CHEMISTRY
A EUROPEAN JOURNAL

Synthesis and Structure of an Unexpected Platinum π Complex Formed from Substituted 1,4-Diamino Ligands through an Elimination Process

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Abstract: An unusual reactivity of *cis*-1,2-bis[(*N*,*N*-dimethylamino)methyl] cyclohexane with $PtCl_2$ was observed, resulting in the formation of a platinum(II) π-olefin complex instead of the conventional square-planar *cis* Pt^{II} coordination complex with the diamino ligand. This behavior was interpreted on the basis of the steric hindrance of the dimethylamino groups whose electron lone pairs are barely accessible to a platinum atom, which can make it difficult for both dimethylamino groups to bind platinum at the same time. This complex has been physically and spectroscopically characterized and its structure has been confirmed by using X-ray diffraction analyses on single crystals.

Keywords: antitumor agents · diamines · elimination · pi complex · platinum

Introduction

Since the discovery of cisplatin as an antitumor agent, many platinum compounds have been synthesized, but only a few are being currently used in clinical therapy (cisplatin, carboplatin, oxaliplatin, and nedaplatin).[1,2] In spite of the great efficiency of the aforementioned platinum complexes against ovarian, bladder, and testicular cancers, these drugs display limited activity against some of the most common tumors in colon and breast cancer. In addition, other limitations are observed in cisplatin chemotherapy, such as a variety of adverse effects and acquired resistance. The great success of cisplatin on the one hand, and these limitations on the other, have motivated efforts to develop new antitumor agents with improved therapeutic properties. The goals for the design of new platinum complexes are the synthesis of compounds that remain active against cisplatin-resistant cells, with a wider spectrum of antitumor activity, and with lower toxicity than cisplatin. In order to explore possibilities of improving antitumor activity of these kind of compounds, we have been working on the design of new platinum(II) complexes with cytotoxic activity to establish structure–activity relationship rules that could contribute to a better understanding of their mechanisms of action and to obtain new hits and leads with promising cytoregulatory properties.

In this context, we have been working on the synthesis of a chemical library of 1,4-diaminoligands with different degrees of substitution on the nitrogen atoms in order to prepare the corresponding platinum(II) complexes to evaluate their cytotoxic activity. When we reacted 1,2-bis(*N*,*N*-dimethylaminomethyl)cyclohexane as a ligand with $PtCl_2$, we obtained an unexpected organometallic compound of platinum(II) instead of the usual seven-membered ring chelate formed by coordination of a platinum atom to both nitrogen atoms of the diamino groups. Formally, one of the dimethylamino groups was lost during the reaction, resulting in the formation of a carbon–carbon double bond that coordinated to platinum(II). These kind of amino–olefin platinum(II) dichloride complexes have been previously reported in the literature,[3,4] but what is really new in the present work, to the best of our knowledge, is the unusual formation process of a π complex from a *N*,*N*-disubstituted 1,4-diamine ligand.

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DOI: 10.1002/chem.200401228

The preparation and structural characterization of the new compound is reported here, and a possible mechanism to explain its formation from the diamino ligand is also proposed. The organometallic compound is being evaluated as a potential antitumor compound due to accepted knowledge that the main pharmacological target of platinum compounds is DNA,[5,2f] so in this case the platinum–carbon bond could facilitate the formation of a DNA adduct[6] because of an enhanced *trans* effect.[3]

