geometry. In the spectra of **9** and **10**, the only ν(CO) band is observed at 1994 cm^{-1}. The lower energy of the band in the bis(phosphine) complexes **9** and **10** can be accounted for in terms of the better σ-donor and poorer π-acceptor ability of two phosphine ligands with respect to the substituted CO and imine ligands in **4**.

Conclusions

Although acetimine is unstable, it can be stabilized by coordination to silver(I). [Ag(NH=CMe_2)$_2$]ClO_4 (**1**) was prepared by reacting $AgClO_4$ and NH_3 in acetone. The use of **1** as a transmetallating agent toward various chloro complexes of Rh(I) opens a new route for the synthesis of acetimino derivatives. The first Rh(I) complexes containing acetimine were prepared and characterized.

Acknowledgment. We thank Ministerio de Ciencia y Tecnología, FEDER (BQU2001-0133), and the Fonds der Chemischen Industrie for financial support. R.G. thanks Cajamurcia (Spain), and I.V.-H. thanks Fundación Séneca for grants.

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

IC035002+

(47) Plappert, E. C.; Mingos, D. M. P.; Lawrence, S. E.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2119.
(48) Blake, A. J.; Champness, N. R.; Howdle, S. M.; Morley, K. S.; Webb, P. B.; Wilson, C. *CrystEngComm* **2002**, *4*, 88.