Inorganica Chimica Acta 395 (2013) 181–188

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Platinum(II) complexes containing unsaturated ligands. Nucleophilic substitution versus nucleophilic attack to ligand: a stereochemistry driven outcome

Daniela Belli Dell'Amico *, Claudio Broglia, Luca Labella, Fabio Marchetti, Daniele Mendola, Simona Samaritani

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, 1-56126 Pisa, Italy

ARTICLE INFO

Article history:
Received 20 July 2012
Accepted 24 October 2012
Available online 16 November 2012

Keywords:
Substitution reactions
Addition reactions
Platinum
Unsaturated ligands

ABSTRACT

The reactivity of mixed complexes $[PtCl_2(L)(L')]$ (L = MeCN, EtCN, CO), L′ = PPh_3; L = η^2-C_2H_4, CO; L′ = MeCN, EtCN) towards diethylamine has been investigated. The processes are chemo- (substitution versus addition) and stereo-selective in dependence of the stereochemistry of the precursor. The structures of [SP4-4]-$[PtCl(CONEt_2)(NHEt_2)(PPh_3)]$, [SP4-4]-**1**, *trans*-$[PtCl_2(NHEt_2)(PPh_3)]$, *trans*-**2**, and *cis*-$[PtCl_2\{(E\text{-})HN{=}C(NEt_2)Me\}(PPh_3)]$, *cis*-**3a**, are reported.

1. Introduction

Metal coordinated unsaturated ligands may undergo attack by suitable nucleophiles, a reactivity widely exploited in coordination and organometallic chemistry, as proved by the number of articles, reviews and book chapters devoted to this topic [1]. Many examples describing the reactions of neutral platinum(II) $PtCl_2L_2$ (L = CO; RCN) and $PtCl_2L$(alkene) (L = neutral ligand) with primary and/or secondary amines, have been reported and it is worth to recall here some of them. *cis*-$[PtCl_2(CO)_2]$ reacts with NH^iPr_2 in molar ratio 1:2 yielding the carbamoyl derivative $[NH_2{}^iPr_2]$*cis*-$[PtCl_2(CON^iPr_2)(CO)]$ [2] (Eq. (1))

$$cis - [PtCl_2(CO)_2] + 2NH^iPr_2 \rightarrow [NH_2^iPr_2]cis\text{-}[PtCl_2(CON^iPr_2)(CO)] \quad (1)$$

Both, *cis*- and *trans*-$[PtCl_2(NCR')_2]$ react with excess of primary or secondary amines yielding the bis-amidine derivatives *cis*- or *trans*-$[PtCl_2\{NH{=}C(R')NR_2\}_2]$, respectively (Eq. (2)) [3]

$$cis\text{-}[PtCl_2(NCR')_2] + 2NHR_2 \rightarrow cis\text{-}[PtCl_2\{NH{=}C(R')NR_2\}_2] \quad (2a)$$

$$trans\text{-}[PtCl_2(NCR')_2] + 2NHR_2 \rightarrow trans\text{-}[PtCl_2\{NH{=}C(R')\times(NR_2\}_2] \quad (2b)$$

Moreover, according to the earliest report by Orchin et al. and to the extensive work by Panunzi and Green, amines attack the coordinated alkene in platinum(II) complexes $[PtCl_2(C{=}C)L]$ (where C=C represents the alkene and L is a neutral ligand) with formation of an alkyl zwitterionic species [4] where the positive and negative charges are localized on the nitrogen and platinum atoms, respectively (Eq. (3)). Reaction 3 is an equilibrium reaction as the amine attached to the alkene skeletal can be easily lost

$$[PtCl]_2(C{=}C)L] + NHR_2 \rightleftharpoons [Pt^-Cl_2(C{-}C{-}N^+HR_2)L] \quad (3)$$

Recently Atwood et al. have re-examined the reactivity of a series of platinum(II) neutral alkene complexes *cis*-$[PtCl_2(C{=}C)(PPh_3)]$, [5] reporting alkene substitution or nucleophilic attack to the unsaturated ligand in dependence of the alkene nature (alkenes with more than four carbon atoms being displaced by $NHEt_2$) and of the temperature (ligand substitution rather than nucleophilic attack being observed also for the smaller alkenes if the reaction mixture, initially at −75 °C, is allowed to reach room temperature too rapidly). Ligand substitution reactions in platinum(II) chemistry are strongly influenced by the "trans effect" [6], exploited for synthetic goals to foresee or justify (with some prudence) the outcome of a reaction [6] or the different behaviour of two geometric isomers [7].

In order to gain a deeper insight into the reactivity towards diethylamine of neutral platinum(II) complexes, $PtCl_2LL'$, containing at least one unsaturated ligand, the present study was carried out with the aim to find the conditions to favour selectively ligand attack or ligand substitution. It appeared attractive to monitor both the chemo- and the regio-selectivity (attack to L versus L′ when both the neutral ligands are unsaturated). The reactions of $NHEt_2$ with both geometrical isomers of $[PtCl_2(CO)(PPh_3)]$, $[PtCl_2(NCR)(PPh_3)]$ and $[PtCl_2(C_2H_4)(NCR)]$ (R = Me, Et) and with *trans*-$[PtCl_2(CO)(NCEt)]$ showed an outcome strictly dependent on the stereochemistry of

* Corresponding author. Tel.: +39 0502219210.
E-mail address: belli@dcci.unipi.it (D. Belli Dell'Amico).

0020-1693/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2012.10.038

the precursor. It appears surprising that clear and simple examples correlating the precursor geometrical isomerism with the chemoselectivity of a process are quite rare in the literature [8].

2. Experimental

2.1. General

All manipulations were performed under a dinitrogen atmosphere, if not otherwise stated. Solvents and liquid reagents were dried according to reported procedures [9]. ^{1}H-, ^{13}C-, ^{31}P and ^{195}Pt NMR spectra were recorded with a Bruker "Avance DRX 400" spectrometer, in $CDCl_3$ solution if not otherwise stated. Chemical shifts were measured in ppm (δ) from TMS by residual solvent peaks for ^{1}H and ^{13}C, from aqueous (D_2O) H_3PO_4 (85%) for ^{31}P and from aqueous (D_2O) hexachloroplatinic acid for ^{195}Pt. A sealed capillary containing C_6D_6 was introduced in the NMR tube to lock the spectrometer to the deuterium signal when non-deuterated solvents were used. FTIR spectra in solid phase were recorded with a Perkin–Elmer "Spectrum One" spectrometer, with ATR technique. FTIR spectra in solution were recorded with a Perkin–Elmer "Paragon 500" or a Perkin–Elmer "Spectrum 100" spectrometers. A 0.1 mm cell supplied with CaF_2 windows was used. Elemental analyses (C, H, N) were performed at Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine.*trans*-[$PtCl_2(C_2H_4)$(NCEt)] was prepared from *trans*-[$Pt(\mu\text{-}Cl)Cl(C_2H_4)]_2$ according to the procedure described for *trans*-[$PtCl_2(C_2H_4)$(NCMe)] [10,11]. *cis*-[$PtCl_2(C_2H_4)$(NCMe)] was prepared (54% yield) by reacting a suspension of $[Pt(\mu\text{-}Cl)Cl(C_2H_4)]_2$ with an excess of MeCN (11.5 mmol) in CH_2Cl_2 as solvent under argon atmosphere. *trans*-[$PtCl_2(C_2H_4)$(NCMe)] isomer is first obtained which slowly isomerizes to the sparingly soluble *cis*-isomer (15 d at room temperature, solution about 1 M, 54% yield). ^{1}H NMR (CD_3CN + $CDCl_3$): 4.64 ($^{2}J_{Pt-H}$ = 62 Hz; 4 H; C$\underline{H}_2$ = C$\underline{H}_2$); 2.44 ($^{4}J_{Pt-H}$ = 13 Hz; 3 H; C$\underline{H}_3$CN). ^{13}C NMR (CD_3CN): 74.8 ($^{1}J_{Pt-C}$ = 163 Hz, $\underline{C}H_2$ = $\underline{C}H_2$); 4.6 ($\underline{C}H_3CN$) in agreement with the literature data [12]. ^{195}Pt NMR (CD_3CN): −2883 ($^{1}J_{Pt-N}$ = 364 Hz). *cis*-[$PtCl_2(PPh_3)$(NCMe)], *cis*-[$PtCl_2(PPh_3)$(NCEt)] and *cis*-[$PtCl_2$(CO)(NCEt)] were prepared according to already reported procedures.[13] *cis*-[$PtCl_2(CO)(PPh_3)$] [14] was prepared (91% yield) by treatment of a propionitrile solution of *cis*-[$PtCl_2$(NCEt)(PPh_3)] with CO ($P_{CO} \approx 1$ atm) at room temperature until complete conversion of the precursor was achieved (24 h, monitored by ^{31}P NMR spectroscopy). ^{31}P NMR: 10.9 ($^{1}J_{P-Pt}$ = 3030 Hz). ^{195}Pt NMR: −4090 ($^{1}J_{P-Pt}$ = 3030 Hz). ^{13}C NMR: 156.4 ($\underline{C}O$), 134.2 (d, J_{C-P} = 10.7 Hz), 132.6 (s) 128.1 (d, J_{C-P} = 12.0 Hz) 126.9 (d, J_{C-P} = 67.5 Hz). IR (ATR): 2104 ($\tilde{\nu}_{CO}$) cm^{-1}.

