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Synthesis of Acetimino Complexes of Pt(II) and Pt(IV) and the First Heteronuclear μ-Acetimido Complexes

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The reactions of $[Ag(NH{=}CMe_2)_2]ClO_4$ with *cis*-$[PtCl_2L_2]$ in a 1:1 molar ratio give *cis*-$[PtCl(NH{=}CMe_2)(PPh_3)_2]ClO_4$ (**1cis**) or *cis*-$[PtCl(NH{=}CMe_2)_2(dmso)]ClO_4$ (**2**), and in 2:1 molar ratio, they produce $[Pt(NH{=}CMe_2)_2L_2](ClO_4)_2$ [L = PPh_3 (**3**), L_2 = tbbpy = 4,4′-di-*tert*-butyl-2,2′-dipyridyl (**4**)]. Complex **2** reacts with PPh_3 (1:2) to give *trans*-$[PtCl(NH{=}CMe_2)(PPh_3)_2]ClO_4$ (**1trans**). The two-step reaction of *cis*-$[PtCl_2(dmso)_2]$, $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$, and PPh_3 (1:1:1) gives [*SP*-4-3]-$[PtCl(NH{=}CMe_2)(dmso)(PPh_3)]ClO_4$ (**5**). The reactions of complexes **2** and **4** with $PhICl_2$ give the Pt(IV) derivatives [*OC*-6-13]-$[PtCl_3(NH{=}CMe_2)_2(dmso)]ClO_4$ (**6**) and [*OC*-6-13]-$[PtCl_2(NH{=}CMe_2)_2$-(dtbbpy)]$(ClO_4)_2$ (**7**), respectively. Complexes **1cis** and **1trans** react with NaH and $[AuCl(PPh_3)]$ (1:10:1.2) to give *cis*- and *trans*-$[PtCl\{\mu\text{-}N(AuPPh_3){=}CMe_2\}(PPh_3)_2]ClO_4$ (**8cis** and **8trans**), respectively. The crystal structures of **4**·0.5Et_2O·0.5Me_2CO and **6** have been determined; both exhibit pseudosymmetry.

Introduction

Although acetimine, $Me_2C{=}NH$, can be identified among the condensation products of acetone and ammonia,[1] it decomposes readily to give acetonine and NH_3.[2] Its difficult synthesis[3,4] and handling may account for the scarcity of acetimino complexes reported so far,[5−8] none of which has been obtained using acetimine itself. We have described the syntheses of $[Au(NH{=}CMe_2)PPh_3]ClO_4$[8] and $[Ag(NH{=}CMe_2)_2]ClO_4$[9] and their use for preparing the first acetimino Rh(I)[9] and Rh(III)[10] complexes; an interesting coupling process between two acetimino ligands was found to occur

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at a Rh(III) center to give a 2-methyl-2-amino-4-iminopentano ligand.[10,11]

While this paper was being written, a paper by Natile et al. has appeared[12] describing the synthesis and in vitro antitumor activity of the first acetimino complexes of platinum, namely, the cis and trans isomers of $[PtX_2(NH{=}CMe_2)_2]$ and $[PtX_2(NH{=}CMe_2)(NH_3)]$ (X = Cl, I), in which the $Me_2C{=}NH$ ligands form from the reaction of coordinated ammonia with acetone in the presence of KOH. Complexes of Pt(IV) with a different type of NH-imine [RR′C═NOC(Me)═NH (R/R′ = Cl/Ar, NH_2/Ph),[13] $Ph_2C{=}NC(R){=}$NH (R = Me, Et),[14] R′OC(R)═NH (R/R′ = Me/Ph, Et/Me, Et/Ph),[15] or $H_2NN{=}C(R')C(Me){=}NOC(R){=}$NH (R/R′ = Me/Ph, Et/Me, Et/Ph)][16] have been obtained by the attack of various nucleophiles on (nitrile)Pt(IV) complexes.

Although many complexes containing terminal ketimido/azavinylidene ligands ($R_2C{=}N$-M/$R_2C{=}N{=}$M/) have been reported,[17] those with an acetimido bridging ligand are scarce, and only homonuclear species have been reported so far.[7,18−24] Nearly as many different synthetic methods as bridging acetimido complexes have been described, none of them being of general application. They involve processes in which the appropriate precursors decompose thermally,[21,22] rearrange,[20] or react with 2-nitropropane and CO,[19] 2-bromo-2-nitrosopropane,[7] or $Me_2C{=}NCl$.[23,24]

In this paper, we show that $[Au(NH{=}CMe_2)PPh_3]ClO_4$[8] and $[Ag(NH{=}CMe_2)_2]ClO_4$[9] can also be used to prepare acetimino complexes of platinum. The new species here described include (i) the first cationic mono- and bis-(acetimino) complexes of Pt(II) (**1**−**5**), (ii) the first Pt(IV) complexes with $NH{=}CR_2$ ligands (**6** and **7**), and (iii) the first heteronuclear μ-acetimido complexes of any metals (**8cis** and **8trans**). Unfortunately, all attempts, in some of these complexes, to provoke an intramolecular coupling process between two acetimino ligands to give a 2-methyl-2-amino-4-iminopentano ligand were unfruitful.

Experimental Section

IR spectroscopy, elemental analyses, and melting point determinations were carried out as described elsewhere.[8] Molar conductivities were measured on ca. 5×10^{-4} M acetone solutions with a Crison Micro CM2200 conductimeter. The expected ranges for the 1:1 and 1:2 electrolytes have been reported.[25] The NMR spectra were recorded on Bruker Avance 200, 300, or 400 MHz spectrometers. Chemical shifts are referred to TMS (^{1}H and $^{13}C\{^1H\}$) or H_3PO_4 ($^{31}P\{^1H\}$). 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 [$PtCl_2$ (Johnson Matthey), $AgClO_4$, NaH (Aldrich, 60%, dispersion in mineral oil), PPh_3, and Me_4NCl (Fluka)] were obtained from commercial sources and used as received. $[Ag(NH{=}CMe_2)_2]ClO_4$,[9] $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$,[8] *cis*-$[PtCl_2(PPh_3)_2]$,[26] *cis*-$[PtCl_2(dmso)_2]$,[27] $[AuCl(PPh_3)]$,[28] and $PhICl_2$[29] were prepared according to literature methods. $[PtCl_2(dtbbpy)]$ was synthesized by being refluxed in acetone (15 mL), a mixture of $PtCl_2$ (500 mg, 1.88 mmol), and dtbbpy (605 mg, 2.26 mmol) until a yellow suspension formed, which was removed by filtration, and the solid was washed with Et_2O (3×5 mL) and suction dried (88% yield).

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

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***cis*-[PtCl(NH=CMe$_2$)(PPh$_3$)$_2$]ClO$_4$ (1cis).** [Ag(NH=CMe$_2$)$_2$]ClO$_4$ (127 mg, 0.39 mmol) was added to a solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (312 mg, 0.39 mmol) in CH_2Cl_2 (20 mL). The resulting suspension was stirred for 30 min and filtered through Celite. The filtrate was concentrated (1 mL), and Et_2O (25 mL) was added to give a suspension, which was stirred for 5 min and filtered. The solid was dried in an oven (70 °C) for 12 h to give **1cis** as a colorless powder. Yield: 321 mg, 88%. mp: 254 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.54 (s, 3H, Me), 2.26 (s, 3H, Me), 7.23−7.60 (m, 30H, Ph), 10.65 (br, 1H, NH). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ 5.2 (d, $^2J_{PP}$ = 19 Hz, $^1J_{PPt}$ = 3112 Hz), 14.1 (d, $^2J_{PP}$ = 19 Hz, $^1J_{PPt}$ = 3710 Hz). ^{13}C{^{1}H} NMR (50 MHz, DMSO-d_6): δ 26.8 (d, Me, $^4J_{CP}$ = 7 Hz), 27.8 (s, Me), 127.2 (vt, *ipso*-C, N = 130 Hz), 128.2 (d, *meta*-C, $^2J_{CP}$ = 10 Hz), 129.0 (d, *meta*-C, $^2J_{CP}$ = 15 Hz), 131.4 (d, *para*-C, $^4J_{CP}$ = 0.2 Hz), 132.1 (d, *para*-C, $^4J_{CP}$ = 0.2 Hz), 133.8 (d, *ortho*-C, $^3J_{CP}$ = 10 Hz), 134.5 (d, *ortho*-C, $^3J_{CP}$ = 10 Hz), 184.3 (s, C=N). IR (cm^{-1}): ν_{NH} 3238, $\nu_{C=N}$ 1674, ν_{PtCl} 306. Λ_M: **1cis** is insoluble in acetone. Anal. Calcd for $C_{39}H_{37}Cl_2NO_4P_2Pt$: C, 51.38; H, 4.09; N, 1.54. Found: C, 51.60; H, 4.14; N, 1.54.

