Reactions of aziridine with platinum(II) nitriles. Formation of (aziridino)amidines and 2-imidazolines and X-ray structure of *trans*-$[PtCl_2\{N(H)=C(Ph)\overline{NCH_2CH_2}\}_2]$

Rino A. Michelin*, Mirto Mozzon and Roberta Bertani

Istituto di Chimica Industriale and Centro di Studio per la Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Facoltà di Ingegneria, Università di Padova, Via F. Marzolo 9, 35131 Padua (Italy)

Franco Benetollo

Istituto di Chimica e Tecnologie Inorganiche dei Materiali Avanzati del CNR, Corso Stati Uniti 4, 35100 Padua (Italy)

Gabriella Bombieri

Istituto di Chimica Farmaceutica, Università di Milano, Viale Duca degli Abbruzzi, 20131 Milan (Italy)

Robert J. Angelici*

Department of Chemistry, Iowa State University, Ames, IA 50011 (USA)

(Received March 22, 1994)

Abstract

The amidine complexes *cis*- and *trans*-$[PtCl_2\{NH=C(R)\overline{NCH_2CH_2}\}_2]$ (R = Me, Ph) (**1–4**) are prepared by reaction of the nitrile complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ with two to four equiv. of aziridine, $H\overline{NCH_2CH_2}$, at room temperature. All complexes were characterized by their IR, ^1H and ^{13}C NMR spectra, and by their microanalytical data and mass spectra. These complexes are all likely associated to form dimers either in the solid state and partially in solution as evidenced by molecular weight measurements carried out for *trans*-$[PtCl_2\{NH=C(Ph)\overline{NCH_2CH_2}\}_2]$ (**3**), and on the X-ray structure investigation of this complex. Complex **3** crystallizes in the monoclinic system with $P2_1/n$ space group, with $a = 11.039(3)$, $b = 10.883(3)$, $c = 34.349(5)$ Å, $\beta = 90.34(4)°$, $V = 4127(1)$ Å^3, $Z = 8$. The structure was solved and refined to $R = 0.025$ and $R_w = 0.028$ for 4748 reflections with $I \geq 3\sigma(I)$. Complex **3** consists of 'dimers' $[Pt_2Cl_4L_4]$ ($L = HN=C(Ph)\overline{NCH_2CH_2}$) formed by two $[PtCl_2L_2]$ units intermolecularly associated through four N–H···Cl hydrogen bond interactions (H···Cl ~ 2.4 Å) involving the chlorines and the amidinic protons. The ^1H and ^{13}C NMR spectra of **1–4** show that there is relatively free rotation around the C–N(aziridine) bond and also that they are formed as a complex mixture of isomers arising either from restricted rotation around the C=N bond or around the Pt–N(amidine) bond. Complex **3** reacts with two equiv. of *cis*-$Ph_2PCH=CHPPh_2$ to give $[Pt(cis\text{-}PPh_2PCH=CHPPh_2)_2](Cl_2)$ and formation of the amidine $NH=C(Ph)\overline{NCH_2CH_2}$ together with 2-(phenyl)imidazoline, $\overline{N}=C(Ph)N(H)\overline{CH_2CH_2}$, which is the only isolated product when the reaction mixture is heated at 90 °C for a few hours or stirred for a few days at room temperature. A mechanism is proposed for the reactions of nitriles with aziridine and the conversion of amidines to 2-imidazolines.

Key words: Crystal structures; Platinum complexes; Amidine complexes; 2-Imidazolines; Nitrile complexes; Aziridine reactions

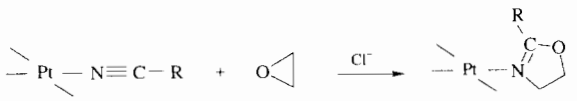
Introduction

Due to their tendency to undergo ring opening reactions, the saturated three-membered heterocycles $\overline{XCH_2CH_2}$ (X = O, S, NR) have been widely used in cycloaddition reactions to electrophilic CO [1], CS [1a] and RNC [2] ligands in transition metal carbonyl, thiocarbonyl and isocyanide complexes, respectively, for the synthesis of five-membered ring carbene complexes. Recently, we have found that oxirane undergoes ring expansion also with electrophilic nitrile ligands in Pt(II) complexes to afford 2-oxazolines (eqn. (1)) [3, 4b]. Closely related to this reaction chemistry is that of Pt(II) nitriles with $^-O–(CH_2)_n–Cl$ ($n = 2$, 3) alkoxides

*Authors to whom correspondence should be addressed.

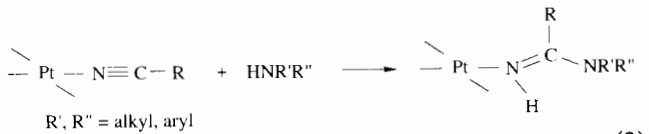
SSDI 0020-1693(94)03925-E

derived from HO–$(CH_2)_n$–Cl/base systems leading to the synthesis of 2-oxazolines [3, 4] and 1,3-oxazines [5], respectively; noteworthy, 1,3-oxazines are not formed using oxetane, $\overline{OCH_2CH_2CH_2}$, under conditions similar to those of eqn. (1).



(1)

Our interest in this area coupled with the well-known reactivity of Pt(II) nitriles with amines to give Pt(II) amidines [6] (eqn. (2)), led us to investigate their reactions with aziridine, $\overline{HNCH_2CH_2}$, with the purpose of exploring whether five-membered imidazoline complexes could form, in analogy with the reactions illustrated in eqn. (1). It was found that the species resulting



R', R'' = alkyl, aryl

(2)

from the reactions with $\overline{HNCH_2CH_2}$ were (aziridino)amidine complexes rather than the aziridine ring-opened products 2-imidazolines, which however were formed upon displacement of the (aziridino)amidine ligands from the metal.

Experimental

General procedures

All reactions were carried out under a dinitrogen atmosphere, but work-up of the reaction products was performed in air. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl; all the other solvents were of reagent grade and used without further purification. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. ^1H and ^{13}C NMR spectra were taken on Bruker AM-400 and Bruker AC-200 spectrometers and ^{31}P NMR spectra were recorded on a Varian FT 80-A spectrometer. The fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB 2F instrument operating with a Xe-atom beam energy of 8 keV using *m*-nitrobenzyl alcohol as a matrix. Molecular weight measurements were made on a Knauer osmometer. The GLC-MS analyses were run on a Carlo Erba QMD 1000 instrument. The elemental analyses were performed by the Department of Analytical Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected.

Starting complexes

The complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = CH_3 [7], C_6H_5 [7], *trans*-$[PdCl_2(NCC_6H_5)_2]$ [8] and the cationic complex *trans*-$[Pt(CF_3)(NCC_2H_5)(PPh_3)_2]BF_4$ [4b] were prepared according to reported procedures.

Synthesis of the complexes

Cis-[PtCl$_2${N(H)=C(Ph)$\overline{NCH_2CH_2}$}$_2$] (1)

A suspension of *cis*-$[PtCl_2(NCPh)_2]$ (0.57 g, 1.22 mmol) in THF (30 ml) at 0 °C was treated with $H\overline{NCH_2CH_2}$ (0.15 ml, 3.05 mmol). The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 1.5 h. After this time, the IR analysis of the solid precipitate did not reveal the $\nu(C{\equiv}N)$ band of the starting complex at 2286 cm^{-1}. Solid **1** was filtered, washed with MeOH (3 ml) and Et_2O (3×5 ml) and dried under vacuum. Yield 0.39 g (58%) m.p. 207–209 °C. *Anal.* Calc. for $C_{18}H_{20}N_4Cl_2Pt$: C, 38.72; H, 3.61; N, 10.03. Found: C, 38.50; H, 3.56; N, 9.58%. FAB mass spectrum (relative intensity): $M^{\cdot+}$ *m/z* 557 (1.06), MH^+ *m/z* 558 (1.54). Compound **1** was also obtained starting from *cis*-$[PtCl_2(NCPh)_2]$ (0.33 g, 0.71 mmol), $[ClCH_2CH_2NH_3]Cl$ (0.19 g, 1.63 mmol) and aziridine (0.08 ml, 1.63 mmol) in THF (70 ml) at 0 °C. A clear solution was obtained after 30 min at 0 °C from which **1** precipitates as a white solid. After 2 h at room temperature, solid **1** was collected by filtration, washed with MeOH (2×5 ml), Et_2O (2×5 ml) and dried under vacuum. Yield 0.14 g (34%).