Results and Discussion

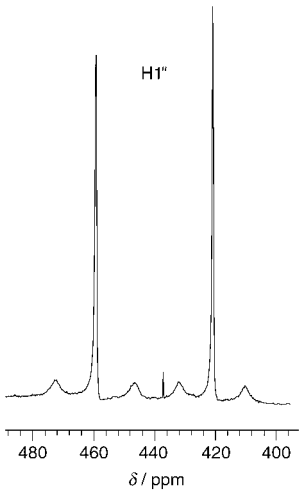
The synthesis of this new compound was carried out starting from commercially available *cis*-3,3,6,6-tetrahydrophthalic anhydride.[7] Hydrolysis of anhydride **1** led to the formation of *cis*-3,3,6,6-tetrahydrophthalic acid **2**, whose amidation was easily accomplished by refluxing it with hexamethylphosphorus triamide (HMPT) in benzene. Diamine **4** was obtained by reduction of diamide **3** with $LiAlH_4$. Catalytic hydrogenation of **4** afforded the desired saturated diamine **5**. The synthetic pathway to prepare ligand **5** and the yields of each step are shown in Scheme 1.

The preparation of platinum(II) complex **6** was carried out by using $PtCl_2$ as reagent and CH_2Cl_2 as solvent (see Scheme 2). Diamine **5** was completely soluble in CH_2Cl_2, but $PtCl_2$ was only partially soluble in it at 25 °C, which explains the low reaction rate (15 days of reaction time were necessary in order to get complete conversion of the substrate). Complex **6** was isolated as a yellow solid and was purified by crystallization in hot acetonitrile, affording yellow crystals suitable for X-ray analysis.

Complex **6** was studied, in the solid state, by using elemental analysis, mass spectrometry, and FTIR spectroscopy and, in solution, by using high-field ^{1}H NMR spectroscopy. Its structure was confirmed by X-ray diffraction analysis.

It is worth noting that only one of the two possible diastereoisomers of π complex **6** has been detected and isolated. Analysis by using molecular modeling suggests that the π complexation of platinum by the other face of the methylidene group should result in modification of the cyclohexane conformation, placing the dimethylamino and the methylidene groups in a quasi-diaxial position, thus energetically unfavorable. Even though the other diastereoisomer could have formed, but was not detected, the isolated and characterized isomer **6** should be the major isomer according to the mass balance. The stereoselection in metal–olefin complexation is well known in the literature when applied to chiral ligands.[8]

NMR studies on complex 6: The assignment of individual proton signals in the ^{1}H NMR spectrum was based on J(H,H) coupling constant values and was confirmed by 2D COSY experiments. The effect of the coordination of the methylidene group ligand to platinum and the back-donation effect were observed by using ^{1}H NMR spectroscopy. Thus, protons H1″ in **6** appeared at higher fields ($\delta = 4.21$ and 4.51 ppm) than similar hydrogens belonging to a typical non-coordinated double bond ($\delta = 4.63$ and 4.88 ppm, respectively). Moreover, ^{195}Pt satellites were observed in the ^{1}H NMR spectrum for the two protons H1″ (^2J(Pt, H1″a) = 65.7 Hz, ^2J(Pt, H1″b) = 76.8 Hz) (see Figure 1).



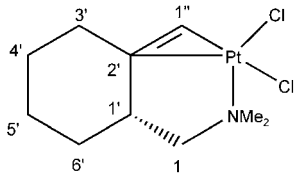
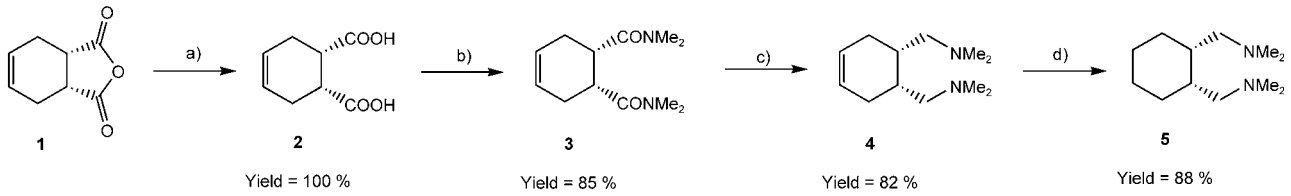


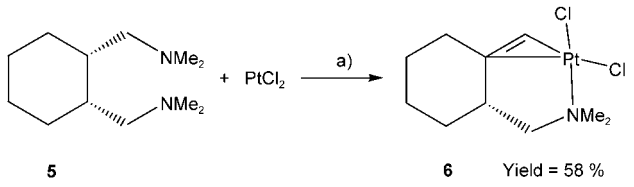
Figure 1. Detail of the ^{195}Pt satellites for the H1″ signal in the ^{1}H NMR spectrum of **6** (300 MHz).