***trans*-[PtCl(NH=CMe$_2$)(PPh$_3$)$_2$]ClO$_4$ (1trans). 2·**H_2O (65 mg, 0.12 mmol) was added to a solution of PPh_3 (65 mg, 0.25 mmol) in acetone (10 mL). The solution was stirred for 1 h and concentrated under vacuum (1 mL), and then Et_2O (20 mL) was added. The suspension was filtered, and the solid was dried first by suction and then in an oven at 60 °C for 24 h to give **1trans** as a colorless powder. Yield: 95 mg, 87%. mp (dec): 143 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.01 (s, 3H, Me), 1.59 (s, 3H, Me), 7.59−7.68 (m, 30H, Ph), 10.53 (br, 1H, NH). ^{31}P{^{1}H} NMR (121 MHz, DMSO-d_6): δ 19.3 (s, $^1J_{PPt}$ = 2604 Hz). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ 26.0 (Me), 28.2 (Me), 127.0 (vt, *ipso*-C, *N* = 60 Hz), 129.1 (vt, *meta*-C, *N* = 8 Hz), 131.8 (s, *para*-C), 134.3 (vt, *ortho*-C, *N* = 8 Hz), 184.4 (C=N). IR (cm^{-1}): ν_{NH} 3192, $\nu_{C=N}$ 1672, ν_{PtCl} 335. Λ_M (Ω^{-1} cm^2 mol^{-1}): 106. Anal. Calcd for $C_{39}H_{37}Cl_2NO_4PPt$: C, 51.38; H, 4.09; N, 1.54. Found: C, 51.05; H, 4.02; N, 1.59.

***cis*-[PtCl(NH=CMe$_2$)$_2$(dmso)]ClO$_4$·H$_2$O (2·H$_2$O).** [Ag(NH=CMe$_2$)$_2$]ClO$_4$ (145 mg, 0.45 mmol) was added to a suspension of *cis*-[PtCl$_2$(dmso)$_2$] (190 mg, 0.45 mmol) in CH_2Cl_2 (30 mL). After it was stirred for 30 min, the reaction mixture was filtered through Celite, and the filtrate was concentrated to dryness. The residue was heated at 70 °C under vacuum for 30 min and dissolved in CH_2Cl_2 (2 mL), and then Et_2O (20 mL) was added to precipitate a sticky material. The solvent was decanted, and when the residue was stirred with Et_2O (3 × 20 mL), a colorless solid formed which was filtered off and suction dried to give **2·**H_2O. Yield: 188 mg, 77%. mp: 118 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ 2.32 (d, 3H, Me, $^4J_{HH}$ = 1 Hz), 2.36 (d, 3H, Me, $^4J_{HH}$ = 1 Hz), 2.58 (s, 3H, Me), 2.59 (s, 3H, Me), 2.80 (s, 2H, H_2O), 3.47 (s+d, $^3J_{HPt}$ = 20 Hz, 6H, Me, DMSO), 9.95 (br, 2 H, NH). ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 27.6 (Me), 27.8 (Me), 28.0 (Me), 28.1 (Me), 43.5 (Me, DMSO, $^2J_{CPt}$ = 55 Hz), 190.6 (C=N), 191.2 (C=N). IR (cm^{-1}): ν_{NH} 3260, $\nu_{C=N}$ 1678, $\nu_{S=O}$ 1190, ν_{PtCl} 349. Λ_M (Ω^{-1} cm^2 mol^{-1}): 102. Anal. Calcd for $C_8H_{22}Cl_2N_2O_6PtS$: C, 17.78; H, 4.10; N, 5.18; S, 5.93. Found: C, 17.48; H, 3.72; N, 5.03; S, 6.02.

***cis*-[Pt(NH=CMe$_2$)$_2$(PPh$_3$)$_2$](ClO$_4$)$_2$·H$_2$O (3·H$_2$O).** [Ag(NH=CMe$_2$)$_2$]ClO$_4$ (163 mg, 0.51 mmol) was added to a solution of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (200 mg, 0.25 mmol) in CH_2Cl_2 (25 mL). The resulting suspension was stirred for 30 min and filtered. The filtrate was concentrated under vacuum (1 mL), and upon the addition of Et_2O (20 mL), the suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and suction dried to give **3** as a colorless powder. Yield: 253 mg, 96%. mp (dec): 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (s, 2H, H_2O), 1.71 (s, 3H, Me), 2.18 (d, 3H, Me, $^4J_{HH}$ = 3 Hz), 7.38−7.54 (m, 15H, Ph), 9.50 (br, 1H, NH). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 2.5 (s, $^1J_{PPt}$ = 3324 Hz). ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ 28.2 (vt, Me, *N* = 3 Hz), 29.0 (Me), 126.6 (vd, *ipso*-C, *N* = 64 Hz), 130.2 (vt, *meta*-C, *N* = 11 Hz), 133.3 (*para*-C), 135.3 (vt, *ortho*-C, *N* = 10 Hz), 192.5 (vd, C=N, *N* = 8 Hz). IR (cm^{-1}): ν_{NH} 3224, $\nu_{C=N}$ 1660, 1644. Λ_M (Ω^{-1} cm^2 mol^{-1}): 258. Anal. Calcd for $C_{42}H_{46}Cl_2N_2O_9P_2Pt$: C, 48.01; H, 4.41; N, 2.67. Found: C, 47.79; H, 4.49; N, 2.75.

[Pt(NH=CMe$_2$)$_2$(dtbbpy)](ClO$_4$)$_2$·H$_2$O (4·H$_2$O). [Ag(NH=CMe$_2$)$_2$]ClO$_4$ (343 mg, 1.07 mmol) was added to a suspension of [PtCl$_2$(dtbbpy)] (259 mg, 0.48 mmol) in CH_2Cl_2 (80 mL). The reaction mixture was stirred for 5 h and filtered through Celite. The filtrate was concentrated under vacuum (1 mL), and Et_2O (20 mL) was added to precipitate a colorless solid, which was filtered, washed successively with CH_2Cl_2 (2 mL) and Et_2O (2 × 5 mL), and suction dried to give **4·**H_2O as a colorless powder. Yield: 265 mg, 70%. mp (dec): 189 °C. ^{1}H NMR (200 MHz, acetone-d_6): δ 1.45 (s, 18H, ^{t}Bu), 2.55 (s, 6H, Me), 2.71 (s, 6H, Me), 2.83 (s, 2H, H_2O), 7.88 (dd, 2H, H5-bpy, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz), 8.59 (d, 2H, H6-bpy, $^3J_{HH}$ = 6 Hz), 8.74 (d, 2H, H3-bpy, $^4J_{HH}$ = 2 Hz), 10.53 (br, 2H, NH). ^{13}C{^{1}H} NMR (50 MHz, acetone-d_6): δ 28.44 (Me), 28.54 (Me), 29.94 (C*Me*$_3$), 36.7 (*C*Me$_3$), 122.4 (C3-bpy), 125.9 (C5-bpy), 150.7 (C6-bpy), 157.0 (C2-bpy), 167.6 (C4-bpy), 193.9 (C=N). IR (cm^{-1}): ν_{OH} 3604, ν_{NH} 3231, $\nu_{C=N}$ 1650, 1621. Λ_M (Ω^{-1} cm^2 mol^{-1}): 170. Anal. Calcd for $C_{24}H_{40}Cl_2N_4O_9Pt$: C, 36.28; H, 5.07; N, 7.05. Found: C, 35.92; H, 4.88; N, 7.06. Crystals of **4·**0.5Et_2O·0.5Me_2CO suitable for an X-ray difraction study were obtained by the liquid diffusion method using acetone and Et_2O.