Cis-[PtCl$_2${N(H)=C(Me)$\overline{NCH_2CH_2}$}$_2$] (2)

Compound **2** was obtained starting from *cis*-$[PtCl_2(NCMe)_2]$ (0.33 g, 0.97 mmol) and $H\overline{NCH_2CH_2}$ (0.19 ml, 3.87 mmol) in THF (20 ml). The reaction was carried out as for **1** and was complete after 15 h at room temperature. Solid **2** was filtered off, washed with CH_2Cl_2 (2×5 ml), MeOH (3×5 ml), Et_2O (2×5 ml) and dried under vacuum. Yield 0.21 g (50%), m.p. 210–211 °C. *Anal.* Calc. for $C_8H_{16}N_4Cl_2Pt$: C, 22.13; H, 3.71; N, 12.90. Found: C, 21.93; H, 3.68; N, 12.45%. FAB mass spectrum (rel. int.): $M^{\cdot+}$ *m/z* 433 (1.12), MH^+ *m/z* 434 (0.96).

Trans-[PtCl$_2${N(H)=C(Ph)$\overline{NCH_2CH_2}$}$_2$] (3)

This compound was obtained starting from *trans*-$[PtCl_2(NCPh)_2]$ (0.23 g, 0.50 mmol) and $H\overline{NCH_2CH_2}$ (0.05 ml, 1.15 mmol) in THF (20 ml) at 0 °C. A clear yellow solution was immediately obtained and no $\nu(C{\equiv}N)$ band was detected in its IR spectrum. Then, the reaction mixture was stirred at room temperature for 7 h. The solvent was then removed *in vacuo* and the residue was treated with Et_2O/n-pentane (1/1) solvent mixture (30 ml). After filtration, the solid portion was washed with MeOH (2×5 ml) and dried *in vacuo*. Yield 0.16 g (57%), m.p. 221–223 °C. *Anal.* Calc. for

$C_{18}H_{20}N_4Cl_2Pt$: C, 38.72; H, 3.61; N, 10.03. Found: C, 38.03; H, 3.71; N, 9.99%. FAB mass spectrum (rel. int.): $M^{\cdot+}$ *m/z* 557 (2.29), MH^+ *m/z* 558 (2.73). Molecular weight measurements in 1,2-bis-dichloroethane gave the average value of 730 amu, indicating that the complex is partially associated in solution. A dimer–monomer equilibrium is also present in the range of concentrations studied ($1.5–0.6\times10^{-2}$ M).

Trans-[$PtCl_2${N(H)=C(Me)$\overline{NCH_2CH_2}$}$_2$] (4)

Compound **4** was obtained starting from *trans*-[$PtCl_2(NCMe)_2$] (0.24 g, 0.69 mmol) and $H\overline{NCH_2CH_2}$ (0.07 ml, 1.45 mmol) in THF (30 ml). The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 15 h. After this time, the IR analysis of the clear pale yellow solution showed the absence of any residual ν(C≡N) absorption. The solution was reduced to 2 ml and Et_2O (20 ml) was added. The yellow precipitate obtained was filtered off and dried *in vacuo*. Yield 0.19 g (63%), m.p. > 200 °C (dec.). *Anal.* Calc. for $C_{18}H_{20}N_4Cl_2Pt$: C, 22.13; H, 3.71; N, 12.90. Found: C, 21.82; H, 3.73; N, 12.38%. FAB mass spectrum (rel. int.): $M^{\cdot+}$ *m/z* 433 (1.63), MH^+ *m/z* 434 (1.09).

Trans-[$PdCl_2(H\overline{NCH_2CH_2})_2$] (5)

To a solution of *trans*-[$PdCl_2(NCC_6H_5)_2$] (0.31 g, 0.80 mmol) in THF (10 ml) was added aziridine (0.08 ml, 1.61 mmol) and the reaction mixture was stirred at 0 °C. After 5 min the ice-water bath was removed and the reaction mixture was allowed to reach room temperature. Over this time a clear solution was formed. The solution was then concentrated under reduced pressure to *c.* 5 ml and n-hexane (20 ml) was added. The yellow solid **5** was filtered off and dried under vacuum. Yield 0.15 g (68%), m.p. 180 °C (dec.). *Anal.* Calc. for $C_4H_{10}N_2Cl_2Pd$: C, 18.23; H, 3.82; N, 10.63. Found: C, 18.86; H, 3.81; N, 10.28%. FAB mass spectrum (rel. int.): $M^{\cdot+}$ *m/z* 261 (1.83).

Trans-[$Pt(CF_3)(H\overline{NCH_2CH_2})(PPh_3)_2$]$BF_4$ (6)

A suspension of *trans*-[$Pt(CF_3)(NCCH_2CH_3)(PPh_3)_2$]-$BF_4$ (0.53 g 0.57 mmol) in THF (20 ml) at 0 °C was treated with $H\overline{NCH_2CH_2}$ (0.03 ml, 0.63 mmol). The ice bath was removed, and stirring was continued at room temperature for 20 min. Over this time a white precipitate of **6** formed. After 2 h an IR spectrum of the solution showed the presence of a ν(C≡N) band at 2246 cm^{-1} due to free CH_3CH_2CN. Stirring was continued for 3 h, then the solid was filtered off and dried under vacuum. Yield 0.46 g (97%), m.p. 141–143 °C. *Anal.* Calc. for $C_{39}H_{35}NP_2PtBF_7$: C, 50.99; H, 3.84; N, 1.52. Found: C, 50.71; H, 4.03; N, 1.49%. FAB mass spectrum (rel. int.): M^+ *m/z* 830 (5.80), MH^+ *m/z* 831 (6.22).

Reaction of trans-[$PtCl_2${N(H)=C(Ph)$\overline{NCH_2CH_2}$}$_2$] with cis-bis-1,2-diphenylphosphinoethylene

trans-[$PtCl_2${N(H)=C(Ph)$\overline{NCH_2CH_2}$}$_2$] (0.158 mg, 0.28 mmol) was dissolved in CH_2Cl_2 (10 ml) and *cis*-$Ph_2PCH=CHPPh_2$ was added (0.230 g, 0.57 mmol) at room temperature. The IR spectrum of the reaction mixture showed the immediate disappearance of the ν(N=C) absorption of **3** at 1607 cm^{-1} with the appearance of a very sharp absorption at 1611 cm^{-1} due to free amidine. After 30 min a whitish solid started to precipitate. The stirring was continued for an additional 8 h. Then the reaction mixture was concentrated to small volume (2 ml) and on addition of Et_2O (10 ml) a white solid formed. It was filtered off, washed with Et_2O (2×3 ml) and dried under vacuum. Yield 0.30 g (99%). The solid was identified as [Pt(*cis*-$Ph_2PCH=CHPPh_2)_2$]$(Cl)_2$ ($^{31}P\{^1H\}$ NMR, $CDCl_3$: δ(P) 50.6, ^1J(PPt) 2535 Hz) [3].

The mother liquors were taken to dryness and the yellow oil was redissolved in 1 ml of $CDCl_3$. The GC-MS spectrum (column PS 264, 25 m, from 100 to 250 °C, 10°/min) of this solution showed the presence of free amidine, HN=C(Ph)$\overline{NCH_2CH_2}$ (r.t. 14.83 min, $M^{\cdot+}$ *m/z* 146 (80%), $[M-\overline{NCH_2CH_2}]^{\cdot+}$ *m/z* 104 (100%)) and of 2-(phenyl)imidazoline, $\overline{N=C(Ph)N(H)CH_2CH_2}$, (r.t. 17.32 min, $M^{\cdot+}$ *m/z* 146 (50%), $[M-C_2H_4]^{\cdot+}$ *m/z* 117 (100%)). The ^1H and ^{13}C NMR spectra of the $CDCl_3$ solution confirmed the presence of both compounds. HN=C(Ph)$\overline{NCH_2CH_2}$, ^1H NMR (δ in ppm, ref. TMS): 2.10 (s, 4H, NCH_2CH_2), 6.72 (s-br, 1H, NH), 7.80–7.29 (5H, Ph); $^{13}C\{^1H\}$ NMR (δ in ppm, ref. TMS): 26.59 (s, CH_2), 172.59 (s, C=N). $\overline{N=C(Ph)N(H)CH_2CH_2}$, ^1H NMR: 3.71 (s, 4H, NCH_2CH_2), 4.50 (br, 1H, NH), 7.66–6.78 (5H, Ph); $^{13}C\{^1H\}$ NMR: 49.85 (s, CH_2), 164.68 (s, C=N).