Structure determination of complex 6 by X-ray crystallography: Details of the structure determination are given in the Experimental Section. Crystallographic data and selected bond distances and angles are quoted in Tables 1 and 2. In Figure 2, an ORTEP view of the X-ray crystal structure of **6** is shown. This molecular representation shows that the structure of **6** corresponds to the diastereoisomer that has the lower steric hindrance between the methyl groups and the cyclohexane ring. Complex **6** adopts a square-planar geometry, in which the C=CH_2 group is located perpendicular to the plane containing the platinum and chlorine atoms. Angles of the C=CH_2 moiety indicate that the double-bond geometry is not exactly coplanar. Moreover, the C2′–C1″ bond length is 1.38 Å. These two experimental data are consistent with a back-donation effect. In addition, it is possible

Abstract in Spanish: *Se ha observado una reactividad inusual de* cis-*1,2-bis*[(N,N-*dimetilamino)metil]ciclohexano con* $PtCl_2$, *que conduce a la formación de un complejo* π-*olefínico de platino (*II*) en lugar del complejo de coordinación convencional* cis *cuadrado plano de* Pt^{II} *con el ligando diaminado. Este comportamiento se puede interpretar sobre la base del impedimento estérico de los grupos dimetilamino, cuyos pares de electrones solitarios son difícilmente accesibles al átomo de platino y este hecho dificulta que ambos grupos dimetilamino puedan coordinarse al platino al mismo tiempo. Este compuesto se ha caracterizado física y espectroscópicamente y su estructura se ha confirmado mediante difracción de rayos X de monocristal.*



Scheme 1. Synthetic pathway of ligand **5**. a) H_2O/HCl, RT, 16 h; b) HMPT, N_2, anhydrous benzene, reflux, 30 min; c) $LiAlH_4$, N_2, anhydrous Et_2O, reflux, 1 h; d) H_2, Pd/C, EtOH, RT, 7 h.



Scheme 2. Synthesis of compound **6**. a) CH_2Cl_2, RT, 15 days.

Table 1. Crystal data for compound **6**.

molecular formula	$C_{10}H_{19}Cl_2NPt$
formula weight [g mol^{-1}]	419.25
T [K]	293(2)
λ ($Mo_{K\alpha}$) [Å]	0.71069
crystallographic system	monoclinic
space group	$P2_1/m$
a [Å]	8.4980(10)
b [Å]	16.5210(10)
c [Å]	9.5350(10)
α [°]	90
β [°]	113.106(10)
γ [°]	90
V [Å^3]	1231.3(2)
Z	4
ρ_{calcd} [Mg m^{-3}]	2.262
μ [mm^{-1}]	11.793
F (000)	792
Θ [°]	2.47–33.40
h, k, l range	$-11 \le h \le 10$, $0 \le k \le 24$, $0 \le l \le 13$
number of registered reflections	7247
number of independent reflections	2960
[R_{int} (on F)]	0.0355
method of refinement	full-matrix least-squares on F^2
number of data	2960
number of parameters	127
goodness-of-fit on F^2	1.117
R final [$I > 2\sigma(I)$]	$R_1 = 0.0317$, $wR_2 = 0.0987$
R index (all data)	$R_1 = 0.0365$, $wR_2 = 0.1021$
largest difference peak and hole [e Å^3]	0.787 and −0.886

Table 2. Selected bond lengths [Å] and angles [°] for compound **6**.