***SP*-4-3]-[PtCl(NH=CMe$_2$)(dmso)(PPh$_3$)]ClO$_4$ (5).** [Au(NH=CMe$_2$)(PPh$_3$)]ClO$_4$ (292 mg, 0.47 mmol) was added to a suspension of *cis*-[PtCl$_2$(dmso)$_2$] (200 mg, 0.47 mmol) in acetone (30 mL). The resulting solution was stirred for 1 h and filtered through Celite. The filtrate was concentrated to dryness, and the residue was stirred with Et_2O (5 × 20 mL) to remove [AuCl(PPh$_3$)]. The suspension was filtered, and the off-white solid was suction dried (**A**, see Results and Discussion). It was then dissolved in acetone (20 mL), and a solution of PPh_3 (123 mg, 0.47 mmol) in acetone (10 mL) was added dropwise over a period of 15 min. The solution was stirred for 1h and concentrated under vacuum to ca. 1 mL, and then Et_2O (20 mL) was added to precipitate a sticky solid. The solvent was decanted, and the residue was dried under vacuum, washed with Et_2O (2 × 10 mL), and recrystallized from CH_2Cl_2/Et_2O to give **5** as a colorless powder. Yield: 280 mg, 82%. mp (dec): 134 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.73 (s, 3H, Me), 2.21 (s, 3H, Me), 3.34 (s+d, $^3J_{HPt}$ = 16 Hz, 6H, *Me*$_2$SO), 7.36−7.84 (m, 15H, Ph), 9.51 (br, 1H, NH). ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$): δ 14.7 (s, $^1J_{PPt}$ = 3677 Hz). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 27.5 (Me), 28.6 (Me), 45.0 (Me, dmso), 125.9 (d, *ipso*-C, $^1J_{C-P}$ = 65 Hz), 129.2 (d, *meta*-C, $^3J_{CP}$ = 10 Hz), 132.5 (d, *para*-C, $^4J_{CP}$ = 5 Hz), 134.2 (d, *ortho*-C, $^2J_{CP}$ = 10 Hz), 187.8 (C=N). IR (cm^{-1}): ν_{NH} 3225, $\nu_{C=N}$ 1668, 1651, $\nu_{S=O}$ 1149, ν_{PtCl} 303. Λ_M (Ω^{-1} cm^2 mol^{-1}): 148. Anal. Calcd for $C_{23}H_{28}Cl_2NO_5PPtS$: C, 37.97; H, 3.88; N, 1.93; S, 4.41. Found: C, 37.77; H, 3.93; N, 1.95, S, 4.12.

***OC*-6-13]-[PtCl$_3$(NH=CMe$_2$)$_2$(dmso)]ClO$_4$ (6).** $PhICl_2$ (158 mg, 0.57 mmol) was added to a solution of *cis*-[PtCl(dmso)(NH=CMe$_2$)$_2$]ClO$_4$ (**2·**H_2O) (100 mg, 0.18 mmol) in CH_2Cl_2 (15 mL). The resulting solution was stirred for 1 h and filtered through Celite, and the filtrate was concentrated under vacuum to ca. 1 mL. Et_2O (20 mL) was added; the suspension was filtered, and the solid was washed with Et_2O (2 × 5 mL) and suction dried to give **6** as a pale yellow powder. Yield: 90 mg, 82%. mp: 153 °C. ^{1}H NMR (400

MHz, acetone-d_6): δ 2.61 (s, 3H, Me), 2.69 (s, 3H, Me), 2.74 (s, 3H, Me), 2.77 (s, 3H, Me), 3.83 (s+d, 6H, Me_2SO, $^3J_{HPt}$ = 14 Hz), 9.71 (t, br, 1H, NH, $^1J_{HN}$ = 56 Hz), 10.37 (t, br, 1H, NH, $^1J_{HN}$ = 55 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, acetone-d_6): δ 25.6 (Me), 25.8 (Me), 30.3 (Me), 30.7 (Me), 41.4 (Me, DMSO, $^2J_{CPt}$ = 28 Hz), 195.4 (C=N), 197.3 (C=N). IR (cm^{-1}): ν_{NH} 3232, $\nu_{C=N}$ 1644, $\nu_{S=O}$ 1176, ν_{PtCl} 377, 351. Λ_M (Ω^{-1} cm^2 mol^{-1}): 142. Anal. Calcd for $C_8H_{20}Cl_4N_2O_5PtS$: C, 16.20; H, 3.40; N, 4.72; S, 5.40. Found: C, 16.14; H, 3.36; N, 4.60; S, 5.05. Crystals of **6** suitable for an X-ray diffraction study were obtained by the liquid diffusion method using acetone and Et_2O.

[*OC*-6-13]-[PtCl$_2$(NH=CMe$_2$)$_2$(dtbbpy)](ClO$_4$)$_2$ (7). $PhICl_2$ (106 mg, 0.39 mmol) was added to a suspension of **4**·H_2O (100 mg, 0.13 mmol) in CH_2Cl_2 (15 mL). After it was stirred for 2 h, the resulting suspension was filtered. The solid was washed with Et_2O (2 × 5 mL) and suction dried to give **7** as a pale yellow powder. Yield: 88 mg, 80%. mp: 226 °C. ^1H NMR (300 MHz, acetone-d_6): δ 1.52 (s, 18H, ^{t}Bu), 2.83 (s+d, 6H, Me, $^4J_{HPt}$ = 7 Hz), 2.94 (s, 6H, Me), 8.25 (dd, 2H, H5-bpy, $^3J_{HH}$ = 9 Hz, $^4J_{HH}$ = 3 Hz), 8.98 (d+dd, 2H, H6-bpy, $^3J_{HH}$ = 6 Hz, $^3J_{HPt}$ = 21 Hz), 9.08 (d, 2H, H3-bpy, $^4J_{HH}$ = 3 Hz), 11.11 (br, 2H, NH). $^{13}C\{^1H\}$ NMR: decomposes in solution. IR (cm^{-1}): ν_{NH} 3259, 3137, $\nu_{C=N}$ 1644, 1621, ν_{PtCl} 370. Λ_M (Ω^{-1} cm^2 mol^{-1}): 174. Anal. Calcd for $C_{24}H_{38}Cl_4N_4O_8Pt$: C, 34.01; H, 4.52; N, 6.61. Found: C, 34.00; H, 5.00; N, 6.76.

***cis*-[PtCl{μ-N(AuPPh$_3$)=CMe$_2$}(PPh$_3$)$_2$]ClO$_4$ (8cis).** Dry CH_2Cl_2 (25 mL) and THF (20 mL) were successively added to a flask previously charged, under nitrogen, with **1cis** (80 mg, 0.09 mmol), [AuCl(PPh_3)] (52 mg, 0.10 mmol) and NaH (60% dispersion in mineral oil, 35 mg, 0.9 mmol), and the reaction mixture was refluxed for 5 h under nitrogen. After it was cooled to room temperature, the mixture was filtered in air through anhydrous $MgSO_4$. The filtrate was concentrated under vacuum to ca. 1 mL, and Et_2O (20 mL) added to precipitate **8cis** as a cream-colored solid which was filtered off and suction dried. Yield: 103 mg, 84%. mp: 161 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 1.68 (s, 3H, Me), 2.26 (s, 3H, Me), 7.10−7.54 (m, 45H, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 6.6 (d, $^2J_{PP}$ = 20 Hz, $^1J_{PPt}$ = 2738 Hz), 16.9 (d, $^2J_{PP}$ = 20 Hz, $^1J_{PPt}$ = 4014 Hz), 30.0 (s, $AuPPh_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 34.0 (dd, Me, $^4J_{CP}$ = 8 Hz, $^4J_{CP}$ = 4 Hz), 34.6 (d, Me, $^4J_{CP}$ = 12 Hz), 128.1 (d, *meta*-C, $^3J_{CP}$ = 11 Hz), 128.5 (d, *meta*-C, $^3J_{CP}$ = 11 Hz), 129.6 (d, *meta*-C, $^3J_{CP}$ = 12 Hz), 130.9 (d, *para*-C, $^4J_{CP}$ = 2 Hz), 131.91 (*para*-C), 132.4 (d, *para*-C, $^4J_{CP}$ = 2 Hz), 133.8 (d, *ortho*-C, $^2J_{CP}$ = 13 Hz), 134.1 (dd, *ortho*-C, $^2J_{CP}$ = 24 Hz, $^4J_{CP}$ = 10 Hz), 134.7 (d, *ortho*-C, $^2J_{CP}$ = 10 Hz), 178.5 (d, CN, $^3J_{CP}$ = 3 Hz). IR (cm^{-1}): $\nu_{C=N}$ 1639, ν_{PtCl} 320. Λ_M (Ω^{-1} cm^2 mol^{-1}): 130. Anal. Calcd for $C_{57}H_{51}AuCl_2NO_4P_3Pt$: C, 49.98; H, 3.75; N, 1.02. Found: C, 49.68; H, 3.87; N, 1.03.