X-ray crystallographic analysis of trans-[$PtCl_2${N(H)=C(Ph)$\overline{NCH_2CH_2}$}$_2$] (3)

The crystal and refinement data for *trans*-[Pt-Cl_2{N(H)=C(Ph)$\overline{NCH_2CH_2}$}$_2$] are summarized in Table 1. A prismatic (yellow) crystal with dimensions of 0.46×0.38×0.26 mm was lodged in a Lindemann glass capillary and centered on a four-circle Philips PW1100 (Febo System) diffractometer with graphite-monochromated Mo Kα radiation. The orientation matrix and preliminary unit cell dimension were determined from 25 reflections found by mounting the crystal at random, varying each of the orientation angles χ and ϕ over a range of 120°, with $7 \leqslant \vartheta \leqslant 9°$. The unit cell was determined from 25 well-centered reflections ($10 \leqslant \vartheta \leqslant 14°$). Integrated intensities for *hkl* reflections in the interval $h = \pm 12$; $k = 0 \rightarrow 11$; $l = 42$ were measured, and two standard reflections 3,1,1 and −5,2,1 were measured every 180 reflections. There were no significant fluctuations of intensities other than those expected

TABLE 1. Crystal data, experimental conditions and refinement for **3**

Formula	$C_{18}H_{20}N_4Cl_2Pt$
Molecular weight	558.38
Crystal system	monoclinic
a (Å)	11.039(3)
b (Å)	10.883(3)
c (Å)	34.349(5)
β (°)	90.34(4)
V (Å^3)	4127(2)
Space group	$P2_1/n$
Z	8
D_{calc} (g cm^{-3})	1.80
$F(000)$	2144
λ (Mo Kα) (Å)	0.71069
μ (Mo Kα) (cm^{-1})	71.4
Transmission coefficient (relative)	56/100
Reflections measured	4860
Scan method	$\theta/2\theta$
Reflections ($I \geq 3\sigma(I)$)	4748
$R = \Sigma[\|F_o\| - \|F_c\|]/\Sigma\|F_o\|$	0.025
$R_w = [\Sigma(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.028
Weighting scheme, w	$[\sigma^2(F_o) + 0.000415(F_o^2)]^{-1}$
Goodness of fit, S	1.32

TABLE 2. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å$^2 \times 10^3$) for **3**

Atom	x	y	z	U_{eq}[a]
Pt(1)	0.02931(2)	0.22433(2)	0.179244(7)	35.6(1)
Pt(2)	0.03796(2)	0.18975(2)	0.079663(7)	41.8(1)
Cl(1)	0.2320(2)	0.1750(1)	0.18456(5)	48.7(6)
Cl(2)	−0.1731(2)	0.2773(2)	0.17368(5)	51.5(6)
Cl(3)	−0.0373(2)	−0.0068(2)	0.08361(5)	58.0(6)
Cl(4)	0.1142(2)	0.3861(2)	0.07334(6)	66.4(8)
N(1)	0.0807(5)	0.4004(4)	0.1724(1)	43(2)
N(2)	0.0945(5)	0.4716(4)	0.2353(2)	42(2)
N(3)	−0.0249(5)	0.0463(4)	0.1804(2)	42(2)
N(4)	−0.0464(5)	0.0031(5)	0.2459(2)	47(2)
N(5)	0.2081(5)	0.1285(5)	0.0895(2)	48(2)
N(6)	0.2543(6)	0.0096(6)	0.0354(2)	64(2)
N(7)	−0.1317(5)	0.2581(5)	0.0774(2)	50(2)
N(8)	−0.1925(6)	0.2531(6)	0.0122(2)	71(3)
C(1)	0.1049(6)	0.4880(5)	0.1958(2)	41(2)
C(2)	0.1546(5)	0.6080(5)	0.1825(2)	42(2)
C(3)	0.1902(6)	0.6976(5)	0.2091(2)	46(2)
C(4)	0.2332(6)	0.8110(6)	0.1968(2)	52(2)
C(5)	0.2415(9)	0.8361(7)	0.1582(3)	84(4)
C(6)	0.2044(10)	0.7493(8)	0.1317(3)	99(5)
C(7)	0.1653(8)	0.6373(7)	0.1430(2)	72(3)
C(8)	0.0152(7)	0.5448(7)	0.2607(2)	59(3)
C(9)	−0.0094(7)	0.4142(6)	0.2542(2)	57(3)
C(10)	−0.0556(5)	−0.0273(5)	0.2072(2)	39(2)
C(11)	−0.1145(6)	−0.1468(5)	0.1986(2)	44(2)
C(12)	−0.0923(8)	−0.2090(6)	0.1637(2)	63(3)
C(13)	−0.1545(10)	−0.3205(7)	0.1572(3)	84(4)
C(14)	−0.2307(8)	−0.3679(7)	0.1843(3)	83(4)
C(15)	−0.2518(8)	−0.3074(8)	0.2178(3)	79(4)
C(16)	−0.1932(6)	−0.1963(6)	0.2256(2)	58(3)
C(17)	0.0167(7)	−0.0697(7)	0.2748(2)	60(3)
C(18)	0.0584(7)	0.0544(7)	0.2646(2)	60(3)
C(19)	0.2838(6)	0.0618(6)	0.0705(2)	52(2)
C(20)	0.1989(8)	0.0818(12)	0.0047(2)	104(5)
C(21)	0.3245(9)	0.0355(10)	0.0002(2)	87(4)
C(22)	0.4045(6)	0.0276(7)	0.0872(2)	56(3)
C(23)	0.4549(9)	−0.0832(10)	0.0781(3)	91(4)
C(24)	0.5638(12)	−0.1172(15)	0.0947(4)	139(8)
C(25)	0.6220(12)	−0.0388(16)	0.1186(5)	142(8)
C(26)	0.5745(10)	0.0725(15)	0.1271(3)	120(6)
C(27)	0.4632(7)	0.1075(9)	0.1112(2)	75(4)
C(28)	−0.2087(7)	0.2868(6)	0.0510(3)	54(3)
C(29)	−0.1869(9)	0.3445(10)	−0.0184(2)	96(5)
C(30)	−0.0811(8)	0.2670(9)	−0.0093(2)	83(4)
C(31)	−0.3244(7)	0.3465(7)	0.0596(2)	60(3)
C(32)	−0.4286(8)	0.3306(9)	0.0371(3)	86(4)
C(33)	−0.5342(9)	0.3819(12)	0.0451(4)	119(6)
C(34)	−0.5419(11)	0.4590(12)	0.0782(4)	124(6)
C(35)	−0.4426(10)	0.4772(10)	0.0999(3)	109(5)
C(36)	−0.3355(8)	0.4227(9)	0.0909(3)	83(3)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

from Poisson statistics. The intensity data were corrected for Lorentz–polarization effects and for absorption, by following the method of North *et al.* [9]. No correction was made for extinction. The structure was solved by using three-dimensional Patterson and Fourier techniques and refined with full matrix least-squares, with anisotropic thermal parameters assigned to all the non-hydrogen atoms. The hydrogens were introduced at calculated idealized positions (d(C–H) = 0.98 Å with U = 0.07 Å^2) and allowed to ride on the attached carbon atoms. The function minimized was $\Sigma w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$. The final refinement cycle resulted in the conventional R factors R = 0.025 and R_w = 0.028 based on the 4748 unique reflections with $I \geq 3\sigma(I)$ and the 452 variables. The anomalous dispersion terms [10] for Pt were taken into account in the refinement. Data processing and computation were carried out using the SHELX 76 program package [11], with atomic scattering factors taken from the International Tables for X-ray Crystallography [10]. The program for the ORTEP drawing was taken from ref. 12. The atomic coordinates are reported in Table 2, while selected bond distances and angles are listed in Table 3.