Pt–N1	2.077(4)	Cl1-Pt-Cl2	95.84(6)
Pt–C1″	2.120(4)	C1-N1-Pt	104.2(3)
Pt–C2′	2.149(6)	C1‴-N1-Pt	114.0(3)
Pt–Cl1	2.2876(18)	C1^{iv}-N1-Pt	115.4(3)
Pt–Cl2	2.3409(14)	C1″-C2′-Pt	70.0(3)
N1–C1	1.463(8)	C1′-C2′-Pt	98.2(4)
N1–C1‴	1.520(6)	C3′-C2′-Pt	124.1
N1–C1^{iv}	1.526(6)	C2′-C1″-Pt	72.3(3)
C1–C1′	1.586(8)	C1-N1-C1‴	108.5(4)
C1′–C6′	1.485(8)	C1-N1-C1^{iv}	108.9(4)
C1′–C7′	1.529(7)	C1‴-N1-C1^{iv}	105.6(5)
C6′–C5′	1.624 (10)	N1-C1-C1′	111.4(4)
C5′–C4′	1.484(10)	C1″-C2′-C1′	118.3(5)
C4′–C3′	1.488(8)	C1″-C2′-C3′	122.0(5)
C3′–C2′	1.550(8)	C6′-C1′-C2′	103.1(5)
C2′–C1″	1.383(6)	C6′-C1′-C1	115.2(4)
N1-Pt-C1″	97.12(18)	C2′-C1′-C1	113.0(4)
N1-Pt-C2′	91.0(2)	C1′-C6′-C5′	113.1(5)
C1″-Pt-C2′	37.79(16)	C4′-C5′-C6′	113.3(5)
N1-Pt-Cl1	179.19(11)	C5′-C4′-C3′	107.4(6)
C1″-Pt-Cl1	82.63(14)	C4′-C3′-C2′	109.3(5)
C2′-Pt-Cl1	88.35(17)	C1′-C2′-C3′	114.5(4)
N1-Pt-Cl2	84.67(14)	H1a″-C1″-H1b″	113.3
C1″-Pt-Cl2	158.98(13)	C2″-C1″-H1a″	116.3
C2′-Pt-Cl2	163.12(12)	C2″-C1″-H1b″	116.3

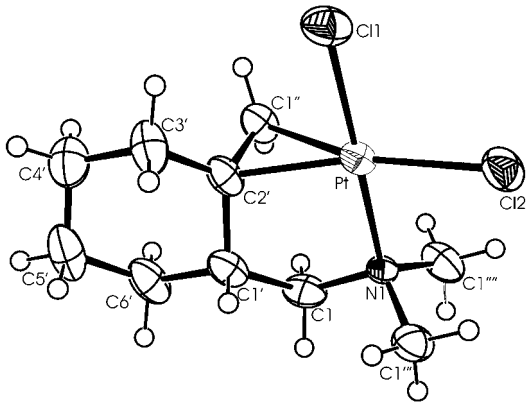
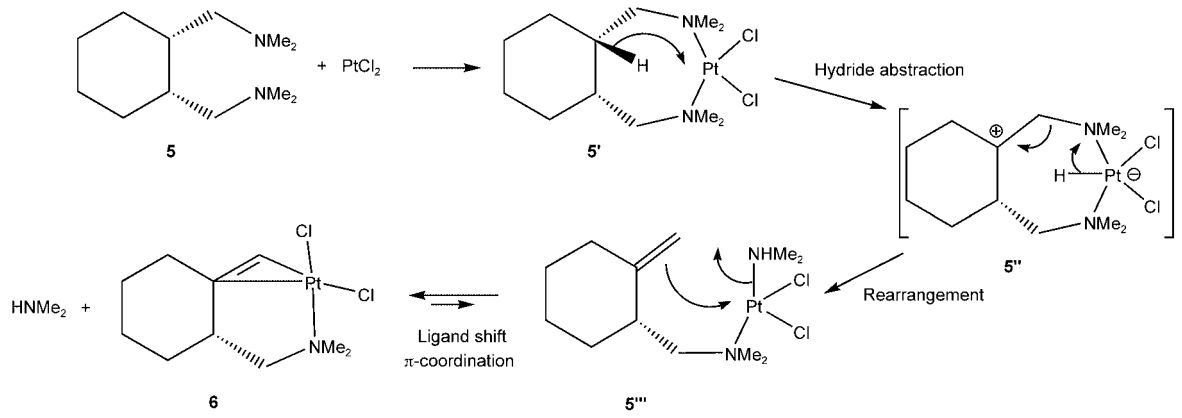