***trans*-[PtCl{μ-N(AuPPh$_3$)=CMe$_2$}(PPh$_3$)$_2$]ClO$_4$ (8trans).** Dry CH_2Cl_2 (40 mL) was added to a Carius tube previously charged, under nitrogen, with **1trans** (125 mg, 0.14 mmol), NaH (60% dispersion in mineral oil, 65 mg, 1.6 mmol), and [AuCl(PPh_3)] (74 mg, 0.15 mmol), and the mixture was heated at 70 °C for 6 h. After it was cooled to room temperature, the mixture was filtered in air through Celite, and the filtrate was concentrated under vacuum to ca. 1 mL. Upon addition of Et_2O (20 mL), **8trans** precipitated as a cream-colored powder which was filtered off and suction dried. Yield: 118 mg, 62%. mp: 152 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 3H, Me), 1.57 (s, 3H, Me), 7.11−7.74 (m, 45H, Ph). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 19.5 (*P*Pt, $^1J_{PPt}$ = 2847 Hz), 27.5 (s, *P*Au). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 34.5 (Me), 35.1 (d, Me, $^4J_{CP(Au)}$ = 8 Hz), 127.7 (d, *ipso*-C, $AuPPh_3$, $^1J_{CP}$ = 62 Hz), 127.9 (vt, *ipso*-C, $PtPPh_3$, *N* = 57 Hz), 128.7 (vt, *meta*-C, $PtPPh_3$, *N* = 11 Hz), 129.7 (d, *meta*-C, $AuPPh_3$, $^3J_{CP}$ = 12 Hz), 131.6 (s, *para*-C, PPh_3), 132.5 (d, *para*-C, $^4J_{CP}$ = 2 Hz), 133.7 (d, *ortho*-C, $AuPPh_3$, $^2J_{CP}$ = 13 Hz), 134.8 (vt, *ortho*-C, $PtPPh_3$, *N* = 12 Hz), 179.4 (C=N). IR (cm^{-1}): $\nu_{C=N}$ 1632. Λ_M (Ω^{-1} cm^2 mol^{-1}): 116. Anal. Calcd for $C_{57}H_{51}AuCl_2NO_4P_3Pt$: C, 49.98; H, 3.75; N, 1.02. Found: C, 49.97; H, 3.79; N, 1.09.

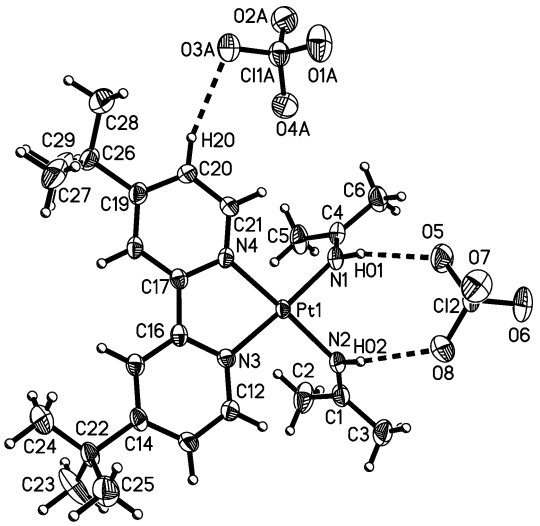


Figure 1. Crystal structure of complex **4** showing the atom numbering. Ellipsoids correspond to 50% probability levels. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) = 2.005(4), Pt(1)−N(2) = 2.012(4), Pt(1)−N(4) = 2.014(4), Pt(1)−N(3) = 2.015(4), N(1)−C(4) = 1.279(7), N(2)−C(1) = 1.273(7); N(1)−Pt(1)−N(2) = 86.75(18), N(1)−Pt(1)−N(4) = 96.39(17), N(2)−Pt(1)−N(3) = 96.29(17), N(4)−Pt(1)−N(3) = 80.54(17).

X-ray Structure Determinations of 4·0.5Et$_2$O·0.5Me$_2$CO and 6. Figures 1 and 2 show the ellipsoid representations, and Table 1 gives a summary of crystallographic data. The crystals were mounted in inert oil on a glass fiber and transferred to the cold stream of the diffractometer (Bruker SMART Apex for **4** and Bruker SMART 1000 CCD for **6**). Absorption corrections were applied using the program SADABS. The structures were refined anisotropically on F^2 (SHELXL, G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included as follows: NH hydrogens refined freely with N−H distance restraints ("SADI"), methyls as rigid groups, others riding.

Special Features of 4. The acetone and ether of solvation are each disordered over an inversion center. The hydrogen atoms of the acetone were not included in the refinement. Compound **4** exhibits pseudosymmetry. The near-equality of the triclinic *b* and *c* axes and β and γ angles means that a C-centered metrically monoclinic cell may be generated. The structure can be solved and refined in this cell [a = 21.4738(8) Å, b = 13.2669(5) Å, c = 12.0762(5) Å, α = 90.406(1)°, β = 100.404(1)°, γ = 90.348(1)°] with a *C*2/*m* space group. However, there are several anomalies. The monoclinic α and γ angles differ appreciably from 90°, and the *R* values (R_{int} = 0.0771, R_2 = 0.0960, and R_1 = 0.0452) are significantly worse than in the triclinic case. For this reason, we prefer the triclinic description. However, unambiguous proof of the correct symmetry is probably impossible to obtain.

Special Features of 6. We thank a referee for suggesting that we should comment in more detail on the pseudosymmetry of this compound. For a large fraction of the structure, the atoms can be grouped into pairs for which the atoms are related by a translation of 0.5 in x (reflections with h odd are very weak), and this halved structure can be solved and refined down to acceptable *R* values (R_2 = ca. 8%). However, difference peaks of ca. 2−3 e/Å^3 are observed in the perchlorate and DMSO groups, and the *U* values