2.2. Reaction between cis-[$PtCl_2$(CO)(PPh_3)] and $NHEt_2$ with formation of [SP4-4]-[PtCl(CONEt$_2$)(NHEt$_2$)(PPh_3)], [SP4-4]-1

A suspension of 0.683 g (1.23 mmol) of *cis*-[$PtCl_2(CO)(PPh_3)$] in 30 mL of toluene, under dinitrogen, was treated with a solution of 0.520 mL of diethylamine (5.03 mmol, $NHEt_2$/Pt molar ratio = 4.09) in toluene (10 mL) under stirring. The liquid phase turned deep yellow in minutes and a white solid appeared. When the complete conversion of the substrate was achieved (2 h, monitored by ^{31}P NMR) the mixture was filtered under dinitrogen to eliminate NH_2Et_2Cl, the filtrate was concentrated (15 mL) under vacuum, treated with heptane (15 mL) and cooled (−30 °C). Light-orange crystals separated out which were filtered and dried under vacuum (0.522 g, 64% yield). Suitable single crystals were selected for X-ray diffraction studies. *Anal.* Calcd. for $C_{27}H_{38}ClN_2OPPt$: N, 4.2; C, 48.5; H, 5.7%. Found: N, 4.1; C, 48.8; H, 5.5%. ^{1}H NMR ($CDCl_3$, T = 50 °C): 7.80–7.20 (15H); 4.30 (m, 1H); 3.78 (br s, 1H); 3.37–2.85 (m, 6H); 2.41 (m, 1H); 1.64 (t, 3H); 1.52 (t, 3H); 0.82 (t) and 0.78 (t, 6H). ^{13}C NMR ($CDCl_3$): 167.7; 134.5 (d, J_{C-P} = 11 Hz); 130.5 (d, J_{C-P} = 61 Hz); 130.4; 127.9 (d, J_{C-P} = 11 Hz); 48.5; 47.7; 43.5; 38.7; 15.0; 14.0; 13.8. For the assignment see Section 3. ^{31}P NMR ($CDCl_3$): 9.6 ($^{1}J_{P-Pt}$ = 4310 Hz). ^{195}Pt NMR ($CDCl_3$): −3949 (d, $^{1}J_{Pt-P}$ = 4310 Hz). IR (ATR): 3212 (w, $\tilde{\nu}_{N-H}$); 1556 (m, $\tilde{\nu}_{CO}$) cm^{-1}.

The reaction between *cis*-[$PtCl_2(CO)(PPh_3)$] and a slight excess of Et_2NH (molar ratio about ¼) was carried out also starting from a temperature of −30 °C in CD_2Cl_2 as solvent and monitored by ^{31}P NMR spectroscopy. Resonances at 9.64, 8.71 and 7.67 ppm ($^{1}J_{P-Pt}$ = 4879, 4349 and 4926 Hz, respectively) were observed at low temperature. Once at room temperature, those at 9.64 and 7.67 ppm progressively disappeared and only the signal due to [SP4-4]-**1** (8.71 ppm) was present after 5 h.

2.3. Reaction between cis-[$PtCl_2$(NCMe)(PPh_3)] and $NHEt_2$

2.3.1. T = −30 °C. Formation of cis-[$PtCl_2${(E–)HN=C(NEt$_2$)Me}(PPh_3)], cis-**3a**

A solution of 0.216 g (0.38 mmol) of *cis*-[$PtCl_2$(NCMe)(PPh_3)] in MeCN (30 mL) was cooled (T = −30 °C), treated with 0.048 mL of diethylamine (0.46 mmol, amine/Pt molar ratio = 1.2) and stirred until room temperature (25 °C) was slowly reached (48 h). Solvent and excess reagents were eliminated under vacuum, the solid residue was dissolved in 1,2-dichloroethane (1,2-DCE) and treated with heptane (15 mL). Pale yellow crystals were filtered, washed with heptane and dried under vacuum (0.173 g, 71% yield). Single crystals were selected for X-ray diffraction studies. *Anal.* Calcd. for $C_{24}H_{29}Cl_2N_2PPt$: C, 44.9; H, 4.6; N, 4.4%. Found: C, 44.6; H, 4.5; N, 4.3%. ^{1}H NMR ($CDCl_3$, T = 50 °C): 7.80–7.35 (15H, aromatic hydrogens); 4.36 (s, 1H, N$\underline{H}$=C(NEt$_2$)CH$_3$; 2.88 (m, 4H, NH=C[N(C$\underline{H}_2$-CH$_3$)$_2$]CH$_3$); 2.30 (s, 3H, NH=C(NEt$_2$)C$\underline{H}_3$); 0.91 (t, 6H, NH=C[N(CH$_2$C$\underline{H}_3$)$_2$]CH$_3$). ^{13}C NMR ($CDCl_3$): 162.6 (s, N=$\underline{C}$); 134.5 (d, J_{C-P} = 11 Hz), 130.9, 128.7 (d, J_{C-P} = 63 Hz) and 128.2 (d, J_{C-P} = 11 Hz) due to aromatic carbon nuclei; 43.7 (NH=C[N(C$\underline{H}_2$-CH$_3$)$_2$]CH$_3$); 22.6 (NH=C(NEt$_2$)$\underline{C}$H$_3$); 13.0 (NH=C[N(CH$_2$C$\underline{H}_3$)$_2$]-CH$_3$). ^{31}P NMR (1,2-DCE): 7.0 ($^{1}J_{P-Pt}$ = 3950 Hz). ^{195}Pt NMR (1,2-DCE): −3421 (d, $^{1}J_{P-Pt}$ = 3950 Hz). IR (ATR): 3298 (m, $\tilde{\nu}_{NH}$); 1592 (s, $\tilde{\nu}_{C=N}$) cm^{-1}.

2.3.2. T = 83 °C. Formation of trans-[$PtCl_2$(NHEt$_2$)(PPh_3)], trans-**2**

A solution of 0.201 g (0.35 mmol) of *cis*-[$PtCl_2$(NCMe)(PPh_3)] in 10 mL of MeCN was refluxed (83 °C) and a solution of diethylamine (0.43 mmol, $NHEt_2$/Pt molar ratio = 1.2) in 5 mL of the same solvent was slowly added under stirring. The solution turned deep yellow and was refluxed until the complete conversion of the precursor was achieved (2 h, monitored by ^{31}P NMR spectroscopy). The solvent was eliminated under vacuum, the solid residue was dissolved in 1,2-DCE (10 mL), treated with heptane (15 mL) and cooled (−30 °C). Yellow crystals of solvated *trans*-[$PtCl_2$(NHEt$_2$)(PPh_3)] were obtained (about 60% yield) which were filtered and dried under vacuum. Suitable single crystals were selected for X-ray diffraction measurements and resulted to have the composition [$PtCl_2$(NHEt$_2$)(PPh_3)]·$C_2H_4Cl_2$. Elemental analyses showed different results in dependence of the length of the treatment under vacuum. The partial loss of the lattice solvent is reasonably responsible of the analytical results. *Anal.* Calcd. for [$PtCl_2$(NHEt$_2$)(PPh_3)]·$C_2H_4Cl_2$; $C_{24}H_{30}Cl_4NPPt$: C, 41.1; H, 4.3; N, 2.0%. *Anal.* Calcd. for [$PtCl_2$(NHEt$_2$)(PPh_3)]·0.5$C_2H_4Cl_2$; $C_{23}H_{28}Cl_3NPPt$: C, 42.4; H, 4.3; N, 2.1%. *Anal.* Calcd. for [$PtCl_2$(NHEt$_2$)(PPh_3)], $C_{22}H_{26}Cl_2NPPt$ C, 43.9; H, 4.4; N, 2.3. Found sample *a*: C, 42.8; H, 4.3; N, 2.1%. Found sample *b*: C, 43.9; H, 4.4; N, 2.4%. ^{1}H NMR ($CDCl_3$): 7.78–7.42 (15H, aromatic protons); 3.63 (br, 1H, N$\underline{H}$), 3.34 (m, 2H, C$\underline{H}_2$); 2.83 (m, 2H, C$\underline{H}_2$); 1.59 (t, 6H, C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$): 134.8 (d, J_{C-P} = 10.5 Hz), 130.7 (d, J_{C-P} = 2.7 Hz), 129.0 (d, J_{C-P} = 63.0 Hz)

and 127.9 (d, J_{C-P} = 10.6 Hz) due to the aromatic carbon nuclei; 47.4 ($\underline{C}H_2$); 14.9 ($\underline{C}H_3$). ^{31}P NMR ($CDCl_3$): 4.3 ($^1J_{P-Pt}$ = 3560). ^{195}Pt NMR ($CDCl_3$): −3612 (d, $^1J_{Pt-P}$ = 3560 Hz). IR (ATR): 3219 cm^{-1} ($\tilde{\nu}_{N-H}$).

2.3.3. T = 25 °C

When the reaction was carried out at room temperature a mixture of *trans*-**2** and *cis*-**3a** was obtained.