Figure 2. ORTEP view of molecule **6**.

to observe that the cyclohexane ring adopts a chair conformation to minimize the steric repulsions. Finally, the C1-N1-C1^{iv} angle (105.6°) is large enough to minimize the steric repulsion between the methyl groups.

Proposed formation mechanism of compound 6: A possible mechanism to explain the formation of complex **6** is shown in Scheme 3. The first step could be the labile ligand coordination on the amino groups by platinum, forming an unstable seven-membered ring chelate **5′**. The second step could be the abstraction of a hydride group by the platinum atom.[9] A third step, involving a molecular rearrangement, is imagined to generate the precursory *cis*-diaminodichloroplatinum(II) complex **5‴**. A final step in which the dimethylamine ligand is shifted by the π system of the methylidene group could afford the final complex **6**. This behavior could



Scheme 3. Proposal of a mechanism for the formation of complex **6**.

be interpreted on the basis of the steric hindrance of the dimethylamino groups that would create high steric strain on the seven-membered ring of the diamino complex **5′**. On the other hand, the electron lone pairs of both nitrogen atoms are barely accessible simultaneously by the platinum atom which could destabilize the diamino complex.

Experimental Section

Materials and methods: All reactants were purchased from commercial suppliers and used without further purification. Reactions that required an inert atmosphere were conducted under dry nitrogen and the glassware was oven dried (120 °C). THF, Et_2O, and benzene were distilled from sodium/benzofenone prior to use. CH_2Cl_2 was dried by refluxing it over CaH_2 under nitrogen. Elemental analyses (C, H, N, S) were carried out on a Carlo Erba EA1108 apparatus. Infrared spectra were recorded on a FTIR NICOLET 510 spectrophotometer in a 4000–400 cm^{-1} range. NMR spectra were obtained on a Varian Gemini-200, a Varian Unity-300 plus, or a Varian VXR-500 apparatus using $CDCl_3$ or [D_6]DMSO as solvent. ^{1}H NMR spectra were obtained at 200, 300, or 500 MHz frequencies and chemical shifts are given in ppm relative to tetramethylesilane (TMS). ^{13}C NMR and distortionless enhancement by polarization transfer (DEPT) experiments were recorded at 50 or 75 MHz and were referenced to the 77.0 ppm resonance of $CDCl_3$. Mass spectra were run on a Fisons VG Quattro triple quadrupole analyzer in the *m*/*z* 1800–200 range, using MeCN–H_2O as solvent under electrospray (ES-MS), or on a Hewlett-Packard 5890 mass spectrometer using a chemical ionization (CI) technique (conditions are specified for each case, DIP = direct insertion probe, FAB-MS = fast atom bombardment mass spectrometry, NBA = 3-nitrobenzyl alcohol). Melting points were measured on a Galenkamp and a Stuart Scientific SMP3 apparatus. Conductivity was measured on CRISON Micro CM 2200 equipment.