Results and discussion

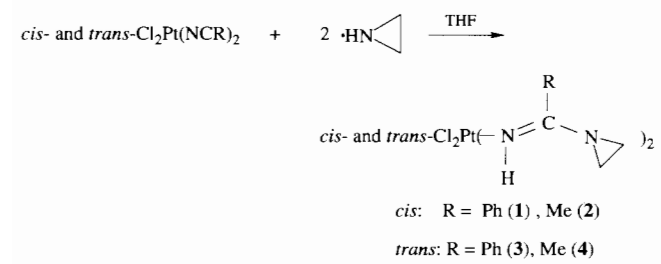
Synthesis, spectroscopic characterization of complexes ***1–6*** *and crystal structure of trans-* $[PtCl_2\{N(H)=C(Ph)NCH_2CH_2\}_2]$ ***(3)***

The reactions between *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = Me, Ph) and aziridine (complex/aziridine molar ratio in the range 1/2 to 1/4) at room temperature in THF result in the formation of the corresponding bis-amidino complexes as illustrated in Scheme 1.

All of the complexes **1–4** were characterized by their IR, ^{1}H and ^{13}C NMR spectra (see below), and by their

TABLE 3. Selected bond lengths (Å) and angles (°) for **3**

Pt(1)–Pt(2)	3.443(1)	Pt(1)–Cl(1)	2.307(2)
Pt(1)–Cl(2)	2.315(2)	Pt(1)–N(1)	2.013(5)
Pt(1)–N(3)	2.028(5)	Pt(2)–Cl(3)	2.299(2)
Pt(2)–Cl(4)	2.308(2)	Pt(2)–N(5)	2.020(5)
Pt(2)–N(7)	2.016(6)	N(1)–C(1)	1.274(8)
N(2)–C(1)	1.371(8)	N(2)–C(8)	1.474(9)
N(2)–C(9)	1.463(9)	N(3)–C(10)	1.268(8)
N(4)–C(10)	1.372(9)	N(4)–C(17)	1.446(9)
N(4)–C(18)	1.435(9)	N(5)–C(19)	1.288(9)
N(6)–C(19)	1.369(9)	N(6)–C(20)	1.448(11)
N(6)–C(21)	1.466(11)	N(7)–C(28)	1.280(9)
N(8)–C(28)	1.394(9)	N(8)–C(29)	1.448(11)
N(8)–C(30)	1.445(11)	C(1)–C(2)	1.491(8)
C(8)–C(9)	1.46(1)	C(10)–C(11)	1.48(1)
C(17)–C(18)	1.47(1)	C(19)–C(22)	1.49(1)
C(20)–C(21)	1.48(1)	C(28)–C(31)	1.46(1)
C(29)–C(30)	1.47(1)		
N(1)–Pt(1)–N(3)	174.4(2)	Cl(2)–Pt(1)–N(3)	87.4(2)
Cl(2)–Pt(1)–N(1)	91.5(2)	Cl(1)–Pt(1)–N(3)	93.6(2)
Cl(1)–Pt(1)–N(1)	87.5(2)	Cl(1)–Pt(1)–Cl(2)	179.0(1)
Pt(2)–Pt(1)–N(3)	85.7(1)	Pt(2)–Pt(1)–N(1)	88.8(1)
Pt(2)–Pt(1)–Cl(2)	88.7(1)	Pt(2)–Pt(1)–Cl(1)	91.2(1)
Pt(1)–Pt(2)–N(7)	88.0(2)	Pt(1)–Pt(2)–N(5)	84.3(2)
Pt(1)–Pt(2)–Cl(4)	90.3(1)	Pt(1)–Pt(2)–Cl(3)	91.8(1)
N(5)–Pt(2)–N(7)	172.2(2)	Cl(4)–Pt(2)–N(7)	89.7(2)
Cl(4)–Pt(2)–N(5)	89.0(2)	Cl(3)–Pt(2)–N(7)	90.5(2)
Cl(3)–Pt(2)–N(5)	91.1(2)	Cl(3)–Pt(2)–Cl(4)	178.0(1)
Pt(1)–N(1)–C(1)	134.1(4)	C(8)–N(2)–C(9)	59.8(5)
C(1)–N(2)–C(9)	124.4(5)	C(1)–N(2)–C(8)	124.6(5)
Pt(1)–N(3)–C(10)	134.2(4)	C(17)–N(4)–C(18)	61.3(5)
C(10–N(4)–C(18)	125.7(6)	C(10)–N(4)–C(17)	124.4(5)
Pt(2)–N(5)–C(19)	135.0(5)	C(20)–N(6)–C(21)	61.2(6)
C(19)–N(6)–C(21)	121.4(7)	C(19)–N(6)–C(20)	120.9(7)
Pt(2)–N(7)–C(28)	136.8(5)	C(29)–N(8)–C(30)	61.2(6)
C(28)–N(8)–C(30)	125.0(7)	C(28)–N(8)–C(29)	121.2(7)
N(1)–C(1)–N(2)	120.6(5)	N(2)–C(1)–C(2)	116.8(5)
N(1)–C(1)–C(2)	122.4(6)	N(2)–C(8)–C(9)	59.7(5)
N(2)–C(9)–C(8)	60.5(5)	N(3)–C(10)–N(4)	122.2(5)
N(4)–C(10)–C(11)	115.7(6)	N(3)–C(10)–C(11)	121.8(6)
N(4)–C(17)–C(18)	59.0(5)	N(4)–C(18)–C(17)	59.7(5)
N(5)–C(19)–N(6)	121.9(7)	N(6)–C(19)–C(22)	116.2(6)
N(5)–C(19)–C(22)	121.7(6)	N(6)–C(20)–C(21)	60.0(6)
N(6)–C(21)–C(20	58.8(5)	N(7)–C(28)–N(8)	121.8(7)
N(8)–C(28)–C(31)	115.3(6)	N(7)–C(28)–C(31)	122.7(7)
N(8)–C(29)–C(30)	59.3(6)	N(8)–C(30)–C(29)	59.5(6)



Scheme 1.

microanalytical and mass spectral data (see 'Experimental'). Complexes **1–4** are all likely associated to form dimers in the solid state which are partially maintained also in solution as evidenced by molecular weight measurements (see 'Experimental') carried out for **3**, which is the more soluble of the complexes prepared, and on the X-ray structure investigation of this complex. Complex **3** consists of 'dimers' $[Pt_2Cl_4L_4]$ ($L = HN{=}C(Ph)\widehat{NCH_2CH_2}$) (see Fig. 1), formed by two $[PtCl_2L_2]$ units intermolecularly held together by four N–H···Cl hydrogen bonds (H···Cl ~ 2.4 Å) involving the chlorines and the amidinic protons; each $[PtCl_2L_2]$ unit is then characterized by a rather distorted square *trans* planar coordination of the ligands. The Cl–Pt–Cl bond angle is almost linear in both units (the Cl(1)–Pt(1)–Cl(2) and Cl(3)–Pt(2)–Cl(4) angles are 179.00(8) and 178.00(7)°, respectively), while the corresponding N(1)–Pt(1)–N(3) and N(5)–Pt(2)–N(7) bond angles are bent (172.2(2) and 173.1(2)°, respectively) in the direction of the corresponding chlorines of the facing unit with contact distances Cl(1)···N(5) of 3.312(6) Å, Cl(2)···N(7) of 3.346(6) Å, Cl(3)···N(3) of 3.375(6) Å and Cl(4)···N(1) of 3.429(6) Å.

The two $[PtCl_2L_2]$ monomers, upon rotation of 90° around an ideal Pt···Pt axis, are approximately mirrored due to the eclipsing of the N–Pt–N of one unit with the Cl–Pt–Cl of the other as shown in Fig. 1 (the torsion angles Cl(1)–Pt(1)···Pt(2)–N(7) and Cl(2)–Pt(1)···Pt(2)–N(5) are −172.1(2) and −174.5(2)°, respectively).