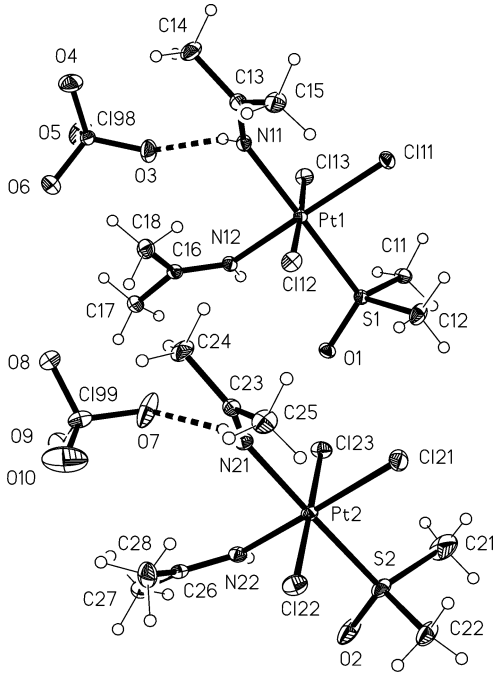


Figure 2. Crystal structure of complex **6** showing the atom numbering. Ellipsoids correspond to 30% probability levels. Selected bond lengths (Å) and angles (deg): Pt(1)−N(12) = 2.037(3), Pt(1)−N(11) = 2.063(3), Pt(2)−N(22) = 2.045(3), Pt(2)−N(21) = 2.056(3), Pt(1)−Cl(11) = 2.3159(8), Pt(1)−Cl(12) = 2.3224(8), Pt(1)−Cl(13) = 2.3189(8), Pt(2)−Cl(21) = 2.3169(9), Pt(2)−Cl(22) = 2.3245(9), Pt(2)−Cl(23) = 2.3117(8), Pt(1)−S(1) = 2.3200(8), Pt(2)−S(2) = 2.3168(8), N(11)−C(13) = 1.280(4), N(12)−C(16) = 1.278(4), N(21)−C(23) = 1.284(4), N(22)−C(26) = 1.285(4), S(1)−O(1) = 1.455(2), S(2)−O(2) = 1.445(3); N(12)−Pt(1)−N(11) = 90.48(11), N(22)−Pt(2)−N(21) = 88.55(11), N(11)−Pt(1)−Cl(11) = 91.64(8), N(21)−Pt(2)−Cl(21) = 92.50(8), N(11)−Pt(1)−Cl(13) = 84.24(8), N(21)−Pt(2)−Cl(23) = 83.96(8), N(11)−Pt(1)−Cl(12) = 95.46(8), N(21)−Pt(2)−Cl(22) = 96.60(8), N(12)−Pt(1)−Cl(13) = 85.07(8), N(22)−Pt(2)−Cl(23) = 84.52(8), N(12)−Pt(1)−Cl(12) = 92.33(8), N(22)−Pt(2)−Cl(22) = 93.95(8), N(12)−Pt(1)−S(1) = 88.17(8), N(22)−Pt(2)−S(2) = 89.73(8), Cl(13)−Pt(1)−Cl(11) = 89.19(3), Cl(23)−Pt(2)−Cl(21) = 90.40(3), Cl(11)−Pt(1)−Cl(12) = 93.42(3), Cl(21)−Pt(2)−Cl(22) = 91.10(4), Cl(11)−Pt(1)−S(1) = 89.51(3), Cl(21)−Pt(2)−S(2) = 88.78(3), Cl(13)−Pt(1)−S(1) = 93.85(3), Cl(23)−Pt(2)−S(2) = 91.12(3), S(1)−Pt(1)−Cl(12) = 86.40(3), S(2)−Pt(2)−Cl(22) = 88.28(3).

of the perchlorate O and DMSO C and O are high. It is possible that these groups are disordered in the smaller cell, but we prefer the larger cell without disorder. The basic ADDSYM command in the program PLATON (A. L. Spek, University of Utrecht, Netherlands) suggests halving the cell, but its EXACT symmetry analysis does not. It is probable that, without a detailed experimental assessment of the weak reflections, the two models cannot be distinguished with absolute confidence.

Results and Discussion

Synthesis of Acetimino Pt(II) and (IV) Complexes. The acetimino Pt(II) complexes, **1**−**5** (Scheme 1), were obtained by transmetalation of acetimine from $[Ag(NH{=}CMe_2)_2]ClO_4$ or $[Au(NH{=}CMe_2)PPh_3]ClO_4$ to the appropriate precursor *cis*-$[PtCl_2L_2]$ (L = PPh_3, DMSO; L_2 = dtbbpy). The results depend on the transmetalating agent, the nature of the L ligands, and the molar ratio used. When equimolar amounts of $[Ag(NH{=}CMe_2)_2]ClO_4$ and *cis*-$[PtCl_2L_2]$ were used, complexes *cis*-$[PtCl(NH{=}CMe_2)(PPh_3)_2]ClO_4$ (**1cis**) or *cis*-$[PtCl(NH{=}CMe_2)_2(dmso)]ClO_4{\cdot}H_2O$ (**2**·H_2O) were obtained in good yields. The precipitation of AgCl produces two free acetimino ligands, one of which occupies a vacant position at the Pt center to give **1cis**. Complex **2** results from the additional substitution of the labile DMSO trans to the chloro ligand by the second imine present in solution. Under the same reaction conditions, $[PtCl_2(dtbbpy)]$ and $[Ag(NH{=}CMe_2)_2]ClO_4$ gave $[PtCl(NH{=}CMe_2)(dtbbpy)]ClO_4$ contaminated with $[Pt(NH{=}CMe_2)_2(dtbbpy)](ClO_4)_2$ (**4**, see below) and another impurity that we could not identify. We failed not only to separate this mixture but also in two other attempts to isolate the monoimino complex.[30] Thus, the reaction of $[PtCl_2(dtbbpy)]$ with $[Au(NH{=}CMe_2)(PPh_3)]ClO_4$ (1:1, 45 min, DMSO; no reaction occurs in CH_2Cl_2) and that of **4**·H_2O with QCl (Q = PPN = $Ph_3P{=}N{=}PPh_3$, 1:1, 2 h; Me_4N, 1:1.2, 12 h) gave the desired $[PtCl(NH{=}CMe_2)(dtbbpy)]ClO_4$ (by ^1H and ^{31}P NMR) as the major product, but it was mixed with other products ($[AuCl(PPh_3)]$ + $[PtCl_2(dtbbpy)]$, or $PPNClO_4$, or $(NMe_4)ClO_4$ + $(NMe_4)Cl$, respectively) that we could not separate.

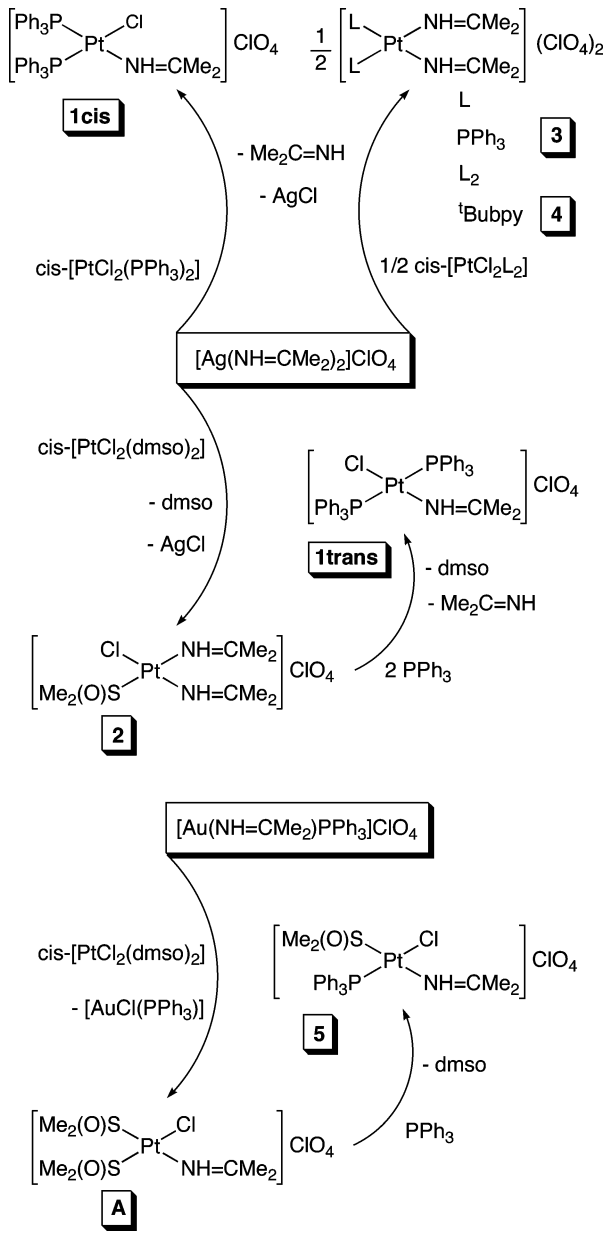
Two equivalents of $[Ag(NH{=}CMe_2)_2]ClO_4$ react with *cis*-$[PtCl_2L_2]$ to give *cis*-$[Pt(NH{=}CMe_2)_2L_2](ClO_4)_2{\cdot}H_2O$ [L =