Synthesis of *cis*-cyclohex-4-ene-1,2-dicarboxylic acid (2): 3,3,6,6-Tetrahydrophthalic anhydride (1.178 g, 7.09 mmol) was dissolved in acetic acid (2 mL) and water (10 mL). To this, four drops of 36% w/w hydrochloric acid were added. The mixture was stirred overnight at room temperature. The solvent was removed under vacuum to give a white solid (1.171 g, 100%). M.p. 169–170 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.36$–2.69 (m, 4H; H3, H6), 3.10 (dd, J_1(H,H) = 5.1, J_2(H,H) = 5.1 Hz, 2H; H1, H2), 5.69 ppm (s, 2H; H4, H5); ^{13}C NMR (50 MHz, CD_3OD): $\delta = 23.2$ (C3, C6), 36.8 (C1, C2), 122.3 (C4, C5), 173.3 ppm (C1′, C1″); IR (KBr): $\tilde{\nu} = 3300$–2300 (COO–H), 1680 cm^{-1} (C=O); MS (70 eV, DIP-CI-NH_3): *m*/*z* (%): 205 (10) [*M*+N_2H_7]$^+$, 188 (100) [*M*+NH_4]$^+$, 171 (3) [*M*+H]$^+$.

Synthesis of *cis*-*N*,*N*,*N*′,*N*′-tetramethylcyclohex-4-ene-1,2-dicarboxamide (3): To a suspension of **2** (300 mg, 1.765 mmol) in anhydrous benzene (2 mL), hexamethylphosphorous triamide (0.32 mL, 1.765 mmol) was added and the mixture refluxed for 30 min. The resulting cloudy solution was allowed to cool down to room temperature and a saturated aqueous solution of $NaHCO_3$ (2 mL) was added under strong stirring. The layers were separated and the aqueous layer was extracted with methylene chloride (4 × 2 mL). The organic phases were combined, dried over $MgSO_4$, filtered, and concentrated to dryness to give a colorless oil that solidified after a few hours to form a white solid. The solid was washed with hexane and purified by crystallization from ether at −78 °C (348 mg, 88%). M.p. 65–70 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.03$–2.12 (m, 2H; H3, H6), 2.31–2.47 (m, 2H; H3, H6), 2.73 (s, 3H; H1‴, H1^{iv}, H1^{v}, or H1^{vi}), 2.75 (s, 3H; H1‴, H1^{iv}, H1^{v}, or H1^{vi}), 2.85 (s, 3H; H1‴, H1^{iv}, H1^{v}, or H1^{vi}), 2.87 (s, 3H; H1‴, H1^{iv}, H1^{v}, or H1^{vi}), 2.85–2.92 (m, 2H; H1, H2), 5.52–5.55 ppm (m, 2H; H4, H5); ^{13}C NMR (50 MHz, CD_3OD): $\delta =$ 26.5 (C3, C6), 35.5 (C1^{iv}, C1^{vi}), 36.0 (C1, C2), 37.4 (C1‴, C1^{v}), 124.9 (C4, C5), 174.0 ppm (C1′, C1″); IR (KBr): $\tilde{\nu} = 3010$, 2930, 1645 (C=O), 1090 cm^{-1}; MS (70 eV, DIP-CI-NH_3): *m*/*z* (%): 225 (100) [*M*+H]$^+$, 180 (12) [*M*−NMe_2]$^+$, 171 (3) [*M*+H]$^+$.