*2.4. Reaction of trans-[PtCl$_2$(NCMe)(PPh$_3$)] prepared "in situ" with diethylamine at −30 °C. Formation of trans-[PtCl$_2$(NHEt$_2$)(PPh$_3$)], trans-**2***

trans-[Pt(μ-Cl)Cl(PPh_3)]$_2$ (0.14 mmol of platinum) was suspended in 50.0 mL of MeCN at 0 °C. A yellow solution was formed in 8 h (^{31}P NMR: *trans*-[$PtCl_2$(NCMe)(PPh_3)], 4.3 ppm, $^1J_{P-Pt}$ = 4076 - Hz; traces of the *cis*-isomer were present) [13]. The solution was concentrated under vacuum (15 mL), cooled (−30 °C) and treated, under stirring, with 0.017 mL of diethylamine (0.17 mmol, $NHEt_2$/Pt molar ratio = 1.2). The mixture was stirred until room temperature was reached, the solvent was eliminated under vacuum and the solid residue was dissolved in $CDCl_3$. ^1H and ^{31}P NMR spectra revealed the formation of *trans*-**2** as the largely prevalent product (only traces of *cis*-**3a** were present).

*2.5. Reaction between cis-[PtCl$_2$(NCEt)(PPh$_3$)] and diethylamine at room temperature with formation of trans-[PtCl$_2$(NHEt$_2$)(PPh$_3$)], trans-**2***

A 1,2-DCE solution (20.0 mL) of *cis*-$PtCl_2$(NCEt)(PPh_3) [13] (0.230 g, 0.40 mmol) was treated with 0.041 mL of diethylamine (0.40 mmol, $NHEt_2$/Pt molar ratio = 1.0) at room temperature. The pale yellow solution turned immediately deep yellow and was maintained under stirring at room temperature (3 h). The solution volume was reduced to 7 mL, 15.0 mL of heptane were added and the obtained solution was cooled (4 °C). Yellow crystals of *trans*-**2**·1,2-DCE were obtained which were filtered, washed with heptane (5.0 mL) and dried under vacuum (0.131 g, 55% yield). Analytical and spectroscopic data (IR and NMR) corresponded to those herein before reported.

When the reaction was carried out at −30 °C a mixture of *trans*-**2** and *cis*-[$PtCl_2${(E−)HN=C(NEt_2)Et}(PPh_3)], *cis*-**3b**, was obtained.

*2.6. Reaction of trans-[PtCl$_2$(CO)(PPh$_3$)] prepared "in situ" with diethylamine: formation of trans-[PtCl$_2$(NHEt$_2$)(PPh$_3$)], trans-**2***

A suspension of *trans*-[Pt(μ-Cl)Cl(PPh_3)]$_2$ (21.0 mg, 4.0×10^{-2} - mmol of Pt) in 2.5 mL of CD_2Cl_2 was cooled (−35 °C) and the suspension was saturated with CO. A yellow–orange solution was obtained (1 h). The solution was frozen and saturated with N_2 after a treatment under vacuum (10^{-2} mmHg). A sample of the mixture was analyzed by ^{31}P NMR spectroscopy and showed a unique signal (15.2 ppm, $^1J_{P-Pt}$ = 3075 Hz), ascribable to *trans*-[$PtCl_2$(CO)(PPh_3)] [15]. The solution was then treated under N_2 atmosphere at −30 °C with a CD_2Cl_2 solution of Et_2NH (5.0 μl in 0.30 mL) and immediately analyzed by ^{31}P NMR: a signal at 4.35 ppm ($^1J_{P-Pt}$ = 3568 Hz) was observed, due to *trans*-**2**, together with minor signals at 9.64, 8.71 and 7.67 ppm ($^1J_{P-Pt}$ = 4879, 4349 and 4926, respectively). Of the last three signals those at 9.64 and 7.67 ppm turned slowly into the one at 8.71 ppm, due to addition product [SP4-4]-**1**.

*2.7. Reaction between trans-[PtCl$_2$(CO)(NCEt)] and diethylamine. Formation of trans-[PtCl$_2$(CO)(NHEt$_2$)], trans-**4***

A solution of 0.082 g (0.24 mmol) of *cis*-[$PtCl_2$(CO)(NCEt)] [13] in freshly distilled 1,2-DCE (10 mL) was stirred at 25 °C until the complete conversion into the *trans* isomer was achieved (24 h, monitored by ^{195}Pt NMR spectroscopy: δ −3426). The orange solution was treated with diethylamine ($NHEt_2$/Pt molar ratio = 1.0) and turned immediately yellow. The solvent was eliminated under vacuum, the residue was dissolved in $CDCl_3$ and NMR spectra were recorded. ^1H NMR: 3.65 (br, 1H, N$\underline{H}$); 3.16 (m, 2H, C$\underline{H}_2$); 2.80 (m, 2H, C$\underline{H}_2$); 1.46 (t, 6H, C$\underline{H}_3$). ^{13}C NMR: 153.5 ($^1J_{C-Pt}$ = 1652 Hz, $\underline{C}$O), 48.3 (NH$\underline{C}H_2$), 14.5 (NHCH$_2\underline{C}H_3$). ^{195}Pt NMR (1,2-DCE): −3421. IR (ATR): 2128 (s, $\tilde{\nu}_{CO}$); 3226 (w, $\tilde{\nu}_{NH}$)cm^{-1}. Elemental analyses were unreliable for the extreme sensitivity of the product to moisture.

2.8. Reaction of trans-[PtCl$_2$(NCR)(C$_2$H$_4$)] with NHEt$_2$

Analogous results were obtained for MeCN and EtCN derivatives. Experiments carried out with MeCN are described.

2.8.1. Amine/platinum molar ratio = 1

The treatment of [Pt(μ-Cl)Cl(C_2H_4)]$_2$ (0.460 g; 0.78 mmol) with acetonitrile (10 mL) afforded a yellow solution of *trans*-[$PtCl_2$(NCMe)(C_2H_4)] [10,11]. $HNEt_2$ (155 μl; 1.49 mmol) was added and after 15 min a ^{195}Pt NMR spectrum was recorded on an aliquot of the reaction mixture: a unique signal at –2987 ppm was observed. After removing the volatiles in vacuum a yellow solid was recovered (0.50 g, 86% yield as *trans*-[$PtCl_2$(C_2H_4)($NHEt_2$)] [10]. ^1H NMR ($CDCl_3$): 4.63 (s, C$\underline{H}_2$C$\underline{H}_2$, 4 H, $^2J_{Pt-H}$ = 60 Hz); 3.3 and 2.9 (m, 4 H, NC$\underline{H}_2$); 1.54 (t, 6 H, NCH$_2$C$\underline{H}_3$) in agreement with the literature data [16]. ^{13}C NMR ($CDCl_3$):74.5 ($\underline{C}H_2$=$\underline{C}H_2$, $^1J_{Pt-C}$ = 158 Hz); 49.0 (PtNH$\underline{C}H_2$CH$_3$); 14.7 (PtNHCH$_2\underline{C}H_3$). ^{195}Pt NMR ($CDCl_3$): −2986. Although the species has been already described [16], at the best of our knowledge its ^{13}C and ^{195}Pt NMR data have not been so far reported.

2.8.2. Amine/platinum molar ratio ⩾ 2

In an experiment monitored by NMR spectroscopy [Pt(μ-Cl)Cl(C_2H_4)]$_2$ (67 mg; 0.11 mmol) was dissolved in CD_3CN (1.0 mL) with formation of *trans*-[$PtCl_2$(C_2H_4)($NCCD_3$)]. Diethylamine (250 μl; 2.42 mmol; amine/Pt molar ratio = 11) was then added. ^1H and ^{13}C NMR spectra of the solution showed signals attributable to *trans*-[$Pt^{(-)}Cl_2$(CH_2–CH_2–$N^{(+)}HEt_2$)($NHEt_2$)]: ^1H NMR: 3.20 (q; Pt–CH_2–CH_2–NH–C$\underline{H}_2$–CH_3); 2.89 and 2.64 (m; C$\underline{H}_2$ of the platinum coordinated amine); 2.78 (t; Pt–CH_2–C$\underline{H}_2$–N); 1.72 (t; $^2J_{Pt-H}$ = 88.2; Pt–C$\underline{H}_2$–CH_2–N); 1.33 (t; Pt–CH_2–CH_2–NH–CH_2–C$\underline{H}_3$); 1.28 (t; platinum coordinated amine C$\underline{H}_3$), in agreement with the literature data [16]. ^{13}C NMR: 59.5 ($^2J_{Pt-C}$ = 37 Hz; Pt–CH_2–$\underline{C}H_2$–N); 47.3 (s) and 47.1(s) (NH–$\underline{C}H_2$–CH_3); 14.8(s) and 9.9(s) (NH–CH_2–$\underline{C}H_3$); −11.3 ($^1J_{Pt-C}$ = 723 Hz; Pt–$\underline{C}H_2$–CH_2–N).

The ^{195}Pt NMR spectrum showed a single resonance at −3168 ppm, unchanged after 24 h.

In other experiments carried out in MeCN (amine/platinum molar ratio ⩾ 2) the ^{195}Pt NMR spectrum of the reaction mixtures showed a single platinum signal at −3168, due to *trans*-[$Pt^{(-)}Cl_2$(CH_2–CH_2–$N^{(+)}HEt_2$)($NHEt_2$)]. In all the experiments, when the solution was evaporated in vacuum and the solid residue was dissolved in $CDCl_3$, ^1H and ^{195}Pt spectra showed the presence of both *trans*-[$PtCl_2$(C_2H_4)($NHEt_2$)] and *trans*-[$Pt^{(-)}Cl_2$(CH_2–CH_2–$N^{(+)}HEt_2$)($NHEt_2$)].

