ELSEVIER

Inorganica Chimica Acta 334 (2002) 437–447

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Addition reactions of primary and secondary aliphatic amines to the benzonitrile ligands in *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ complexes. X-ray structure of the amidine complex *trans*-$[PtCl_2\{Z\text{-}N(H)=C(NHBu^t)Ph\}_2]$

Umberto Belluco [a], Franco Benetollo [b], Roberta Bertani [a], Gabriella Bombieri [c], Rino A. Michelin [a,*], Mirto Mozzon [a], Oliviero Tonon [a], Armando J.L. Pombeiro [d], Fatima Costa Guedes da Silva [d]

[a] *Dipartimento di Processi Chimici dell'Ingegneria and Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Università di Padova, Via F. Marzolo 9, 35131 Padova, Italy*

[b] *ICIS, Area di Ricerca del CNR, Corso Stati Uniti 4, 35020 Padova, Italy*

[c] *Istituto di Chimica Farmaceutica, Università di Milano, Viale Abruzzi 42, 20131 Milan, Italy*

[d] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal*

Received 30 January 2002; accepted 4 March 2002

Dedicated to Professor Andrew Wojcicki on the occasion of his retirement from The Ohio State University

Abstract

The reactions of *cis*-$[PtCl_2(NCPh)_2]$ with a fivefold excess of the primary aliphatic amines RNH_2 (R = Me, Et, Pr^i) in CH_2Cl_2 at −10 °C afford in high yield the di-amidine complexes *cis*-$[PtCl_2\{N(H)=C(NHR)Ph\}_2]$. The reaction of *cis*-$[PtCl_2(NCPh)_2]$ with Bu^tNH_2 yields the di-amidine complex *trans*-$[PtCl_2\{Z\text{-}N(H)=C(NHBu^t)Ph\}_2]$ which has been characterized also by an X-ray diffraction analysis. The corresponding reactions of *trans*-$[PtCl_2(NCPh)_2]$ with a fivefold excess of RNH_2 (R = Me, Et) afford the di-amidine derivatives *trans*-$[PtCl_2\{N(H)=C(NHMe)Ph\}_2]$, while the reactions of Pr^iNH_2 and Bu^tNH_2 lead, for the former, to a mixture of the mono-amidine derivative *trans*-$[PtCl_2(NCPh)\{N(H)=C(NHPr^i)Ph\}]$ and the di-amine dicationic species derivative *trans*-$[Pt(Pr^iNH_2)_2\{N(H)=C(NHPr^i)Ph\}[Cl]_2$ and, for the latter, to the mono-amidine complex derivative *trans*-$[PtCl_2(NCPh)\{N(H)=C(NHBu^t)Ph\}]$. The reactions of *cis*- or *trans*-$[PtCl_2(NCPh)_2]$ di-nitrile complexes with the secondary aliphatic amine Me_2NH yields the di-amidine complexes *cis*- or *trans*-$[PtCl_2\{N(H)=C(NMe_2)Ph\}_2]$, while the corresponding reactions with RR′NH (R, R′ = Me, Et; R = Me, R′ = Bu^t) produce the mono-amidine complexes *cis*- or *trans*-$[PtCl_2(NCPh)\{N(H)=C(NRR'^t)Ph\}]$. The stereochemistry of the amidine ligands in the final products has been investigated by ^1H NMR spectroscopy. © 2002 Published by Elsevier Science B.V.

Keywords: Platinum complexes; Nitrile complexes; Amidine complexes; X-ray structure

1. Introduction

Transition metal-coordinated organonitriles RCN have been reported to exhibit a rich reaction chemistry, which often results from the activation of the nitrile to electrophilic or nucleophilic attack upon coordination to a low-valent electron-rich or an high-valent electron-poor metal center, respectively [1]. In particular, the metal-promoted addition reactions of protic nucleophiles such as water [1,2], alcohols [1,3], oximes [4], amines [1,5] and imines [6] to the C≡N triple bond of the nitrile afford the corresponding amidates, imido esters, iminoacylated species, amidines and 1,3-diaza-1,3-dienes, respectively, which represent products of valuable synthetic and pharmacological interest. Thus, for instance, platinum(II)-imino ester complexes of the

* Corresponding author. Tel.: +39-049-827 5522; fax: +39-049-827 5525.

E-mail address: rino.michelin@unipd.it (R.A. Michelin).