Synthesis of dimethyl-({(1*R,6*S**)-6-[(dimethylamino)methyl]cyclohex-3-en-1-yl}methyl)amine (4)**: To a suspension of lithium aluminum hydride (70 mg, 1.837 mmol) in anhydrous diethyl ether (2 mL), a solution of diamide **3** (300 mg, 1.531 mmol) in dry THF (1 mL) was added. The mixture was refluxed for 1 h and was then quenched by slow and cautious addition of water (0.12 mL) in an ice bath. Afterwards, NaOH aqueous solution (15% w/w, 0.12 mL) and water (0.38 mL) were successively added. The resulting white precipitate was filtered off, washed twice with ether, and discarded. The organic solutions were combined together, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness under vacuum to give a colorless oil (300 mg, 82%). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.20$ (s, 12H; H1‴, H1^{iv}, H1^{v}, H1^{vi}), 1.87–2.30 (m, 10H; H1′, H2′, H5′, H6′, H1, H1″), 5.64 ppm (s, 2H; H3′, H4′); ^{13}C NMR (50 MHz, CD_3OD): $\delta = 28.3$ (C2′, C5′), 33.0 (C1′, C6′), 46.0 (C1‴, C1^{iv}, C1^{v}, C1^{vi}), 60.6 (C1, C1″), 125.9 ppm (C3′, C4′); IR (film): $\tilde{\nu} = 3020$, 2970, 2940, 2900, 2860, 2820, 2770, 1650, 1095 cm^{-1}; MS (70 eV, DIP-CI-NH_3): *m*/*z* (%): 214 (3) [*M*+NH_4]$^+$, 197 (33) [*M*+H]$^+$, 184 (100) [*M*−Me]$^+$.

Synthesis of dimethyl-({(1*R,2*S**)-2-[(dimethylamino)methyl]cyclohexyl}methyl)amine (5)**: A solution of diamine **4** (150 mg, 0.765 mmol) in absolute ethanol (5 mL) was added under a nitrogen atmosphere to a 10% Pd/C catalyst (30 mg). The reaction mixture was pumped out and backfilled with hydrogen four times in order to remove traces of oxygen which could passivate the catalyst. A hydrogen atmosphere was established and the reaction mixture was stirred strongly for 7 h. The catalyst was removed by filtration through Celite® and the organic solution concentrated to dryness to give a colorless oil (133 mg, 88%). The conversion and the chemical selectivity were observed to be complete by using TLC and GC analyses but the yield was not quantitative due to the adsorption of a certain amount of product onto the fine particles of catalyst, even though we tried to release it by suspending the catalyst fine powder in

ethanol in a sonication ultrasound bath. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.34–1.56 (m, 8H; H3′, H4′, H5′, H6′), 1.94–2.03 (m, 2H; H1′, H2′), 2.19 (s, 12H; H1‴, H1^{iv}, H1^{v}, H1^{vi}), 2.25–2.32 ppm (m, H1; H1″); ^{13}C NMR (50 MHz, CD_3OD): δ = 23.6 (C4′, C5′), 27.6 (C3′, C6′), 35.4 (C1′, C2′), 45.7 (C1‴, C1^{iv}, C1^{v}, C1^{vi}), 60.0 ppm (C1, C1″); IR (film): $\tilde{\nu}$ = 2927, 2855, 2815, 2763, 1458, 1261, 1169, 1040 cm^{-1}; MS (70 eV, DIP-CI-NH_3): *m*/*z* (%): 200 (15) $[M+H]^+$, 199 (100) $[M+H]^+$, 184 (37) $[M-Me]^+$.