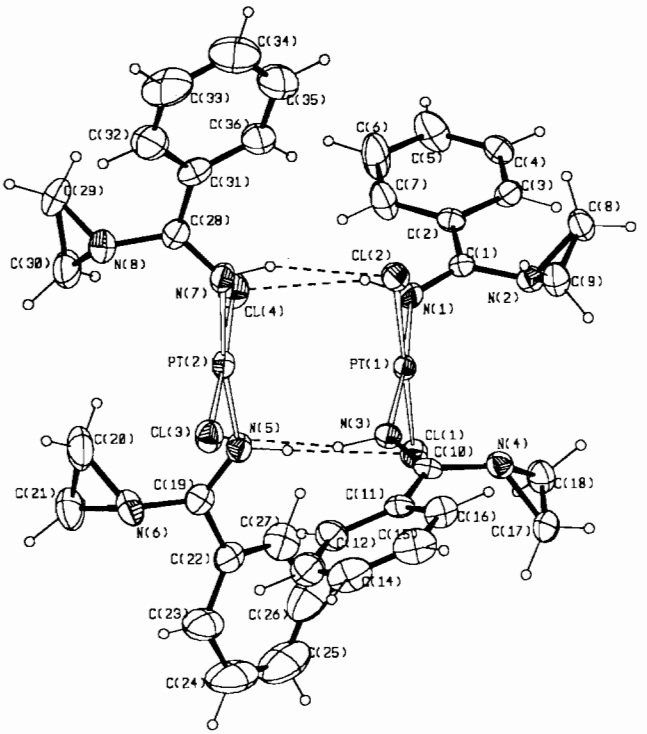


Fig. 1. An ORTEP drawing of the complex *trans*-[$PtCl_2\{N(H){=}C(Ph)\widehat{NCH_2CH_2}\}_2$] (**3**) with the atom-numbering scheme.

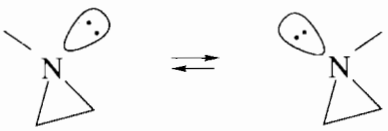
The Pt(1)···Pt(2) contact distance of 3.4430(5) Å is not short enough to justify a metal–metal interaction as found in the bis(benzamido)Pt(II) compound bis-[bis(1-imino-1-hydroxy-2,2-dimethylpropane)dichloro-platinum(II)], *cis*-$[PtCl_2\{HN{=}C(OH)Bu^t\}_2]_2$ [13], (Pt···Pt 3.165(1) Å), the structure of which consists of dimers with a staggered conformation of the two *cis*-$[PtCl_2L'_2]$ (L′ = benzamido ligand) units. These results suggest that for **3** the driving force to the dimer formation arises from the four hydrogen bond intermolecular interactions rather than a metal–metal interaction; however, the Pt–Pt bond appears to predominate in the formation of the above mentioned bis(benzamido)Pt(II) complex.

It is worthwhile noting that the Pt–Cl (2.299(2), 2.315(2) Å) and Pt–N (2.013(5), 2.028(5) Å) bond distances in the *trans* complex **3** (Table 3) are similar to those found in the previously mentioned *cis*-bis(benzamido)Pt(II) derivative (Pt–Cl 2.314(7), 2.337(6) Å, Pt–N 1.970(21), 2.056(20) Å), despite the different stereochemical arrangements of the ligands and the different strengths of the metal–metal interactions.

The nujol mull IR spectra of **1–4** (Table 4) show strong ν(C=N) bands in the range 1594–1624 cm^{-1} and medium absorptions around 3220 cm^{-1} due to the ν(N–H) mode. The IR spectrum in CH_2Cl_2 of **3** shows a strong broad absorption at 3237 cm^{-1}, which may indicate the partial presence also in solution of the dimers described above [14]. It is noteworthy that a strong tendency to associate through intermolecular N–H···Cl hydrogen bonds was previously discussed on the basis of the IR spectra of primary amine Pt(II) complexes of the type *trans*-$[PtCl_2(NH_2R)_2]$ (R = alkyl, aryl) [14b]. The ν(Pt–Cl) vibrations give rise to two absorptions for the *cis* compounds **1** and **2** and also for the *trans* complex **3**, but not **4**, thus paralleling the spectroscopic behavior previously observed for other *cis*- and *trans*-$[PtCl_2L_2]$ systems (L = an N-coordinated ligand such as oxazoline, imido-ester or nitrile) [3, 7, 6d]. A medium absorption in the range 3054–3070 cm^{-1} characteristic of the CH asymmetric mode of the aziridine ring [15] is also well detectable in the IR spectra of **1–4**.

At room temperature, in the ^{1}H NMR (Table 4) spectra the $-CH_2CH_2-$ protons of the aziridine ring appear as singlets in the range 2–3 ppm, indicating their magnetic equivalence possibly due to relatively free rotation around the C–N(aziridine) bond. Similarly, the ^{13}C NMR spectra (Table 5) show singlets for the two aziridine carbons and their chemical shifts fall in the range 25–30 ppm, as expected for N-substituted aziridines (i.e. for *N*-(methyl)aziridine), $\delta(CH_2) = 28.5$) [16]. Noteworthy, the ^1J(CH) values (of ~174 Hz) in the coupled ^{13}C NMR spectra confirm the presence of the three-membered ring of aziridine, since this coupling constant is sensitive to the ring size of a saturated N-heterocycle; in particular, it is reported that ^1J(CH) decreases on going from a three- (~170 Hz) to four- (~140 Hz), five- (139 Hz) and six- (137 Hz) membered rings [16]. In the ^{13}C NMR spectra, the amidinic–N=*C*– carbons fall in the range 174–182 ppm and their values closely match those previously reported for other transition metal N-coordinated amidines [17], imido esters [6d] and 2-oxazolines [3–5].

The NMR data also indicate that **1–4** are formed as complex mixtures of isomers, since, for instance, four or up to seven singlets due to the aziridine protons are observed in their ^{1}H NMR spectra (Table 4). However, as a general feature, only one of the isomers formed by each of the complexes **1–4** is much more abundant (average 80%) than the others. It is likely that some of these isomers arise from a restricted rotation around the C=N bond and, in this respect, **1–4** parallel the behavior shown by imido ester derivatives of the type *cis*- and *trans*-$[PtCl_2\{N(H){=}C(R)OCH_2CH_2Cl\}_2]$ (R = Me, Ph) [3], which were obtained from the reactions of the corresponding Pt(II) nitriles with $^-OCH_2CH_2Cl$ [3]. The additional isomers may originate from restricted rotation around the Pt–N(amidine) bond either due to ligand association in solution, as previously discussed for **3**, or due to mutual steric effect of the coordinated amidine ligands, which eventually may result in the formation of atropisomers. A further possibility, as suggested by a reviewer, is that the additional isomers might be due to inversion of the aziridine nitrogen, i.e.



We were unable to detect the magnetic inequivalence of the $-CH_2-$ groups of aziridine even at low temperature; thus, for instance, the five $-\overline{NCH_2}\dot{C}H_2$ singlets of **1**, that are observed at room temperature, are present as only one resonance at 212 K with an activation free energy of the process ($\Delta G^{\neq}_{212\,K}$) of 9.2 ± 0.5 kcal mol^{-1} in CD_2Cl_2 [18]. This value is in agreement with those reported for barriers to rotation in free amidines [19] or in related organo-metallic derivatives of the type *cis*-$[Pt(NH{=}C(Ph)N(Bu^t)CH_2CH_2NH(Bu^t)]Cl_2(NCPh)$ [6d] and $Re(Cp)(CO)_2[C(p\text{-tolyl}){=}\overline{NCH(CH_3)}\dot{C}H_2]$ (Cp = η^5-C_5H_5) [20]. On further lowering the temperature to 187 K only a broadening of the $-\overline{NCH_2}\dot{C}H_2$ signals is observed. A similar behavior is observed also for **2**; in this case, together with the four resonances of the aziridine protons, the ^{1}H NMR spectrum at room temperature shows up four singlets for the CH_3