2.9. NMR study of the reaction of cis-[PtCl$_2$(C$_2$H$_4$)(NCMe)] with diethylamine

Solutions of *cis*-[$PtCl_2$(C_2H_4)($NCCH_3$)] in CD_3CN were prepared in NMR tubes under argon. Each solution was treated with a different amount of diethylamine, in order to study the outcome of the reactions with different amine/Pt molar ratios. Each sample was monitored through ^1H and ^{195}Pt NMR spectra in order to follow the evolution of the systems with time. The addition of the first

Table 1
Crystal data and structure refinements.

	[SP4-4]-**1**	*trans*-**2**·$C_2H_4Cl_2$	*cis*-**3a**
Empirical formula	$C_{27}H_{36}ClN_2OPPt$	$C_{24}H_{30}Cl_4NPPt$	$C_{24}H_{29}Cl_2N_2PPt$
Formula weight	666.09	700.35	642.45
Crystal system	monoclinic	triclinic	triclinic
Space group	*Cc* (No. 9)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	16.6781(5)	9.3545(1)	8.624(1)
b (Å)	12.3373(4)	9.5028(2)	11.285(2)
c (Å)	14.9107(5)	16.6356(3)	13.963(2)
α (°)	-	99.930(1)	102.22(1)
β (°)	114.1040(10)	101.180(1)	107.86(1)
γ (°)	-	100.443(1)	96.61(1)
U (Å^3)	2800.55(16)	1393.29(4)	1240.2(3)
Z	4	2	2
D_{calc} (Mg m^{-3})	1.580	1.669	1.720
μ (mm^{-1})	5.184	5.489	5.950
No. measured	29272	22017	6168
No. unique (R_{int})	6387 [0.0281]	6023 [0.0225]	5112 [0.0243]
No. parameters	302	259	271
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0189, 0.0379	0.0269, 0.0785	0.0376, 0.0829
R_1, wR_2 [all data][a]	0.0229, 0.0390	0.0326, 0.0892	0.0513, 0.0881
Goodness of fit [a] on F^2	0.988	1.075	1.035

[a] $R(F_o) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $Rw(F_o^2) = [\Sigma[w(F_o^{2e}-F_c^2)^2]/\Sigma[\ w(F_o^2)^2]]^{½}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [MAX(F_o^2,0) + 2F_c^2]/3$; GOF = $[\Sigma\ [w(F_o^2 - F_c^2)^2]/(N-P)]^{½}$, where *N*, *P* are the numbers of observations and parameters, respectively.

amine equivalent caused the fast formation of the zwitterionic complex *cis*-[Pt$^-$Cl$_2$ ($CH_2CH_2N^+HEt_2$)(NCMe)]. A slow reaction, monitored by ^{1}H, ^{13}C and ^{195}Pt NMR spectra, followed the addition of the second equivalent. Spectroscopic data suggest the addition of the amine to the coordinated nitrile with formation of the amidine complex *cis*-[Pt$^-$Cl$_2$($CH_2CH_2N^+HEt_2$)(E-){NHC(NEt$_2$)Me}]. For the discussion of the spectra, see Section 3.

2.10. X-ray structure determinations

The X-ray diffraction experiments were carried out at room temperature (*T* = 293 K) using Mo Kα radiation with the samples sealed in glass capillaries under a dinitrogen atmosphere. Geometric and intensity data of *cis*-**3a** were collected by means of a Bruker P4 diffractometer, those of [SP4-4]-**1** and *trans*-**2**·$C_2H_4Cl_2$ by means of a Bruker Smart Breeze 4 K CCD detector diffractometer. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a semi-empirical methods.[1] The more relevant crystal parameters for the three compounds are listed in Table 1.

The structure solutions were obtained by means of the automatic direct methods contained in SHELXS97 [17]. In the structure of *trans*-**2**·$C_2H_4Cl_2$ a solvent molecule (1,2-DCE) was localised in a cavity centred at 0.60, 0.60, 0.15. After the introduction of this molecule in the structural model several maxima were still present around them in the difference Fourier map. This was considered an evidence of disorder in this part of the structure and a second orientation of the solvent molecule was added to the model superimposed to the first one by fixing to 1.0 the total occupancy of the site. The following least squares refinement cycles were done with constraints in the isotropic thermal factors of the atoms of disordered solvent, but leaving free their occupancy factor. His final value suggested that one limit position was assumed for the 66.8% of times while the other for the 33.2%. All hydrogen atoms were added in idealized positions. All non hydrogen atoms not involved in disorder were refined with anisotropic displacement parameters. The least squares refinements were done by using SHELXL97 programme [17]. Some other utilities contained in the WINGX suite [18] were also used. The more relevant parameters of structure refinements are listed in Table 1.

[1] The absorption correction for the data of [SP4-4]-1 and *trans*-2·$C_2H_4Cl_2$ were done by the multi-scan method (G.M. Sheldrick, SADABS, version 2008/2. Program for Empirical Absorption Correction of Area Detector Data. Univ. of Göttingen: Göttingen, Germany, 1996); those of *cis*-**3a** by a Psi-scan method (G.M. Sheldrick, XPREP, version 5.1/NT. Program for Redaction of Diffractometer Data. Bruker AXS Inc., Madison, Wisconsin, USA, 2000).

3. Results and discussion

The two geometrical isomers *cis*- and *trans*-[$PtCl_2$(CO)(PPh_3)] react differently with $NHEt_2$, the former with attack to CO and the latter with substitution of CO (see Eqs. (4) and (5), respectively). The reaction of *cis*-[$PtCl_2$(CO)(PPh_3)] with a small excess of $NHEt_2$ proceeds smoothly in toluene at room temperature under dinitrogen without any evidence of CO evolution affording [SP4-4]-[PtCl($CONEt_2$)($NHEt_2$)(PPh_3)], [SP4-4]-**1**, and NH_2Et_2Cl (Eq. (4))

$$\textit{cis}\text{-}[PtCl_2(CO)(PPh_3)] + 3NHEt_2 \rightarrow \underset{[SP4\text{-}4]\text{-}1}{[SP4\text{-}4]\text{-}[PtCl(CONEt_2)(NHEt_2)(PPh_3)]} + NH_2Et_2Cl \quad (4)$$

$$\textit{trans}\text{-}[PtCl_2(CO)(PPh_3)] + NHEt_2 \rightarrow \underset{\textit{trans}\text{-}2}{\textit{trans}\text{-}[PtCl_2(PPh_3)(NHEt_2)]} + CO \quad (5)$$

The crystalline product has been recovered in good yield and characterized by elemental analysis, single crystal X-ray diffraction, IR and NMR spectra (see Table 3 for ^{31}P and ^{195}Pt NMR). The molecular structure of [SP4-4]-**1** is shown in Fig. 1 and selected geometric parameters are listed in Table 2. The structure is similar to that of the five Pt-carbamoyl derivatives reported in the chemical literature [2,19]. The Pt(II) centre shows the usual square planar coordination geometry with the NCO group of the carbamoyl ligand lying on a plane perpendicular to it. The Cl ligand *trans* to the carbamoyl group shows in our compound a distance from the platinum centre significantly longer than the mean value, 2.33 Å, usually encountered in Pt(II) derivatives. No significant intermolecular interactions are observed.

Table 2
Bond lenghts (Å) and angles (°) around Pt atoms in [SP4-4]-**1**.

Pt–Cl	2.4167(9)	O–C(19)	1.228(5)
Pt–P	2.2251(8)	C(19)–N(1)	1.367(5)
Pt–C(19)	2.002(4)	N(1)–C(20)	1.425(7)
Pt–N(2)	2.139(3)	N(1)–C(22)	1.482(7)
Cl–Pt–P	92.88(3)	Pt–N(2)–C(24)	115.8(3)
Cl–Pt–N(2)	83.34(9)	Pt–N(2)–C(26)	115.9(3)
N(2)–Pt–C(19)	90.53(13)	Pt–C(19)–O	118.5(3)
C(19)–Pt–P	93.09(10)	Pt–C(19)–N(1)	121.5(3)
P–Pt–N(2)	175.75(9)	O–C(19)–N(1)	120.0(4)
Cl–Pt–C(19)	172.48(11)		

Table 3
^{31}P and ^{195}Pt NMR data.