Synthesis of dichloro{η^2-dimethyl[(2-methylidenecyclohex-1-yl)methyl]-amino}platinum(II) (6): A solution of **5** (170 mg, 0.859 mmol) in dry CH_2Cl_2 (20 mL) was added to a brown suspension of $PtCl_2$ (228 mg, 0.859 mmol) in CH_2Cl_2 (50 mL), in the dark. The reaction mixture was stirred at room temperature (25 °C) for fifteen days. After this time, the formation of metallic platinum (Pt^0) was observed. The suspension was filtered to remove metallic platinum particles and stirred for two additional days. A yellow solid then formed, which was filtered out and dried. The mother liquor from the filtration was concentrated to dryness to obtain an orange oil that was lixiviated with acetonitrile at room temperature. The remaining residue on the flask was a homogeneous yellow solid of the same composition as the solid obtained by filtration. Both solids were combined together, dissolved in hot acetonitrile, and left to stand at room temperature for two days to obtain yellow crystals (201 mg, 58 %). M.p. 223–225 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 1.11 (dddd, J_1(H,H) = 3.8, J_2(H,H) = J_3(H,H) = J_4(H,H) = 12.1 Hz, 1H; H6′a), 1.35 (ddddd, J_1(H,H) = J_2(H,H) = 3.9, J_3(H,H) = J_4(H,H) = J_5(H,H) = 12.7 Hz, 1H; H4′a), 1.59 (ddddd, J_1(H,H) = J_2(H,H) = 3.9, J_3(H,H) = J_4(H,H) = J_5(H,H) = 12.9 Hz, 1H; H4′b), 1.75–1.80 (m, 1H; H5′a), 1.93–2.02 (m, 2H; H5′b, H6′b), 2.22 (dd, J_1(H,H) = 4.3, J_2(H,H) = 12.2 Hz, 1H; H1a), 2.27–2.29 (m, 1H; H3′b), 2.40 (ddd, J_1(H,H) = 4.1, J_2(H,H) = J_3(H,H) = 12.3 Hz, 1H; H3′b), 2.67 (dddd, J_1(H,H) = J_2(H,H) = 3.9, J_3(H,H) = J_4(H,H) = 12.3 Hz, 1H; H1′), 2.79–2.96 (m, 1H; H1b), 2.83 (s, 3H; H1‴), 2.92 (s, 3H; H1^{iv}), 4.21 (s, 1H; H1″a), 4.21 (d, J(Pt,H) = 65.7 Hz, 1H; H1″a), 4.59 (s, 1H; H1″b), 4.59 ppm (d, J(Pt,H) = 76.8 Hz, 1H; H1″b); IR (KBr): $\tilde{\nu}$ = 3070 (C_{sp^2}–H, st), 2927, 2855, 1650 (C=C, st), 1508, 1462, 1451, 1119, 1009, 926, 831 cm^{-1}; FAB-MS (NBA) *m*/*z*: 498, 460, 383; elemental analysis calcd (%) for $C_{10}H_{19}Cl_2NPt$ (419.25 g mol^{-1}): C 28.65, H 4.57, N 3.34; found: C 28.96, H 4.79, N 3.45.

X-ray diffraction analysis: A [$PtCl_2L'$] prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a MAR345 image plate detector system. Unit-cell parameters were determined from automatic centering of 6697 reflections ($3 < \Theta < 31°$) and refined by using the least-squares method. Intensities were collected with graphite monochromatized $Mo_{K\alpha}$ radiation. 7247 reflections were measured in the range $2.47 < \Theta < 33.40$, 2960 of which were non-equivalent by symmetry (R_{int} (on *I*) = 0.035). 2543 reflections were assumed as observed by applying the condition $I > 2\sigma(I)$. Lorentz polarization and absorption corrections were made.

The structure was solved by direct methods using the SHELXS computer program[10] and refined by using the full-matrix least-squares method with the SHELXS-96 computer program,[11] using 2960 reflections (very negative intensities were not assumed to be present). The function minimized was: $\Sigma w[F_o^2 - F_c^2]^2$, where $w = [\sigma^2(I) + (0.0745P)^2 + (0.4463P)]^{-1}$, and $P = [F_o^2 + 2F_c^2]/3$; *f*, *f*′, and *f*″ were taken from the International Tables of X-ray Crystallography.[12] All the H atoms were computed and refined using a riding model with isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atoms which are linked. The final *R*(on *F*) factor was 0.031, *wR*(on $[F]^2$) was 0.098, and goodness of fit was 1.117 for all observed reflections. The number of refined parameters was 127. The maximum shift/esd = 0.00 and the mean shift/esd = 0.00. The maximum and minimum peaks in the final difference synthesis were 0.787 and −0.886 e Å^{-3}, respectively.

CCDC-257127 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

We thank the Spanish Ministry of Education and Science for financial support (Projects PB-98-1236 and BQU2002-00601). A fellowship to M.G. from the University of Barcelona is also gratefully acknowledged.

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Received: November 30, 2004
Published online: February 15, 2005