TABLE 4. IR and ^{1}H NMR data for compounds **1–6**

Compound	IR[a] (cm^{-1})				^{1}H NMR[b]		
	ν(C=N)	ν(NH)	ν(PtCl)	ν(other)	δ(NCH_2)	δ(NH)	δ(other)
1	1594(s)	3231(s)	318(m) 328(m)	3054(m)[c]	3.019(s) 2.969(s)[d] 2.505(s) 2.287(s) 2.112(s)[f]	8.55(br) 8.64(br)[d] 8.35(br) 7.90(br)	7.37–7.66(m)[e] 8.5–8.6(m)[e]
2	1622(s)	3220(s)	319(m) 328(m)	3068(m)[c]	2.581(s)[h] 2.589(s)[h] 2.794(s)[d] 2.787(s)[f]	8.89(br) 8.30(br) 8.70(br) 8.41(br)	2.213(s)[g] 2.192(s)[i,g] 2.205(s)[f,g] 2.203(s)[d,g]
3	1599(s)	3228(s)	304(m) 324(m)	3057(m)[c]	3.034(s)[d] 2.959(s) 2.769(s)[f] 2.528(s)[f] 2.285(s)[f] 2.245(s)[f] 2.114(s)[f]	9.00(br)	7.74–7.36(m)[e]
4	1624(s)	3216(s)	304(m)	3070(m)[c]	2.821(s)[j] 2.553(s)[k] 2.546(s) 2.465(s) 2.460(s)[l]	6.85(br) 7.27(br) 7.45(br)	2.257(s)[g,d] 2.215(s)[g] 2.208(s)[g]
5		3255(s)		353(m)[m] 480(m)[n]	2.102(m) 1.888(m)	1.40(br)	
6[o]		3258(s)		3053(m)[c]	1.025(m) 0.799(m)	1.959(br)	7.86–7.53(m)

[a]Nujol mulls; abbreviations: s = strong, m = medium. [b]In CD_2Cl_2; the signals are referred to $MeSi_4$; δ in ppm; J in Hz; abbreviations: s = singlet, m = multiplet, br = broad. [c]ν_{as}(C–H) or aziridine ring. [d]More abundant isomer. [e]Phenyl protons. [f]Less abundant isomer. [g]Me protons. [h]^5J(HPt) 9.4 Hz. [i]^4J(HPt) 30 Hz. [j]^5J(HPt) 4.5 Hz. [k]^5J(HPt) 6.4 Hz. [l]^5J(HPt) 13.4 Hz. [m]ν(PdCl). [n]ν(Pd–N). [o]^{31}P NMR (CD_2Cl_2): δ 25.43 q (^3J(PF) 18.5, ^1J(PPt) 3024.8 Hz); abbreviations: q = quartet.

protons (Table 4), which give rise to only one resonance at 200 K with a $\Delta G^{\neq}_{200\,K} = 10.6 \pm 0.5$ kcal mol^{-1}, a value close to that found for the rotational barrier in the aforementioned Re–carbene(aziridine) complex [20]. The ^{1}H NMR of **2** at room temperature shows also four broad singlets of the NH protons in the range 8.4–8.9 ppm, but on lowering the temperature to 200 K only two of them sharpen (8.80 and 8.20 ppm). It is worthwhile noting that the ^{1}H NMR spectrum of **2** at 80 MHz shows that the singlet at δ 2.587 of the aziridine protons is flanked by ^{195}Pt satellites (^5J(HPt) 9.4 Hz), indicating a remote agostic coupling and suggesting an arrangement with the $-NCH_2-$ protons close to the metal; this feature is also in agreement with the X-ray findings of **3**. This coupling was observed also for some of the $-NCH_2CH_2$ resonances of **4**; in particular, the isomer at δ 2.460 shows an exceptionally high value of J(PtH) (13.4 Hz) [21]. This remote agostic coupling J(HPt) coupling is not observed when the ^{1}H NMR spectra were run at 400 or 200 MHz; in fact it is well documented that there is a field dependence of the nuclear magnetic relaxation so that coupling constants with heavy metal ions (in the present case ^{195}Pt) are better detected on a 80 than 200 MHz or higher field instruments, owing to a shortening of the T_1 relaxation times with increasing magnetic field [22].

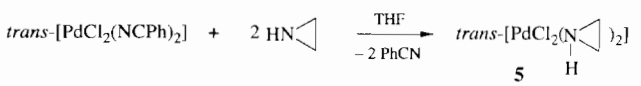
The FAB mass spectra of **1–4** (Table 6) show molecular ions, accompanied by mono- and bis-protonated species, which subsequently lose $Cl^{\cdot}$ and HCl giving rise to ionic species containing the amidine ligands. The further loss of one amidine ligand from ionic species of the type $[M - Cl^{\cdot} - HCl]^+$, $[M - 2HCl]^{\cdot+}$ and $[M - 2Cl^{\cdot}]^{\cdot+}$ is favored more for those having an amidine ligand with a Me (i.e. species at m/z 361, 362 and 363) than a Ph group. This feature suggests that the Pt–N–C–Ph delocalization would increase to some extent the Pt–N bond strength, thus making its rupture more difficult. An analogous behavior was previously observed for some N-coordinated Pt(II) aryl- and alkyl-oxazine compounds [5]. No ionic species arising from fragmentation of the amidine ligands or due to aziridine ring breaking are observed.

TABLE 5. ^{13}C NMR data for compounds **1–6**

Compound	^{13}C NMR[a]		
	$\delta(NCH_2)$	$\delta(NHC)$	δ(other)
1	30.32	176.30	132.29[b], 129.17[b], 127.29[b], 127.11[b]
2	28.64[c,d]	171.37[c]	24.00[c,e]
	27.60[c,f]	175.91[c]	22.44[c,e]
	27.55	177.08	24.04[e]
	28.38	175.73	22.58[e]
3	29.94[c]	174.72[c]	134.41[b], 132.07[b], 128.95[b], 127.58[b]
	30.33	175.99	132.37[b], 129.15[b], 127.37[b]
4	27.55[g,c]	182.27	4.36[c,h,e]
	28.61[j]	178.94	22.96[k,e]
	25.38[i]	176.15	22.94[l,e]
	27.61	177.25	
5	23.55		
6	30.03		136.54[b], 136.42[b], 136.29[b]
			133.80[b], 131.25[b], 131.15[b]
			131.04[b], 130.39[b]

[a]In CD_2Cl_2; the signals are referred to Me_4Si by taking the chemical shift of CD_2Cl_2-d_2 as +53.80 ppm; δ in ppm; J in Hz; the signals are all singlets in the $^{13}C\{^1H\}$ spectrum. [b]Phenyl carbons. [c]More abundant isomer. [d] $^1J(CH)$ 174.09. [e]CH_3 carbon. [f] $^1J(CH)$ 173.70. [g] $^1J(CH) = 173.97$. [h] $^1J(CH)$ 137.87. [i] $^1J(CH)$ 173.30. [j] $^1J(CH)$ 180.39. [k] $^1J(CH)$ 130.55. [l] $^1J(CH)$ 130.91.

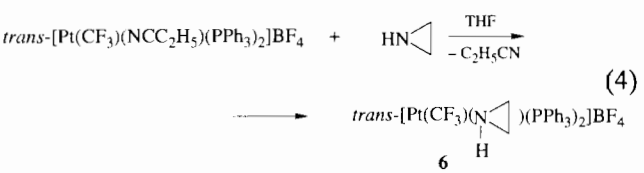
The reaction of Pd(II) nitriles such as *trans*-$[PdCl_2(NCPh)_2]$ with aziridine proceeds differently from those with the corresponding Pt(II) complexes since displacement of the benzonitrile ligands rather than nucleophilic attack at the nitrile carbon occurs, with formation of the bis(aziridine)Pd(II) complex (eqn. 3)).



(3)

The IR spectrum of **5** shows one band at 353 cm^{-1} typical of two *trans* chlorine atoms and a medium absorption at 480 cm^{-1} attributable to the ν(Pd–N) absorption [14a]. Its ^1H NMR spectrum shows two complex multiplets centered at δ 2.102 and 1.888 due to the four NCH_2CH_2 protons which appear magnetically inequivalent, while the two NH protons appear as a broad resonance at 1.40 ppm. The $^{13}C\{^1H\}$ NMR of **5** shows a single resonance at δ 23.55 for the two aziridine carbons. The FAB mass spectrum shows the molecular ion at m/z 261 and fragmentation species due to loss of $Cl^{\cdot}$ (ion at m/z 226) and further loss of $\overline{NCH_2CH_2}$ yielding ions at m/z 184.