Table 1. Crystal Data for Compounds **4**·0.5Et_2O·0.5Me_2CO and **6**

	4·0.5Et_2O·0.5Me_2CO	**6**
formula	$C_{27.5}H_{46}Cl_2N_4O_9Pt$	$C_8H_{20}Cl_4N_2O_5PtS$
cryst size (mm^3)	0.30 × 0.15 × 0.14	0.30 × 0.25 × 0.15
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	12.0737(7)	14.3033(8)
b (Å)	12.5843(8)	10.4115(6)
c (Å)	12.6521(8)	25.5757(14)
α (deg)	63.420(2)	90
β (deg)	81.402(2)	105.820(4)
γ (deg)	80.928(2)	90
V ($Å^3$)	1690.87(18)	3664.4(4)
Z	2	8
ρ_{calcd} (Mg/m^3)	1.655	2.151
M_ρ	842.67	593.21
T (K)	100(2)	133(2)
F(000)	846	2272
μ(Mo Kα) (mm^{-1})	4.361	8.372
θ range (deg)	1.81−26.37	1.48−30.19
abs correction	semiempirical from equivalents	semiempirical from equivalents
reflns collected	18 512	69 312
independent reflns	6854	10 221
R_{int}	0.0283	0.0297
completeness (%)	99.4 (θ = 26.00°)	95.4 (θ = 30.00°)
transm	0.5803/0.3545	0.367/0.213
data/restraints/params	6854/76/445	10221/6/404
GOF on F^2	1.166	1.087
final R indices [$I > 2s(I)$]	R_1 = 0.0362, R_2 = 0.0838	R_1 = 0.0239 R_2 = 0.0518
R indices (all data)	R_1 = 0.0390 R_2 = 0.0850	R^1 = 0.0354 R_2 = 0.0567
largest diff. peak and hole (e.$Å^{-3}$)	2.790 and −1.441	1.460 and −0.935
wavelength (Å)	0.71073	0.71073
index ranges	$-14 \le h \le 14$ $-15 \le k \le 15$ $-15 \le l \le 15$	$-19 \le h \le 20$ $-14 \le k \le 14$ $-35 \le l \le 35$
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2

(30) ^1H NMR (200 MHz, $CDCl_3$): δ 1.43 (s, 9H, Me, ^{t}Bu), 1.47 (s, 9H, ^{t}Bu), 2.49 (s, 3H, Me), 2.60 (s, 3H, Me), 7.61 (dd, 1H, H5 or 5′, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 3 Hz), 7.68 (dd, 1H, H5 or 5′, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 3 Hz), 8.19 (d, 1H, H6 or H6′, $^4J_{HH}$ = 3 Hz), 8.21 (d 1H, H6 or H6′, $^4J_{HH}$ = 3 Hz), 8.79 (d, 1H, H3 or H3′, $^3J_{HH}$ = 6 Hz), 9.28 (d, 1H, H3 or H3′, $^3J_{HH}$ = 6 Hz), 10.53 (br, 1H, NH).

Scheme 1



PPh_3 (**3**·H_2O), L_2 = dtbbpy (**4**·H_2O)**]** in good yield. In the latter case, an excess of the silver complex must be used to prevent the formation of a mixture of **4** with [PtCl(NH═CMe_2)(dtbbpy)]ClO_4 and [$PtCl_2$(dtbbpy)], which we could not resolve. The analogous reaction between [Ag(NH═CMe_2)$_2$]ClO_4 and *cis*-[$PtCl_2$(dmso)$_2$] led to extensive decomposition suggesting that the resulting complexes, [Pt(NH═CMe_2)$_x$(dmso)$_{4-x}$]$^{2+}$, are unstable in solution.

The 2-methyl-2-amino-4-iminopentano ligand has been shown to form from the coupling of two acetimino ligands at a Rh(III) center facilitated by the presence of catalytic or stoichiometric amounts of various labile ligands.[10,11] However, neither the reaction of **3**·H_2O with Ph_2C═NH nor those of **6** with $AsPh_3$, Ph_2C═NH, or PPNCl produce, under similar reaction conditions (1:1, CH_2Cl_2, 24 h), any detectable (^{1}H NMR) amount of the condensed amino−imino ligand.

We have studied the reactivity of **2**·H_2O toward (i) [Au(NH═CMe_2)(PPh_3)]ClO_4 (1:1), (ii) [Ag(NH═CMe_2)$_2$]ClO_4 (1:1), (iii) PPNCl (1:1), and (iv) PPh_3 (1:1 and 1:2). The aim of these reactions was to coordinate additional acetimino ligands to platinum (i and ii) or to see which of the three different ligands present in **2** is more labile toward its substitution by chloro (iii) or phosphine ligands (iv). Unfortunately **2**·H_2O does not react with [Au(NH═CMe_2)(PPh_3)]ClO_4 and gives unresolvable mixtures upon reacting with [Ag(NH═CMe_2)$_2$]ClO_4 or with PPNCl. However, the slow addition of 1 equiv of PPh_3 to a solution of **2**·H_2O in acetone led to a mixture of several compounds including **2** and *trans*-[PtCl(NH═CMe_2)(PPh_3)$_2$]ClO_4 (**1trans**) among others (by NMR). The 1:2 reaction between **2**·H_2O and PPh_3 allowed the synthesis of pure **1trans** in good yield after the replacement of one DMSO and one acetimino ligand by PPh_3**.** It seems reasonable that upon substitution of the labile DMSO ligand by PPh_3, an intermediate mono(phosphino) complex formed, in which the PPh_3 ligand would strongly labilize the trans imino ligand, promoting its fast substitution by another PPh_3 ligand to give finally **1trans**.

In an attempt to prepare a bis(dmso)acetimino complex, we reacted *cis*-[$PtCl_2$(DMSO)$_2$] and [Au(NH═CMe_2)PPh_3]ClO_4 (1:1, Scheme 1). The other product [AuCl(PPh_3)] was removed because of its moderate solubility in Et_2O and isolated in almost quantitative yield. The residue (96% yield) was shown by ^{1}H NMR to be [PtCl(NH═CMe_2)(dmso)$_2$]ClO_4 (**A**)[31] contaminated with a small amount of [PtCl(NH═CMe_2)$_2$(dmso)]ClO_4 (**2**) that we could not separate even after repeated recrystallizations. The crude complex **A** reacts with PPh_3 (1:1) to give [*SP*-4-3]-[PtCl(NH═CMe_2)(DMSO)(PPh_3)]ClO_4 (**5**) which can also be obtained in excellent yield by reacting in two steps [$PtCl_2$(dmso)$_2$], [Au(NH═CMe_2)PPh_3]ClO_4, and PPh_3 (1:1:1) as stated in the Experimental Section. These are new examples of the increasing use of gold(I) complexes as transmetalating agents.[8,32]

The reactions between complexes **2**·H_2O or **4**·H_2O and an excess of $PhICl_2$ (1:3) lead to the first (acetimino)Pt(IV) complexes reported so far, [*OC*-6-13]-[$PtCl_3$(DMSO)(NH═CMe_2)$_2$]ClO_4 (**6**) or [*OC*-6-13]-[$PtCl_2$(NH═CMe_2)$_2$(dtbbpy)]-(ClO_4)$_2$ **(7)**, respectively (Scheme 2). An excess of $PhICl_2$ was necessary to avoid contamination of the Pt(IV) com-

(31) ^{1}H NMR (200 MHz, acetone-d_6): δ 2.42 (d, 3H, Me, $^4J_{HH}$ = 1.5 Hz), 2.62 (s, 3H, Me), 3.69 (s+d, 6H, Me, dmso, $^3J_{HPt}$ = 21 Hz), 3.70 (s+d, 6H, Me, dmso, $^3J_{HPt}$ = 25 Hz), 9.98 (s, 1H, NH)]. Anal. Calcd for $C_7H_{19}Cl_2NO_6PtS_2$: C, 15.47; H, 3.52; N, 2.58; S, 11.80. Found: C, 16.07; H, 3.69; N, 2.76; S, 11.20.