Compound	^{195}Pt δ/ppm	^{31}P δ/ppm	$^1J_{Pt-P}$/Hz	Solvent
[SP4-4]-**1**		10.5	4380	toluene
	−3949	9.6	4310	$CDCl_3$
		8.7	4349	CD_2Cl_2
trans-**2**	−3612	4.3	3560	$CDCl_3$
cis-**3a**	−3421	7.0	3950	1,2-DCE
cis-**3b**		7.4	3860	$CDCl_3$
trans-**4**	−3421	–	–	1,2-DCE
cis-**5**	−3465	–	–	CD_3CN
cis-**6**	−3214	–	–	CD_3CN

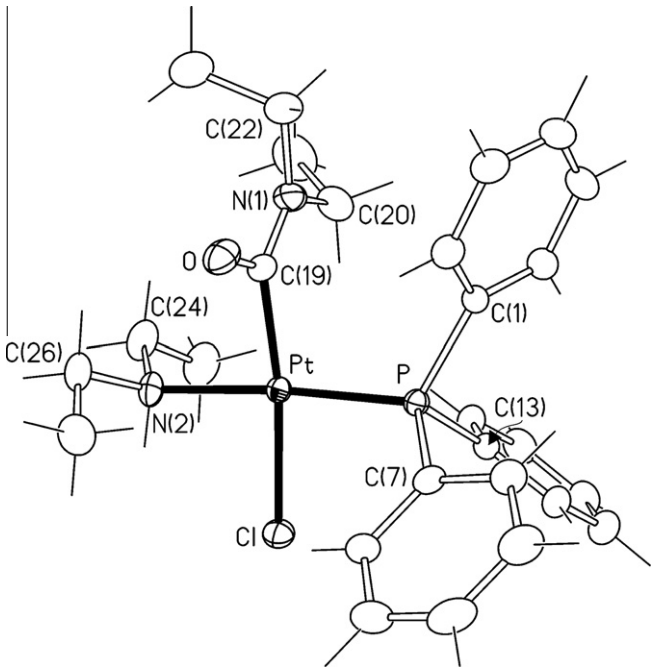


Fig. 1. View of the molecular structure of [SP4-4]-**1**. Thermal ellipsoids are at 20% probability.

Although three stereoisomers of **1** could be obtained, only the isomer [SP4-4]-**1** forms at room temperature as proved by the ^{31}P NMR spectrum recorded on the reaction mixture, showing a single signal at 10.5 ppm ($^{1}J_{Pt-P}$ = 4380 Hz). Reasonably the reaction proceeds through $NHEt_2$ nucleophilic attack to carbon monoxide followed by transfer of a proton to a second amine to get the ionic intermediate **a**, $[NH_2Et_2]$*cis*-$[PtCl_2(CONEt_2)(PPh_3)]$ (Eq. (6a)) and subsequent substitution of a chloride by a third molecule of amine (Eq. (6b)), favoured by the precipitation of $[NH_2Et_2]Cl$. The geometric isomer [SP4-2]-**1** (intermediate **b**), with an amine *trans* to -$CONEt_2$, is expected to be the kinetic product of the reaction (the carbamoyl group should have a stronger *trans* effect than PPh_3, as usually carbon-donor ligands have [6]). Intermediate **b** quickly converts to the more stable [SP4-4]-**1** isomer (Eq. (6c)). Such a proposal is reminiscent of what reported for the reaction between *cis*-$PtCl_2(CO)_2$ and NH^iPr_2 (1:2 molar ratio) producing $[NH_2{}^iPr_2]$*cis*-$[PtCl_2(CON^iPr_2)(CO)]$ [2]

$$cis\text{-}[PtCl_2(CO)(PPh_3)] + 2\ NHEt_2 \rightarrow [NH_2Et_2]cis\text{-}[\underset{\mathbf{a}}{PtCl_2(CONEt_2)}(PPh_3)] \quad (6a)$$

$$[NH_2Et_2]cis\text{-}[PtCl_2(CONEt_2)(PPh_3)] + NHEt_2 \rightarrow [\underset{\mathbf{b}}{SP4\text{-}2}]\text{-}[PtCl(CONEt_2)(NHEt_2)(PPh_3)] + NH_2Et_2Cl \quad (6b)$$

$$[SP4\text{-}2]\text{-}[PtCl(CONEt_2)(NHEt_2)(PPh_3)] \rightarrow [\underset{[SP4\text{-}4]\text{-}\mathbf{1}}{SP4\text{-}4}]\text{-}[PtCl(CONEt_2)(NHEt_2)(PPh_3)] \quad (6c)$$

Furthermore, the presence of two intermediates in the course of the reaction has been confirmed by monitoring the reaction carried out at −30 °C by ^{31}P NMR spectroscopy. Resonances at 9.6, 8.7 and 7.7 ppm ($^{1}J_{P-Pt}$ = 4879, 4349 and 4926 Hz, respectively) were observed. At room temperature those at 9.6 and 7.7 ppm progressively disappeared and only the signal due to [SP4-4]-**1** (8.7 ppm) was present after 5 h.

In the IR spectrum (solid state) the product shows bands at 3212 cm^{-1}, attributable to the N–H stretching vibration of the coordinated amine, and at 1556 cm^{-1} due to the carbonyl stretching vibrations of the carbamoyl group. The ^{1}H NMR spectrum recorded at 25 °C appeared rather complicated, probably for the hindered rotation around the C(O)–NEt_2 bond of the carbamoyl group and the steric hindrance of the phosphine. The spectrum recorded at 50 °C showed the signals of the aromatic protons (7.80–7.20 ppm), a broad resonance at 3.78 ppm, attributed to the NH proton of the coordinated amine and complicated multiplets at 4.30 (1H), 3.11 (6H) and 2.41 (1H) that have been assigned to the methylene protons of the ethyl groups of the carbamoyl moiety and of the amine (methylene protons of the coordinated $NHEt_2$ are diastereotopic). The two triplets at 1.64 and 1.52 (6H) ppm are assigned to the methyl protons of the carbamoyl moiety, while those at 0.82 and 0.78 (6H) ppm to the amine methyl protons. Although the spectrum recorded at 50 °C shows a higher signal resolution, nevertheless the equivalence of the alkyl groups is not reached. The ^{13}C NMR spectrum recorded at room temperature shows a signal at 167.7 ppm due to the carbamoyl (CON) and resonances of the aromatic nuclei at 134.5, 130.5, 130.4 and 127.9 ppm. Four signals at 48.5, 47.7, 43.5 and 38.7 ppm are due to the CH_2 of the four magnetically non equivalent ethyl groups, while three resonances observed at 15.0, 14.0, 13.8 are assigned to the four non-equivalent methyl carbon atoms, assuming the overlapping of two signals.*trans*-$[PtCl_2(CO)(PPh_3)]$ [15] was prepared in situ by reacting *trans*-$[PtCl(\mu\text{-}Cl)(PPh_3)]_2$ with CO in CH_2Cl_2 at low temperature (Eq. (7)). It is the kinetic product of the reaction and care has to be taken to avoid its isomerisation to the more stable *cis*-isomer

$$trans\text{-}[PtCl(\mu\text{-}Cl)(PPh_3)]_2 + 2\ CO \rightarrow 2\ trans\text{-}[PtCl_2(CO)(PPh_3)] \quad (7)$$

When it was reacted with an excess of $NHEt_2$ at −30 °C *trans*-$[PtCl_2(NHEt_2)(PPh_3)]$, *trans*-**2**, was obtained as the main product, as reported in Eq. (5). Notwithstanding the low temperature, traces of [SP4-4]-**1** were observed, reasonably due to isomerisation of the precursor, catalysed by the addition of the amine [15]. The main product is easily recovered after work-up of the reaction mixture and has been characterized in the course of this work by ^{31}P and ^{195}Pt NMR (see Table 3) and X-ray diffraction methods. Compounds of the type *trans*-$[PtCl_2(PPh_3)(amine)]$ are known [20] and the structure of *trans*-$[PtCl_2(PPh_3)(NH_2{}^iPr)]$ has been reported [20b]. The molecular structure of *trans*-**2** is shown in Fig. 2 and the bonding geometry around the metal is listed in Table 4. The structure is tightly related to that of [SP4-4]-**1**, the only difference being the substitution of the carbamoyl moiety by the chloride ligand. The Pt–Cl bond lengths have here the usual values. The diethylamine orientation is very similar to that shown in [SP4-4]-**1** with the amine hydrogen lying approximately on the Pt coordination plane. A quick look at CCDC database [21] shows that in all the diethylamine coordination compounds of Pt(II) of known structure the N–H bond makes small angles with the metal coordination plane. Molecules are paired in couples related by inversion centres, pointing the NH hydrogen toward the Cl(1) atom of the partner (Fig. 3) with a N–H···Cl distance of 2.68 Å, slightly shorter than the sum of the van der Waals radii.

It is worth to note that the Cl(1) atom involved in this interaction shows a bond length from Pt significantly longer than Cl(2). This interaction is reasonably responsible of the amine orientation.

The different reactivity of the two stereoisomers *cis*- and *trans*-$[PtCl_2(CO)(PPh_3)]$ can be justified with the stronger *trans*-effect of the phosphine in comparison with that of the chloride, the displacement of CO by $NHEt_2$ in the *trans*-isomer being driven by the lability of CO *trans* to PPh_3.