Substitution of the nitrile ligand by aziridine is observed also in cationic Pt(II) nitrile complexes (eqn. (4)). The *trans* geometry of **6** has been deduced by



(4)

its ^{31}P NMR spectrum, which displays a quartet for the coupling of the two equivalent P atoms with the CF_3 group flanked by ^{195}Pt satellites. The ^1H NMR spectrum of **6** shows two complex multiplets centered at 0.799 and 1.025 ppm of the inequivalent $\overline{NCH_2CH_2}$ protons together with a broad signal at 1.959 ppm of the NH proton. The ^{13}C NMR spectrum of **6** shows the $\overline{NCH_2CH_2}$ carbons as a singlet at 30.03 ppm. The CF_3 carbon is not detected owing to the relatively low solubility of **6**; this feature was previously observed in the ^{13}C NMR spectra of other (trifluoromethyl)Pt(II) derivatives with N-donor ligands [23, 4b, 5], where C–F, C–Pt and C–Pt–P couplings cause the signal intensity to be too low to be observed, being spread over a number of peaks. The FAB mass spectrum of **6** shows the molecular cation at m/z 830, from which ions at m/z 802 are formed due to the loss of $CH_2{=}CH_2$ arising from aziridine ring breaking. Abundant ions at m/z 788 corresponding to the loss of aziridine from the molecular cations are present; these latter ions lose $CF_3^{\cdot}$ giving rise to a fragmentation pattern characteristic of the $Pt(PPh_3)_2$ moiety [24].

TABLE 6. FAB mass spectra of compounds **1–6**

Compound *m/z*[a,b]										
	$M^{\cdot+}$	$[M+H]^+$	$[M+2H]^{\cdot+}$	$[M-Cl]^+$	$[M-HCl]^{\cdot+}$	$[M-Cl^{\cdot}-HCl]^+$	$[M-2HCl]^{\cdot+}$	$[M-2Cl]^{\cdot+}$	$[M-Cl^{\cdot}-HCl\text{-amd}]^+$	$[M-2HCl\text{-amd}]^{\cdot+}$	$[M-2Cl^{\cdot}\text{-amd}]^{\cdot+}$
1[c]	557(1.06)	558(1.54)	559(1.79)	522(1.28)	521(1.21)[d]	486(2.29)	485(2.13)	487(1.34)	340(3.44)		
2	433(1.12)	434(0.96)	435(0.96)	398(1.0)	397(1.60)	362(2.56)	361(2.88)	363(4.8)	278(19.50)	277(4.70)	279(19.60)
3	557(2.29)	558(2.73)	559(2.82)[e]	522(0.93)	521(1.03)[d]	486(3.24)		487(3.61)	340(2.94)		
4	433(1.63)	434(1.09)	435(0.8)	398(0.6)	397(0.8)	362(1.6)	361(2.2)	363(4.6)	278(9.5)	277(23.12)	279(10.9)
5	261(1.83)			226(1.75)[f]							
6[g]	830(5.80)	831(6.22)									

[a]Nominal molecular weight using the ^{194}Pt isotope; amd = amidine ligand. [b]Relative intensities (% in parentheses) are normalized to the most intense ion. [c]Ions at *m/z* 411 (0.47) due to the loss of aziridine from $M^{\cdot+}$ are present. [d]The ions at *m/z* 444 (1.98) for **1** and (1.53) for **3** due to the loss of Ph$^{\cdot}$ from ions at *m/z* 521 are observed. [e]Ions at *m/z* 523 (1.19) due to the loss of HCl from ions at *m/z* 522 are observed. [f]Ions at *m/z* 184 (1.80) due to the loss of $\dot{N}CH_2CH_2$ from ions at *m/z* 226 are observed. [g]Ions at *m/z* 802 (3.60) are due to the loss of C_2H_4 from the molecular ions; ions at *m/z* 788 (43.55) are due to the loss of aziridine from the molecular ions: subsequent loss of $CF_3^{\cdot}$ yields ions at *m/z* 718 (9.8) corresponding to $[Pt(PPh_3)_2]^{\cdot+}$.

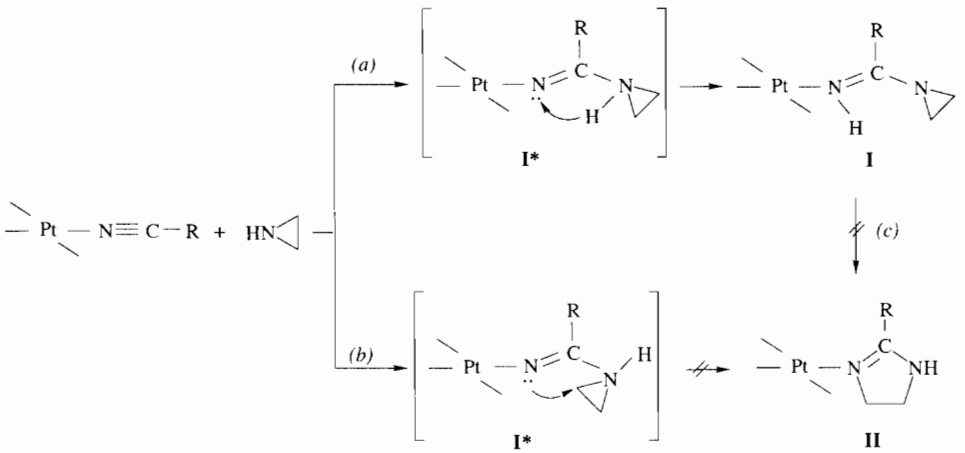
Mechanism and formation of 2-imidazolines

Previous mechanistic studies on the reactions of primary [25a, b] and secondary amines [25c] with Pt(II) nitrile complexes to afford amidine derivatives have shown that these reactions proceed by nucleophilic attack of the amine on the nitrile carbon followed by hydrogen transfer to the nitrile amino nitrogen. It is likely that the reactions of aziridine proceed similarly as illustrated in Scheme 2.

Of the two possible reaction pathways, (a) and (b), only (a) is operative. Thus, H transfer to the nitrogen atom α to Pt of intermediate **I***, derived by nucleophilic attack of aziridine, predominates over the ring closure of **I*** by intramolecular nucleophilic attack of the N-atom on the aziridine ring (path (b)). A plausible reason for the observed reactivity may be the low nucleophilicity of the α-nitrogen atom coordinated to the strong electron-withdrawing Pt(II) ion.

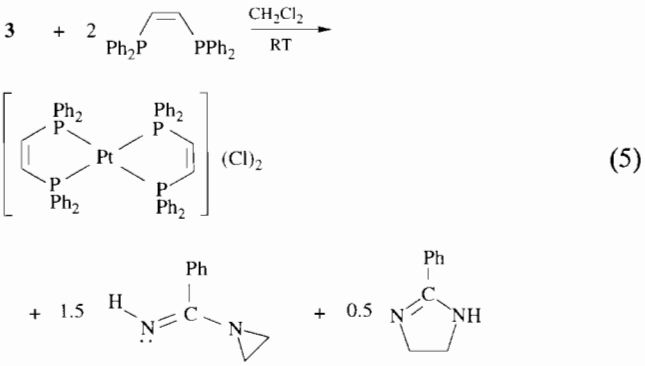
Attempts to generate five-membered imidazoline complexes either from the amidine complexes **I** (path (c) of Scheme 2) or by reaction of $[PtCl_2(NCR)_2]$ complexes with $[H_3NCH_2CH_2Cl]Cl$ in the presence of a base, which would generate 2-chloroethylamine as reported for some related cyclization reactions of Pt(II) isocyanides [26], were unsuccessful. It was also hoped that ring opening of aziridine and subsequent ring closure in complexes of type **I** could be favored by a base (which would deprotonate the N–H bond, thus making the imino nitrogen more nucleophilic) and/or Cl^- ions (which would attack the aziridine ring, as reported for other aziridine reactions [1b, 27]). However, upon treating **3** with equivalent amounts of n-BuLi in THF, NaOH in MeOH or NaOMe in THF/MeOH, even at reflux for several hours, the starting material was always recovered; the same results were obtained upon reaction of **3** with excess Cl^- ions in the presence of 'catalytic' amounts of NaOH in MeOH. The observed lack of reactivity of the amidine N–H bond with bases appears to be somewhat related to the formation of strong N–H$\cdots$Cl hydrogen bonds, as mentioned earlier. Complexes **1** and **3** are thermally stable and did not rearrange or decompose upon refluxing in 1,2-dichloromethane for 8 h even in the presence of 2 equiv. of a base such as NEt_3 or n-BuLi. Similarly, the reactions of *cis*-$[PtCl_2(NCPh)_2]$ with $[H_3NCH_2CH_2Cl]Cl$ in the presence of aziridine, which had been successfully used in similar cycloaddition reactions with carbonyl ligands [1] to form five-membered carbene rings, gave the amidine complex **1**. When the same reaction was performed using $[H_3NCH_2CH_2Cl]Cl$ and n-BuLi as the base, untractable solids formed, which could not be identified spectroscopically.