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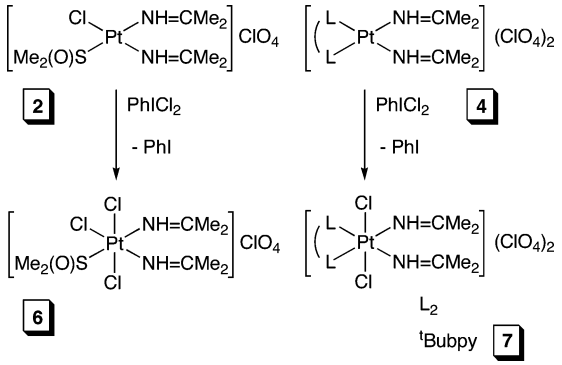
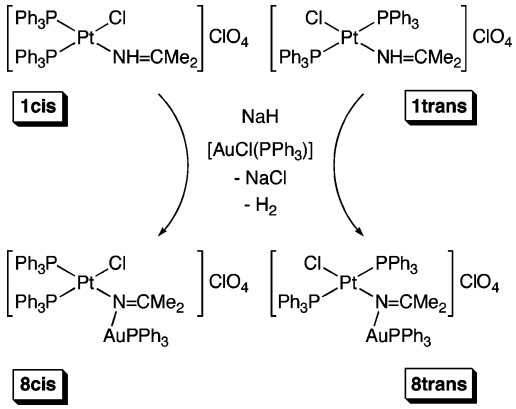
Scheme 2



Scheme 3



plexes with the unreacted Pt(II) derivatives. Although both **6** and **7** were isolated in this way as analytically pure compounds, **7** slowly decomposes in solution, losing chlorine to give **4** as shown by its ^{1}H NMR spectrum after a few hours. This prevented the measurement of the ^{13}C NMR spectrum of **7**. In the case of **6**, no decomposition was observed. The attempted oxidation of complexes **1cis**, **1trans**, or **4**·H_2O by reacting them with $PhICl_2$ gave complex mixtures that we could not separate.

Synthesis of (μ-acetimido)Pt^{II}Au^{I} Complexes. The reactions of **1cis** or **1trans** with NaH and [AuCl(PPh_3)] (1:10:1.2) in a mixture of CH_2Cl_2 and THF (5 h refluxing under N_2) or in CH_2Cl_2 (5 h at 70 °C) gave the corresponding cis (**8cis**) or trans (**8trans**) isomers, respectively, of the (μ-acetimido) complex [PtCl{μ-N(AuPPh$_3$)=CMe$_2$}(PPh_3)$_2$]ClO_4 in a good or moderate yield. The replacement of the NH proton in **1cis** or **1trans** by the isolobal $AuPPh_3^+$ fragment requires both heating and the use of an excess of NaH and [AuCl(PPh_3)]. When $NHEt_2$ was used instead of NaH no reaction was observed. Although the formation of **8cis** was also detected by NMR in the room-temperature reactions of **1cis** with [Au(acac)(PPh_3)] (1:1) or with [{μ_3-O(AuPPh$_3$)$_3$}]ClO_4 (1:0.5), the presence of the byproducts [Pt(acac)(PPh_3)$_2$]ClO_4 or [Au(PPh_3)$_2$]ClO_4 and [AuCl(PPh_3)], respectively, which we could not remove completely, made these reactions unsuitable for the synthesis of **8cis**. Reactions of **1cis** with NaH, Tl(acac), ^{n}BuLi, Ag_2O, Ag_2CO_3, or NaOMe were attempted with the aim of producing a dehydrohalogenation reaction that could give rise to the [{Pt(PPh_3)$_2$}$_2${μ-N=CMe$_2$}$_2$] complex. Unfortunately, complex mixtures were obtained in all cases, the NMR of which did not prove the presence of μ-acetimido ligands.

Crystal Structures of [Pt(NH=CMe$_2$)$_2$(dtbbpy)](ClO$_4$)$_2$·0.5Et$_2$O·0.5Me$_2$CO (4·0.5Et$_2$O·0.5Me$_2$CO) and *cis*-[PtCl$_3$(DMSO)(NH=CMe$_2$)$_2$]ClO$_4$ (6). The crystal structure of **4**·0.5Et_2O·0.5Me_2CO (Figure 1) shows that the unit cell contains two [Pt(NH=CMe$_2$)$_2$(dtbbpy)] cations, four perchlorate anions, and one molecule each of Et_2O and Me_2CO. In the cation, the platinum atom is in a square planar environment, distorted by the small bite of the tbbpy ligand and the narrow N(1)−Pt(1)−N(2) bond angle [86.75(18)°] compared to N(2)−Pt(1)−N(3) and N(1)−Pt(1)−N(4) [96.29(17) and 96.39(17)°, respectively] which could be caused by steric repulsion between the hydrogen atoms on the imino Me groups and those on the 6 and 6′ positions in the dtbbpy ligand. The imino ligands are planar, mutually perpendicular, and rotated with respect to the coordination plane by approximately 70°. The C=N bond distances [1.273(7) and 1.279(7) Å] are in the range found for the other structurally characterized acetimino complexes (1.25−1.30 Å).[33] Each of the NH hydrogen atoms is involved in a classical N−H···O hydrogen bond with one perchlorate anion. Additionally, one dtbbpy C−H takes part in a C−H···O hydrogen bond with the other perchlorate anion (Figure 1).

The crystal structure of **6** (Figure 2) involves two independent formula units; the cations [$PtCl_3$(dmso)(NH=CMe$_2$)$_2$]$^+$ display only small differences in bond distances and angles, but the DMSO and one acetimino ligand (trans to Cl) display somewhat different torsion angles: the root-mean-square (rms) deviation of a fit of all non-H atoms, except DMSO O and C and the relevant acetimino methyl C, was 0.06 Å. The platinum atoms display slightly distorted octahedral enviroments with the chloro ligands in a *meridional* disposition and the imines in a cis disposition. The Pt−N bond distances trans to DMSO [2.063(3) or 2.056(3) Å] are slightly longer than those trans to chloro [2.037(3) or 2.045(3) Å], and all of them are longer than those found in **4**·0.5Et_2O·0.5Me_2CO (see above), suggesting that the trans influence decreases in the series DMSO > Cl > NH=CMe$_2$ ≈ dtbbpy. The C=N bond distances [from 1.278(4) to 1.285(4) Å] are similar to those found in **4**·0.5Et_2O·0.5Me_2CO and other acetimino complexes.[33] Each of the acetimino ligands is essentially planar and lies diagonally with respect to the octahedral planes [the interplanar angles between the acetimino planes and the central Pt, S, N, N, Cl planes of the octahedra are 47.3(1) and 46.4(1)° for cation 1 and 47.1(1) and 55.5(1)° for cation 2]. As in **4**, each of the NH hydrogen atoms is involved in a classical N−H···O hydrogen bond with one perchlorate anion, leading to inversion-symmetric tetramers of **6**. Additionally, some methyl hydrogen atoms from both the NH=CMe$_2$ and DMSO ligands participate in intra- and intermolecular C−H···O and C−H···Cl hydrogen bonds (see Supporting Information). The S=O [S(1)−O(1) = 1.455(2) Å, S(2)−O(2) = 1.445(3) Å] and Pt−S [Pt(1)−S(1) = 2.3200(8) Å, Pt(2)−S(2) =

(33) *Cambridge Structural Database*, version 5.27; Cambridge Crystallographic Data Center: Cambridge, U,K., 2005; www.ccdc.cam.ac.uk.