The reactions of the two geometric isomers of $[PtCl_2(PPh_3)(NCR)]$ (R = Me, Et) [13] proceed with attack to or substitution of

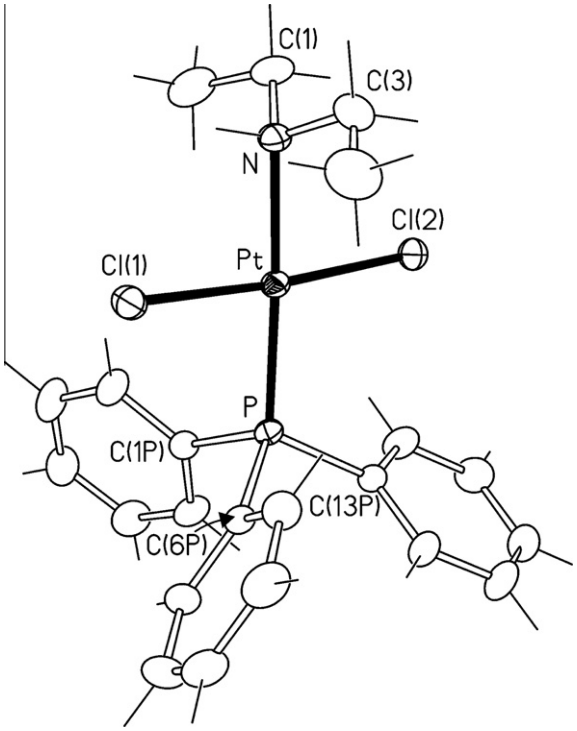


Fig. 2. View of the molecular structure of *trans*-**2**. Thermal ellipsoids are at 20% probability.

Table 4
Bond lenghts (Å) and angles (°) around Pt atoms in *trans*-**2**.

Pt–Cl(1)	2.3071(13)	Pt–Cl(2)	2.2891(12)
Pt–N	2.134(4)	Pt–P	2.2368(11)
Cl(1)–Pt–N	86.30(13)	Cl(2)–Pt–P	94.29(5)
Cl(1)–Pt–P	90.90(5)	Cl(1)–Pt–Cl(2)	174.77(5)
Cl(2)–Pt–N	88.51(13)	N–Pt–P	177.15(12)

the unsaturated ligand for the *cis*- and the *trans* isomer, respectively. The geometric isomers of the precursor, at variance with those of $[PtCl_2(PPh_3)(CO)]$, present a quite similar stability and are usually both present in equilibrium in solution with similar concentrations: solutions of a pure isomer can be obtained only if care is taken to avoid isomerisation. By operating at an initial temperature of −30 °C, *cis*-$[PtCl_2(NCMe)(PPh_3)]$ isomerisation is inhibited and it reacts with a slight excess of $NHEt_2$ in MeCN as solvent, with addition of the nucleophile to the coordinated nitrile and formation of the amidino-complex *cis*-$[PtCl_2\{(E)\text{-}HN{=}C(NEt_2)\text{-}Me\}(PPh_3)]$, *cis*-**3a** (Eq. (8))

$$\textit{cis}\text{-}[PtCl_2(NCMe)(PPh_3)] + NHEt_2 \rightarrow \underset{\textit{cis}\text{-}\mathbf{3a}}{\textit{cis}\text{-}[PtCl_2\{(E)\text{-}HN{=}C(NEt_2)Me\}(PPh_3)]} \quad (8)$$

If the reaction is carried out at about 80 °C only *trans*-$[PtCl_2(NHEt_2)(PPh_3)]$, *trans*-**2**, is obtained, as observed by monitoring the system by ^{31}P NMR. Finally, by operating at room temperature a mixture of *trans*-**2** and *cis*-**3a** is produced. As at high temperature the *cis* isomer of the precursor is still largely prevalent (*cis*/*trans* molar ratio about 95/5), reasonably both the precursor isomerisation (Eq. (9)) and the substitution reaction on the *trans*-isomer (Eq. (10)) have to be faster than the amine addition to the *cis*-isomer (Eq. (8)). At room temperature the reaction rates are probably similar with formation of the mixture of products

$$\textit{cis}\text{-}[PtCl_2(NCMe)(PPh_3)] \rightleftharpoons \textit{trans}\text{-}[PtCl_2(NCMe)(PPh_3)] \quad (9)$$

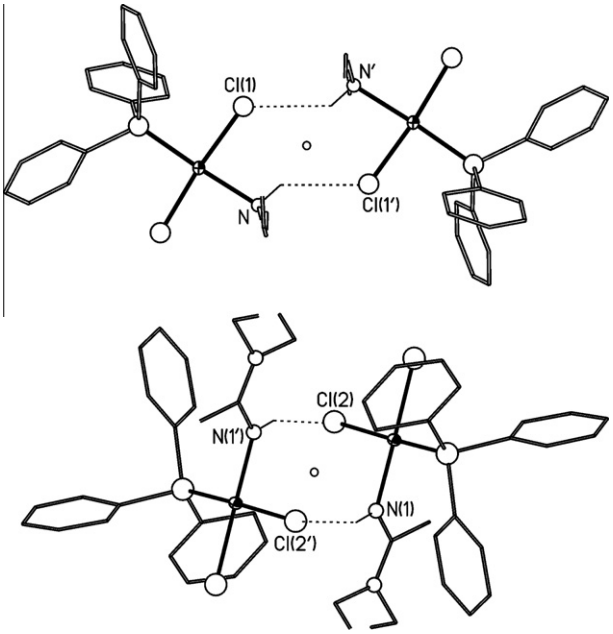


Fig. 3. Pairing of molecules through hydrogen interaction in the structures of *trans*-**2** (above) and *cis*-**3a** (below).

$$\textit{trans}\text{-}[PtCl_2(NCMe)(PPh_3)] + NHEt_2 \rightarrow \underset{\textit{trans}\text{-}\mathbf{2}}{\textit{trans}\text{-}[PtCl_2(NHEt_2)(PPh_3)]} + MeCN \quad (10)$$

To check if the *trans*-isomer reacts with nitrile substitution also at low temperature, an experiment was performed where *trans*-$[PtCl_2(NCMe)(PPh_3)]$ was produced in situ by reacting the dinuclear *trans*-$[PtCl(\mu\text{-}Cl)(PPh_3)]_2$ with MeCN at 0 °C. The solution, containing only traces of *cis*-$[PtCl_2(NCMe)(PPh_3)]$, was cooled at −30 °C and treated with $NHEt_2$. The reaction was monitored by ^{31}P NMR: *trans*-**2** was obtained as final product with only traces of *cis*-**3a**. Results comparable with those obtained with *cis*-$[PtCl_2(NCMe)(PPh_3)]$ were observed for the reaction of the propionitrile derivative *cis*-$[PtCl_2(NCEt)(PPh_3)]$ with $NHEt_2$, with the difference that the temperature threshold to avoid isomerisation of the precursor was lower, and also at −30 °C some *trans*-**2** was formed together with *cis*-$[PtCl_2\{(E)\text{-}HN{=}C(NEt_2)Et\}(PPh_3)]$, *cis*-**3b**, while at room temperature complete conversion to *trans*-**2** was observed. *cis*-**3a** was recovered in good yield and characterized by elemental analysis, single crystal X-ray diffraction, IR and NMR spectra. Significant bands in its IR spectrum at 1592 and 3298 cm^{-1} are attributable to the C=N and N–H stretching vibrations, respectively. Its ^1H NMR spectrum shows, besides the signals due to the phosphine aromatic protons, a broad singlet at 4.36 ppm, due to the amidine HN=C proton and a singlet at 2.30 ppm due to the amidine N=C–CH_3 methyl group, in the region typical of the E configuration of the ligand [3c]. The two magnetically equivalent ethyl groups produce two signals at 2.88 (CH_2) and 0.91 (CH_3) ppm. The ^{13}C NMR spectrum shows signals of aromatic nuclei, a resonance due to HN=C at 162.6 ppm, and a resonance attributable to the N=C–CH_3 methyl at 22.6 ppm. Signals due to the ethyl groups are at 43.7 (CH_2) and 13.0 (CH_3) ppm. The molecular structure of *cis*-**3a** is shown in Fig. 4 and the geometrical parameters of the metal bonding are listed in Table 5. The N–C=N–H plane of amidine ligand is almost perpendicular (81.5°) to the platinum coordination plane and this orientation can be explained, besides the steric hindrance of the phosphine, by the intermolecular interaction requirements. The *cis*-**3a** molecules are, in fact, packed in pairs related by inversion centres (Fig. 3). Each molecule of a pair points its N–H toward

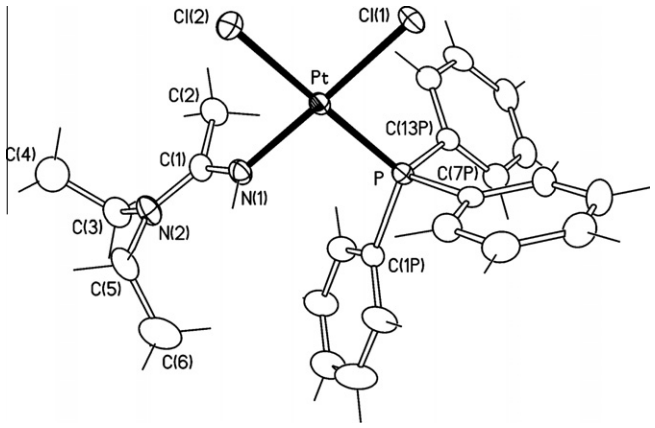


Fig. 4. View of the molecular structure of *cis*-**3a**. Thermal ellipsoids are at 30% probability.

the Cl(2) atom of the coupled molecule with a N–H···Cl(2) distance of 2.74 Å and the Pt–Cl(2) bond length is significantly longer than Pt–Cl(1) one.