Compound **3** reacts with 2 equiv. of *cis*-Ph_2P-$CH{=}CHPPh_2$ to give $[(cis\text{-}Ph_2PCH{=}CHPPh_2)_2Pt](Cl)_2$, free amidine and 2-(phenyl)imidazoline according



Scheme 2.

to reaction (5).



(5)

When this reaction was performed in toluene at 90 °C for a few hours or in $CHCl_3$ for 3 days at room temperature, 2-(phenyl)imidazoline was the only detected product. The free (aziridino)amidine and 2-(phenyl)imidazoline were characterized by IR, ^1H NMR and GC-MS data (see 'Experimental'). While the basic mechanistic features of this reaction still deserve further investigation, the formation of the heterocyclic ligand only upon displacement of the coordinated amidine may be reasonably explained considering that in this process the electron-withdrawing Pt(II) fragment is being removed, thus making the amidino nitrogen sufficiently basic to attack intramolecularly the aziridine ring. The conversion of the coordinated amidine to 2-imidazoline is likely to be promoted by the Pt(II) Lewis acid, since this reactivity would parallel that observed in the organic synthesis of Δ^2-imidazolines from aziridines and nitriles, which is known to be catalyzed by acids [27b, c].

Conclusions

The reactions of aziridine with electrophilic nitrile complexes proceed markedly different from those of isoelectronic carbonyl and isocyanide complexes [1, 2], since aziridine, in spite of its high strain energy (113 kcal mol^{-1}) [14], does not undergo ring opening with RCN ligands as is otherwise observed with CO and RNC ligands. The primary products of these reactions are in fact (aziridino)amidine complexes, but it is noteworthy that the heterocyclic 2-imidazolines can be formed upon displacement of the coordinated amidines. Further investigation of this type of reactivity and a possible catalytic conversion of nitriles to imidazolines by Pt(II) complexes in the presence of aziridine is under study.

Supplementary material

Listing of anisotropic thermal parameters for non-hydrogen atoms and fractional coordinates of H atoms (2 pages) and a list of observed and calculated structure factors (27 pages) are available from author F.B. on request.

Acknowledgements

R.A.M. and R.J.A. are grateful to NATO for a grant (CRG 931224). R.A.M. also thanks MURST and CNR for financial support.

References

1 (a) M.M. Singh and R.J. Angelici, *Inorg. Chem., 23* (1984) 2691; (b) *23* (1984) 2699; (c) L. Zanotto, R. Bertani and R.A. Michelin, *Inorg. Chem., 29* (1990) 3265.

2 (a) R. Bertani, M. Mozzon and R.A. Michelin, *Inorg. Chem., 27* (1988) 2809; (b) R. Bertani, M. Mozzon, R.A. Michelin, F. Benetollo, G. Bombieri, T.J. Castilho and A.J.L. Pombeiro, *Inorg. Chim. Acta, 189* (1991) 175.

3 R.A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo and R.J. Angelici, *Organometallics, 10* (1991) 1751.

4 (a) R.A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo and R.J. Angelici, *J. Chem. Soc., Dalton Trans.*, (1993) 959; (b) R.A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri and R.J. Angelici, *Organometallics, 13* (1994) 1341.

5 R.A. Michelin, U. Belluco, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri and R.J. Angelici, *Inorg. Chim. Acta, 220* (1994) 21.

6 (a) B.N. Storhoff and H.C. Lewis, *Coord. Chem. Rev., 23* (1977) 1; (b) R. Ros, J. Renaud and R. Roulet, *J. Organomet. Chem., 104* (1976) 271; (c) K.B. Nolan and R.W. Hay, *J. Chem. Soc., Dalton Trans.*, (1974) 914; (d) L. Maresca, G. Natile, F.P. Intini, F. Gasparini, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Am. Chem. Soc., 108* (1986) 1180.

7 D. Fraccarollo, R. Bertani, M. Mozzon, U. Belluco and R.A. Michelin, *Inorg. Chim. Acta, 201* (1992) 15.

8 J.R. Doyle, P.E. Slade and H.B. Jonassen, *Inorg. Synth., 6* (1960) 216.

9 A.C.T. North, D.C. Phillips and F.S. Matthews, *Acta Crystallogr., Sect. A, 24* (1968) 351.

10 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974.

11 G.M. Sheldrik, *SHELX-76*, program for crystal structure determination, University of Cambridge, UK, 1976.

12 C.K. Johnson, ORTEP-II, *Rep. ORNL-5138,* Oak Ridge National Laboratory, TN, 1976.

13 R. Cini, F.P. Fanizzi, F.P. Intini, L. Maresca and G. Natile, *J. Am. Chem. Soc., 115* (1993) 5123.

14 (a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 1986, p. 158; (b) J. Chatt, L.A. Ducanson and L.M. Venanzi, *J. Inorg. Nucl. Chem., 8* (1958) 67.

15 A. Padwa and A.D. Woolhouse, in A.R. Katritzky and C.W. Rees (eds.), *Comprehensive Heterocyclic Chemistry,* Vol. 7, Pergamon, New York, 1984, Ch. 5.04.

16 H.-O. Kalinowski, S. Berger and S. Braun, *Carbon-13 NMR Spectroscopy,* Wiley, Chichester, UK, 1988.

17 S.G. Feng, P.S. White and J.L. Templeton, *Organometallics, 12* (1993) 1765.

18 H. Günther, *NMR Spectroscopy,* Wiley, New York, 1980, Ch. VIII.

19 L.M. Jackman, in L.M. Jackman and F.A. Cotton (eds.), *Dynamic Nuclear Magnetic Resonance Spectroscopy,* Academic Press, New York, 1975, p. 203.

20 L.A. Mercando, B.M. Handwerker, H.J. MacMillan, G.L. Geoffroy, A.L. Rheingold and B.E. Owens-Waltermire, *Organometallics, 12* (1993) 1559.

21 A. Albinati, P.S. Pregosin and F. Wombacher, *Inorg. Chem., 29* (1990) 1812.

22 (a) J.Y. Lellemand, J. Soulvé and J.C. Chottard, *J. Chem. Soc., Chem. Commun.*, (1980) 436; (b) C.G. Anklin and P.S. Pregosin, *Magn. Reson. Chem., 23* (1985) 671; (c) R.M. Hawk and R.R. Sharp, *J. Chem. Phys., 60* (1974) 1522.

23 T.G. Appleton, R.D. Berry, J.R. Hall and D.W. Neale, *J. Organomet. Chem., 342* (1988) 399.

24 R. Bertani, M. Mozzon, R.A. Michelin, R. Seraglia and P. Traldi, *Org. Mass Spectrom., 27* (1992) 1187.

25 (a) C.A. Amodio and K.B. Nolan, *Inorg. Chim. Acta, 113* (1986) 27; (b) P. Uguagliati, U. Belluco, R.A. Michelin and P. Guerriero, *Inorg. Chim. Acta, 81* (1984) 61; (c) L. Calligaro, R.A. Michelin and P. Uguagliati, *Inorg. Chim. Acta, 76* (1983) L83.

26 R.A. Michelin, L. Zanotto, D. Braga, P. Sabatino and R.J. Angelici, *Inorg. Chem., 27* (1988) 93.

27 (a) J.R. Malpass, in D.H.R. Barton and W.D. Ollis (eds.), *Comprehensive Organic Chemistry,* Vol. 2, Pergamon, Oxford, 1979, Ch. 6.1, p. 52; (b) p. 541, and refs. therein; (c) M.R. Grimmett, in A.R. Katritzky and C.W. Rees (eds.), *Comprehensive Heterocyclic Chemistry,* Vol. 5, Pergamon, Oxford, 1984, Ch. 4.08, p. 487.