2.3168(8) Å] bond distances are in the ranges reported in the literature.[34]

NMR Spectra. The ^{1}H NMR spectra of complexes **1**−**8** show the resonances expected for the inequivalent acetimino or μ-acetimido Me groups (see Experimental Section). Only in complexes **2** and **3** do the Me protons trans to NH give doublets with $^4J_{HH}$ values of 1−3 Hz similar to those previously found by us in other acetimino complexes.[6,8] In complex **7**, one of the Me resonances (δ 2.83) displays ^{195}Pt satellites ($^4J_{HPt}$ = 7 Hz). The chemical shifts of these Me protons are in the intervals of 1.01−1.73 or 2.21−2.94 ppm and seem to depend on the presence or absence of a PPh_3 ligand in their proximity. We have found that, (i) in complexes without phosphine ligands (**2**, **4**, **6**, and **7**), the two observed Me resonances are in the range of 2.34−2.94 ppm, (ii) in complexes bearing only one PPh_3 (**5**) or two such ligands in a mutually cis disposition (**1cis**, **3**, and **8cis**), only one of the imino Me groups is appreciably shielded (1.54−1.71 ppm) while the other remains in the 2.18−2.26 ppm range, and (iii) in complexes bearing two mutually trans PPh_3 ligands, both Me resonances appear at low frequency (**1trans**, 1.01 and 1.59; **8trans**, 1.27 and 1.57 ppm). We suggest that this effect could be attributed in part to the anisotropic shielding of the phosphine phenyl rings. The similar chemical shifts found for the Me protons in complexes **1trans** and **8trans**, despite the different moieties, NH═CMe_2 and N($AuPPh_3$)═CMe_2, respectively, suggest the shielding effect of the PPh_3 bonded to gold to be at best limited. The NH protons are observed in the ^{1}H NMR spectra of complexes **1**−**7** as broad resonances in the 9.5−11.1 ppm range. Although two such resonances are expected for complexes **2** and **6**, only one, rather broad, is observed for **2**, while **6** displays two 1:1:1 triplets at δ 9.71 and 10.37 ppm ($^1J_{HN}$ = 56.6 and 53.7 Hz) which can be attributed to coupling to ^{14}N.[8]

The ^{13}C{^{1}H} NMR spectra show the expected resonances. The Me carbons appear in the 25.6−35.1 ppm interval, the highest frequencies corresponding to the μ-acetimido complexes (**8cis**, 34.0 and 34.6; **8trans**, 34.5 and 35.1 ppm). Some Me resonances split into a doublet (**1cis**, 2.68; **8cis**, 34.6; **8trans**: 35.1 ppm), a doublet of doublets (**8cis**, 34.0 ppm), or an apparent triplet (**3**, 28.2 ppm) because of the coupling with the PPh_3 ligands. The N═C carbons give a resonance in the 178.5−197.3 ppm interval, the lowest frequencies corresponding, as expected, to the μ-acetimido complexes (**8cis**, 178.5; **8trans**, 179.4 ppm). This shielding is of 5−6 ppm with respect to their parent complexes, **1cis** and **1trans**, respectively.

The ^{31}P{^{1}H} NMR spectra of the complexes **1cis** and **8cis** bearing a "Pt(PPh_3)$_2$" fragment show two doublets with $^2J_{PP}$ values of about 20 Hz indicating their cis geometry (see Experimental Section). These resonances display ^{195}Pt satellites (**1cis**, $^1J_{PPt}$ = 3112 and 3710 Hz; **8cis**, $^1J_{PPt}$ = 2738 and 4014 Hz). However, both the monophosphino complex, **5**, and the "*trans*-Pt(PPh_3)$_2$" complexes, **3**, **1trans**, and **8trans**, display one singlet resonance with ^{195}Pt satellites. In addition, complexes **8cis** and **8trans** show a singlet resonance from the $AuPPh_3$ fragment (**8cis**, 30.0; **8trans**, 27.5 Hz).

Since the $^1J_{PPt}$ coupling constants are known to increase with the decreasing trans influence of the trans ligand,[35] the *J* values can be used to assign the geometry of the (phosphino)Pt complexes, on the basis of previously available data,[35,36] and to classify different ligands in a series of trans influence. Thus, the *SP*-4-3 geometry has been assigned to complex **5** because its $^1J_{PPt}$ is almost identical to that found in *cis*-[$PtCl_2(PPh_3)_2$] (3670 Hz). On the other hand, the $^1J_{PPt}$ values (in Hz) for our complexes with PPh_3 trans to Cl [3710 (**1cis**), 3677 (**5**), and 4014 (**8cis**)], trans to Me_2C═NH [3112 (**1cis**) and 3324 (**3**)], or trans to P [2604 (**1trans**) and 2847 (**8trans**)] are similar to those found in other platinum(II)-related complexes with phosphine, nitrogen-donor, or chloro ligands and that for the P trans to Me_2C═N($AuPPh_3$) in **8cis** (2738 Hz) is in the range of those trans to P. These values suggest the following decreasing series of trans influence: $PPh_3 \approx N(AuPPh_3)$═CMe_2 > NH═CMe_2 > Cl.

IR Spectra. One (**7**) or two broad ν_{NH} bands of medium intensity are observed (3130−3260 cm^{-1}) in the IR spectra of complexes **1**−**7** and are absent in those of **8cis** and **8trans,** as expected after the replacement of the NH hydrogen by an isolobal "$AuPPh_3$" fragment. The vibrational spectra of NH═CMe_2[2] itself shows two weak ν_{NH} bands (Raman, 3326 and 3260 cm^{-1}) and two $\nu_{C=N}$ bands (IR, 1658, 1670 sh cm^{-1}). One (**1cis**, **1trans**, **2, 6**, **8cis**, and **8trans**) or two (**3**, **4**, **5**, and **7**) medium to intense absorptions in the 1620−1680 cm^{-1} region could be attributed to $\nu_{C=N}$ modes, even though the number of absorptions in this region seems to not be related in an obvious manner to the number or disposition of the acetimino ligands, as we have previously observed in other acetimino−gold, −silver, and −rhodium(I) complexes.[8,11]

The chlorocomplexes, **1**, **2**, and **5**−**8** show one or two (**6**) medium bands in the 302−377 cm^{-1} region that we tentatively assign to ν_{PtCl} modes. The energy of these bands depends on the disposition of the chloro ligand and is found to increase in the series "$\nu_{PtCl\ trans\ to\ PPh3}$" (**1cis**, 306; **5**, 302; **8cis**, 309 cm^{-1}) < "$\nu_{PtCl\ trans\ to\ N(AuPPh3)=CMe2}$" (**8trans**, 320 cm^{-1}) < "$\nu_{PtCl\ trans\ to\ NH=CMe2}$" (**1trans**, 335; **2**, 349; **6**, 351 cm^{-1}) < "$\nu_{PtCl\ trans\ to\ Cl}$" (**6**, 377; **7**, 369 cm^{-1}), thus supporting the trans influence series proposed above on the basis of NMR data. In the cases where the comparison is possible, it can be observed that the ν_{PtCl} bands appear at slightly higher frequency for the Pt(IV) complexes than those for the analogous Pt(II) complexes, although this effect is only marginal. The presence in the IR spectra of complexes **2**, **5,** and **6** of a strong band in the 1149−1190 cm^{-1} region is indicative[34,37] of the S coordination of the Me_2S═O ligand, as is the case in all the (DMSO)Pt complexes structurally characterized[33] with the single exception of [Pt(S-DMSO)$_2$-

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$(O\text{-}DMSO)_2](CF_3SO_3)_2$.[38] The IR of all our cationic complexes show bands characteristic of the perchlorate anion at around 1100 and 620 cm^{-1}.

Conclusions

We have found complexes $[Ag(NH{=}CMe_2)_2]ClO_4$ and $[Au(NH{=}CMe_2)PPh_3]ClO_4$ to be efficient transmetalating agents toward $[PtCl_2(PPh_3)_2]$, $[PtCl_2(DMSO)_2]$, and $[PtCl_2$-(dtbbpy)]. Their use allowed us to prepare the first cationic acetimino complexes of Pt(II). The oxidative addition of chlorine to some (acetimino)Pt(II) complexes to give the corresponding Pt(IV) derivatives was achieved by use of $PhICl_2$. The reactions of some (acetimino)Pt(II) complexes with NaH and $[AuCl(PPh_3)]$ produced the first heteronuclear μ-acetimido complexes of any metals, resulting from the substitution of the NH proton by the isolobal $Au(PPh_3)$ fragment. $[Pt(NH{=}CMe_2)_2(dtbbpy)](ClO_4)_2{\cdot}0.5Et_2O{\cdot}0.5Me_2CO$ and [*OC*-6-13]-$[PtCl_3(NH{=}CMe_2)_2(DMSO)]ClO_4$ are the first acetimino complexes of Pt to be structurally characterized.

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Supporting Information Available: Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and CIF files for complexes **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060489I

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