The systems $PtCl_2LL'/NHEt_2$ with both L and L′ unsaturated ligands (L = CO, C_2H_4; L′ = MeCN, EtCN) revealed to be rather complex, not only because the outcome of the reactions depends on the amine/precursor molar ratio, but also because the involved complexes, especially carbonyl complexes, are quite air sensitive. Nevertheless specific points have been established. When *trans*-$[PtCl_2(NCR)L]$ [L = C_2H_4, CO] is reacted with diethylamine in molar ratio 1, in principle four outcomes are possible: (a) L substitution, (b) nitrile substitution, (c) nucleophilic attack to L, (c) nucleophilic attack to nitrile. By reacting *trans*-$[PtCl_2(NCR)(C_2H_4)]$ [11] with a stoichiometric amount of $NHEt_2$ at room temperature in RCN as solvent, nitrile substitution is observed with formation of *trans*-$[PtCl_2(NHEt_2)(C_2H_4)]$ (Eq. (11)) as single product. The high *trans*-effect of the alkene justifies this outcome. Further addition of $NHEt_2$ causes the already reported [4c] nucleophilic attack to the coordinated ethylene with formation of the alkyl zwitterionic complex (Eq. (12))

$$\underset{R=Me,\ Et}{\textit{trans}\text{-}[PtCl_2(NCR)(C_2H_4)]} + NHEt_2 \rightarrow \textit{trans}\text{-}[PtCl_2(NHEt_2)(C_2H_4)] + RCN \quad (11)$$

$$\textit{trans}\text{-}[PtCl_2(NHEt_2)(C_2H_4)] + NHEt_2 \rightleftharpoons \textit{trans}\text{-}[Pt^{-}Cl_2(NHEt_2)(CH_2\text{-}CH_2N^{+}HEt_2)] \quad (12)$$

Similarly, the reaction of *trans*-$[PtCl_2(EtCN)(CO)]$ with $NHEt_2$ (molar ratio 1), carried out at room temperature in 1,2-dichloroethane (1,2-DCE) or CH_2Cl_2 as solvent, proceeds with nitrile substitution affording a single platinum complex containing $NHEt_2$ and CO as ligands, $[PtCl_2(NHEt_2)(CO)]$, **4** (Eq. (13)). Since no isomerisation evidence was detected by monitoring the reaction mixture (IR and ^{195}Pt NMR), substitution is expected to occur with retention of configuration, as usual for platinum(II) complexes, producing the *trans*-isomer, *trans*-**4**

$$\textit{trans}\text{-}[PtCl_2(NCEt)(CO)] + NHEt_2 \rightarrow \underset{\textit{trans}\text{-}\mathbf{4}}{\textit{trans}\text{-}[PtCl_2(NHEt_2)(CO)]} + EtCN) \quad (13)$$

The IR spectrum of the product in solid phase shows bands at 3226 and 2128 cm^{-1} attributable to N–H and C–O stretching vibrations, respectively. For instance the C–O stretching vibration in *trans*-$PtCl_2(CO)$(amine) is reported at 2139, 2123 and 2121 cm^{-1} with amine = NH_3, py, $PhNH_2$ [22a] and in the range 2128–2147 cm^{-1} when the amine is a para-substituted pyridine [22b]. In the ^{1}H NMR spectrum the signals due to the coordinated amine are observed. The broad singlet at 3.65 ppm is assigned to N<u>H</u>, the multiplets at 3.16 and 2.80 ppm to the diastereotopic C<u>H</u>$_2$ and the triplet at 1.46 ppm to methyl protons. The ^{13}C NMR spectrum shows the signal due to coordinated CO at 153.5 ($^1J_{C-Pt}$ = 1652 Hz) to be compared with the data 151.10 ppm ($^1J_{C-Pt}$ = 1670 Hz) reported for $PtCl_2(CO)$py [22c]. For ^{195}Pt NMR data see Table 3.

Preliminary results have been obtained for the system *cis*-$[PtCl_2(MeCN)(C_2H_4)]/NHEt_2$. The reactions were performed in CD_3-CN at room temperature and monitored by ^{195}Pt , ^{13}C and ^{1}H NMR. The addition of the first equivalent of the amine produced the fast formation of the zwitterionic complex *cis*-$[Pt^{-}Cl_2(NCMe)(CH_2CH_2\text{-}N^{+}HEt_2)]$, *cis*-**5** (Eq. (14)). After 1 h from the amine addition the ^{195}Pt resonance due to the precursor (−2883 ppm, $^1J_{Pt-N}$ 364 Hz, $^4J_{Pt-H}$ 13 Hz) is not observable anymore while a broad signal attributable to the product appears at −3465 ppm

$$\textit{cis}\text{-}[PtCl_2(NCMe)(C_2H_4)] + NHEt_2 \rightleftharpoons \underset{\textit{cis}\text{-}\mathbf{5}}{\textit{cis}\text{-}[Pt^{-}Cl_2(NCMe)(CH_2CH_2N^{+}HEt_2)]} \quad (14)$$

Selected ^{13}C and ^{1}H NMR signals are reported, with their attribution, in Table 6. The coordinated nitrile does not exchange with the solvent and the platinum–hydrogen coupling ($^4J_{Pt-H}$) is observed. Furthermore, signals due to coordinated ethylene are not present anymore while the resonances at 2.95 and 1.57 ppm in the ^{1}H spectrum and those at 54.4 and –12.7 ppm in the ^{13}C spectrum can be assigned to the methylene nuclei of the fragment Pt–CH_2CH_2–N. The high field signal due to C_a (see scheme in Table 6) reveals a coupling constant to the ^{195}Pt nucleus of 638 Hz, as expected for an α-carbon atom of a platinum-alkyl group [23]. H_a nuclei produce a triplet with satellites showing coupling to platinum. When the solution is treated *in vacuo* equilibrium 14 is displaced to the left, preventing the product isolation.

The addition of an excess of $NHEt_2$ to *cis*-$[PtCl_2(C_2H_4)(NCMe)]$ (molar ratio 4) causes the rapid formation of the zwitterionic complex *cis*-**5** followed by a slower reaction. Spectroscopic data suggest that the amidino complex *cis*-$[Pt^{-}Cl_2\{NH{=}C(Me)NEt_2\}(CH_2CH_2N^{+}HEt_2)]$, *cis*-**6** (Eq. (15)) is formed

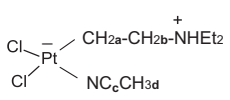
$$\textit{cis}\text{-}[PtCl_2(NCMe)(CH_2CH_2NHEt_2)] + NHEt_2 \rightarrow \underset{\textit{cis}-\mathbf{6}}{\textit{cis} - [Pt^{-}Cl_2NH{=}C(Me)NEt_2(CH_2CH_2N^{+}HEt_2)]} \quad (15)$$

In the ^{195}Pt NMR spectrum the initial signal at –3465 ppm, due to *cis*-**5**, slowly (24 h) disappears with concomitant formation of a signal at −3214 ppm assigned to *cis*-**6**. Selected ^{13}C and ^{1}H NMR resonances with their attribution are reported in Table 6. Signals due to coordinated nitrile have disappeared and new resonances at 163.6 ppm and 23.2 ppm in the ^{13}C spectrum are assigned to the NH=C–CH_3 unsaturated and saturated carbon atoms, respectively. The signal at 2.52 ppm in the ^{1}H spectrum is attributable to the methyl protons of the same group; its chemical shift value suggests the E configuration for the amidino [3c]. Attempts to

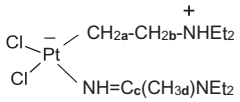
Table 5
Bond lenghts (Å) and angles (°) around Pt atoms in *cis*-**3a**.

Pt–Cl(1)	2.3170(16)	N(1)–C(1)	1.316(9)
Pt–Cl(2)	2.3540(18)	C(1)–C(2)	1.497(10)
Pt–N(1)	2.016(6)	C(1)–N(2)	1.337(9)
Pt–P	2.2069(17)		
Cl(1)–Pt–Cl(2)	90.64(7)	Cl(2)–Pt–P	175.52(7)
Cl(1)–Pt–P	87.57(6)	Pt–N(1)–C(1)	126.5(5)
Cl(2)–Pt–N(1)	87.69(18)	N(1)–C(1)–N(2)	122.4(7)
P–Pt–N(1)	94.11(17)	N(1)–C(1)–C(2)	118.5(6)
Cl(1)–Pt–N(1)	178.32(18)	C(2)–C(1)–N(2)	119.0(7)

Table 6
Selected ^{1}H and ^{13}C NMR signals of *cis*-**5** (see Eq. (14)) and *cis*-**6** (see Eq. (15)) in CD_3CN.



cis-**5**



cis-**6**

	^{1}H: δ/ppm (J/Hz)		^{13}C: δ/ppm (J/Hz)	
cis-**5**			115.0	C_c
	2.95 t	CH_{2b}	54.4	C_b
	2.35 s ($^{4}J_{Pt-H}$ = 16)	CH_{3d}	4.7	C_d
	1.57 t ($^{2}J_{Pt-H}$ = 76)	CH_{2a}	−12.7 ($^{1}J_{Pt-C}$ = 638)	C_a
cis-**6**			163.6	C_c
	2.85 t	CH_{2b}	55.3	C_b
	2.52 s	CH_{3d}	23.2	C_d
	1.40 t ($^{2}J_{Pt-H}$ = 51)	CH_{2a}	−13.0 ($^{1}J_{Pt-C}$ = 738)	C_a

recover the reaction product as a solid were unsuccessful for the poor miscibility of MeCN with other solvents and for the formation of sticky residues when volatiles were eliminated in vacuum. Nevertheless, according to the spectroscopic data it clearly appears that the reaction of *cis*-[$PtCl_2$(NCMe)(C_2H_4)] with $NHEt_2$ does not involve displacement of the ligands and proceeds with a rapid attack to the coordinated ethylene followed by a slow attack to the nitrile.

4. Conclusions

Geometrical isomers of neutral complexes $PtCl_2L_TL$ where L_T is a ligand with a rather strong *trans*-effect and L is an unsaturated ligand have different reactivity towards diethylamine. While *trans*-$PtCl_2L_TL$ complexes (L_T = PPh_3, L = CO, MeCN, EtCN; L_T = CO, L = EtCN; L_T = C_2H_4, L = MeCN) react with substitution of L by the amine, the *cis*-isomers (L_T = PPh_3, L = CO, MeCN) react with attack to the unsaturated ligand. Moreover, *cis*-$PtCl_2(CH_2{=}CH_2)$(NCMe) reacts with a fast attack to the alkene followed by a slow attack to the nitrile. This straightforward behaviour is respected unless partial isomerisation of the precursor takes place before the reaction occurs. Therefore, the stereo-isomerism of the precursor appears to be pivotal in addressing the chemo-selectivity of the process. About the results reported in the literature [5] for the systems *cis*-$PtCl_2(PPh_3)$(alkene)/$NHEt_2$ (see Introduction) the substitution of the alkene (favoured raising the temperature or for alkenes with more of 4 carbon atoms), may be due to a prior partial (even quite small) *cis* → *trans* isomerisation of the precursors, although no evidence of *trans*-$PtCl_2(PPh_3)$(alkene) has been found.

Acknowledgements

We gratefully acknowledge the *Ministero dell'Università e della Ricerca Universitaria* (MIUR), *Progetti di Ricerca di Rilevante Interesse Nazionale* (PRIN 2007) for financial support. We thank Chimet S.p.A., I–52041 Badia al Pino (Arezzo), for a loan of platinum.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.10.038.

References

[1] (a) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, in: Principles and Applications of Organotransition Metal Chemistry, 2nd ed., University Science Books, Mill Valley, California, 1987; (b) J.F. Hartwig, in: Organotransition Metal Chemistry. From Bonding to Catalysis. University Science Books, Mill Valley, CA, 2010.
[2] D. Belli Dell'Amico, F. Calderazzo, G. Pelizzi, Inorg. Chem. 4 (1979) 1165.
[3] (a) L. Maresca, G. Natile, F.P. Intini, F. Gasparrini, A. Tiripicchio, M. Tiripicchio-Camellini, J. Am. Chem. Soc. 108 (1986) 1180;
(b) R. Bertani, D. Catanese, R.A. Michelin, M. Mozzon, G. Bandoli, A. Dolmella, Inorg. Chem. Commun. 3 (2000) 16;
(c) R.A. Michelin, R. Bertani, M. Mozzon, A. Sassi, F. Benetollo, G. Bombieri, A.J.L. Pombeiro, Inorg. Chem. Commun. 4 (2001) 275;
(d) U. Belluco, F. Benetollo, R. Bertani, G. Bombieri, R.A. Michelin, M. Mozzon, A.J.L. Pombeiro, F.C. Guedes da Silva, Inorg. Chim. Acta 330 (2002) 229;
(e) U. Belluco, F. Benetollo, R. Bertani, G. Bombieri, R.A. Michelin, M. Mozzon, O. Tonon, A.J.L. Pombeiro, F.C. Guedes da Silva, Inorg. Chim. Acta 334 (2002) 437;
(f) A.J.L. Pombeiro, V.Yu. Kukushkin, Comprehensive Coordination Chemistry II 2 (2004) 639;
(g) A. Bacchi, D. Belli Dell'Amico, F. Calderazzo, L. Labella, G. Pelizzi, F. Marchetti, S. Samaritani, Inorg. Chim. Acta 363 (2010) 2467.
[4] (a) P.D. Kaplan, P. Schmidt, M. Orchin, J. Am. Chem. Soc. 90 (1968) 4175; (b) R. Palumbo, A. De Renzi, A. Panunzi, G. Paiaro, J. Am. Chem. Soc. 91 (1969) 3874; (c) A. Panunzi, A. De Renzi, R. Palumbo, G. Paiaro, J. Am. Chem. Soc. 91 (1969) 3879; (d) A. Panunzi, A. De Renzi, G. Paiaro, J. Am. Chem. Soc. 92 (1970) 3488; (e) E. Benedetti, A. De Renzi, G. Paiaro, A. Panunzi, C. Pedone, Gazz. Chim. Ital. 102 (1972) 744; (f) A. De Renzi, B. Di Blasio, A. Panunzi, C. Pedone, A. Vitagliano, J. Chem. Soc., Dalton Trans. (1978) 1392; (g) I.M. Al-Najjar, M. Green, J. Chem. Soc., Chem. Commun. (1977) 926; (h) I.M. Al-Najjar, M. Green, J. Chem. Soc., Dalton Trans. (1979) 1651; (i) I.M. Al-Najjar, M. Green, J.K.K. Sarkan, Inorg. Chim. Acta 44 (1980) L213; (j) M. Green, J.K.K. Sarkan, I.M. Al-Najjar, J. Chem. Soc., Dalton Trans. (1981) 1565; (k) J.K.K. Sarkan, M. Green, I.M. Al-Najjar, J. Chem. Soc., Dalton Trans. (1984) 771.
[5] R. Pryadun, D. Sukumaran, R. Bogadi, J.D. Atwood, J. Am. Chem. Soc. 126 (2004) 12414.
[6] (a) R.G. Wilkins, in: Kinetics and Mechanism of Reactions of Transition Metal Complexes, WCH Verlagsgesellschaft, Weinheim and WCH Publishers, Inc., New York, 1991 and references therein; (b) L.M. Tobe, J. Burgess, in: Inorganic Reaction Mechanisms, Longman, New York, 1999 and references therein.
[7] (a) T.V. Hambley, Coord. Chem. Rev. 166 (1997) 181; (b) M. Knipp, A.V. Karotki, S. Chesnov, G. Natile, P.J. Sadler, V. Brabec, M. Vašák, J. Med. Chem. 50 (2007) 4075.
[8] F. Ozawa, T. Hikida, Organometallics 15 (1996) 4501.
[9] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, Butterworth-Heinemann, 1996.
[10] L. Spaulding, B.A. Reinhardt, M. Orchin, Inorg. Chem. 11 (1972) 2092.
[11] S. Otto, A. Roodt, L.I. Elding, Inorg. Chem. Commun. 12 (2009) 766.
[12] T. Weil, L. Spaulding, M. Orchin, J. Coord. Chem. 1 (1971) 25.
[13] D. Belli Dell'Amico, L. Labella, F. Marchetti, S. Samaritani, Dalton Trans. 41 (2012) 1389.
[14] (a) J. Chatt, N.P. Johnson, B.L. Shaw, J. Chem. Soc. (1964) 1662;
(b) L. Manojlovic-Muir, K.W. Muir, R. Walker, J. Organomet. Chem. 66 (1974) C21;
(c) D. Belli Dell'Amico, F. Calderazzo, G. Dell'Amico, Gazz. Chim. Ital. 107 (1977) 101.
[15] G.K. Anderson, R.J. Cross, J. Chem. Soc., Dalton (1980) 1988.
[16] D. Hollings, M. Green, D.V. Claridge, J. Organomet. Chem. 54 (1973) 399.
[17] G.M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis (Release 97–2). Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
[18] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[19] (a) U. Abram, D. Belli Dell'Amico, F. Calderazzo, L. Marchetti, J. Strähle, J. Chem. Soc., Dalton Trans. (1999) 4093.;
(b) T.-M. Huang, J.-T. Chen, G.-H. Lee, Y. Wang, Organometallics 10 (1991) 175;
(c) T.-M. Huang, Y.-J. You, C.-S. Yang, W.-H. Tzeng, J.-T. Chen, M.-C. Cheng, Y. Wang, Organometallics 10 (1991) 1020.
[20] (a) G.K. Anderson, H.C. Clark, J.A. Davies, Inorg. Chem. 20 (1981) 944;
(b) F.J. Ramos-Lima, A.G. Quiroga, B. Garcia-Serrelde, F. Blanco, A. Carnero, C. Navarro-Ranninger, J. Med. Chem. 50 (2007) 2194.
[21] F.H. Allen, Acta Cryst. B58 (2002) 380.
[22] (a) P.H. Hall, D.A. Thornton, G.A. Foulds, Polyhedron 6 (1987) 85;
(b) A.R. Brause, M. Rycheck, M. Orchin, J. Am. Chem. Soc. 89 (1967) 6500;
(c) D.G. Cooper, J. Powell, Inorg. Chem. 16 (1977) 142.
[23] (a) C. Hahn, P. Morvillo, E. Herdtweck, A. Vitagliano, Organometallics 21 (2002) 1807;
(b) P. Ganis, I. Orabona, F. Ruffo, A. Vitagliano, Organometallics 17 (1998) 2646.