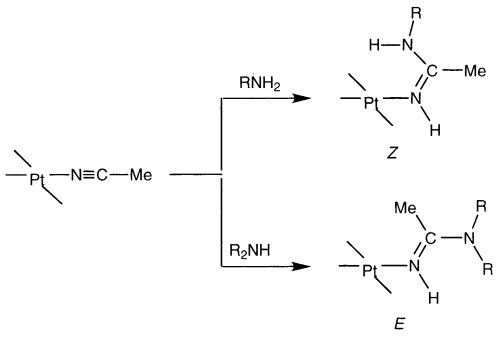
0020-1693/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0020-1693(02)00866-6

general formula *cis*- and *trans*-[$PtCl_2${N(H)=C(OR′)R}$_2$] (R′ = alkyl, R = alkyl, aryl) [3] show unusual antitumor activity [8,9] with the *trans* isomers more active than the corresponding *cis* derivatives.

Our interest in the reactions of Pt(II) organonitriles [1a,5b,5c,5g,7] and those of transition metal cyanamide (N≡CNH_2), organocyanamide (N≡CNR_2; R = Me, Et), and cyanoguanidine (N≡C–N=$C(NH_2)_2$) derivatives [10], led us recently to undertake a detailed investigation [11,12] on the addition of primary and secondary aliphatic amines to Pt(II) nitrile complexes of the type *cis*- and *trans*-[$PtCl_2(NCMe)_2$] to form di- and monoamidine complexes of the type *cis*- and *trans*-[$PtCl_2${*Z* or *E*-N(H)=C(NR′R″)Me}$_2$] and *cis*- and *trans*-[$PtCl_2$(NCMe){*Z* or *E*-N(H)=C(NR′R″)Me}] (R′, R″ = H, alkyl), respectively. The results of this study indicate that the additions of aliphatic amines to the C≡N triple bond of the acetonitrile ligands proceed in a selective manner. Thus, primary amines afford amidine complexes *exclusively* with *Z* configuration, while secondary amines yield amidine complexes *only* with *E* configuration, corresponding to the *trans* or *cis* addition of the amine along the C≡N triple bond, respectively (Scheme 1).

The *Z* configuration of the amidine ligands appears to be determined by the formation of strong intramolecular hydrogen bonds between each chlorine atom and the amino proton of the NHMe moiety forming a six-membered ring. This experimental evidence would explain the lack of *Z* to *E* isomerization as otherwise observed [3a,3b] in the base-catalyzed addition reactions of alcohols to one or both the coordinated nitriles of *cis*- and *trans*-[$PtCl_2(NCR)_2$] (R = Me, Ph). In particular, a detailed investigation [3b] of the mechanism and stereochemistry of the addition reactions of MeOH revealed that the *Z*-imido ester isomers are kinetically favored, then undergoing isomerization to the thermodynamically more stable *E* form.

In this work, we report the study of the addition reactions of primary RNH_2 (R = Me, Et, Pr^i, Bu^t) and secondary R_2NH (R = Me, Et) aliphatic amines to *cis*- and *trans*-[$PtCl_2(NCPh)_2$] complexes with the aim to determine what factors such as the type of amine (primary or secondary), the nature of the R group(s) of the amine and the geometry of the nitrile Pt(II) complexes influence the stereochemistry of the resulting amidine products in comparison with the analogous reactions carried out with *cis*- and *trans*-[$PtCl_2(NCMe)_2$].



Scheme 1.

2. Experimental

2.1. General procedures and materials

All work was carried out with the exclusion of atmospheric oxygen under a N_2 atmosphere using standard Schlenck techniques. Solvents were distilled under N_2 prior to use; CH_2Cl_2 was distilled from CaH_2, Et_2O and THF were distilled from sodium benzophenone. IR spectra were taken on a Perkin–Elmer 983 (Nujol mulls), FT-IR AVATAR 320 of the Nicolet Instrument Corporation (KBr or polyethylene (PE)) spectrophotometers; the wavenumbers (ν) are given in cm^{-1}. ^1H and ^{13}C {^1H} NMR spectra were run at 298 K, unless otherwise stated, on a Bruker 200 AC spectrometer operating at 200.13 and 50.32 MHz, respectively. Peak positions are relative to Me_4Si and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). ^{195}Pt NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature and the ^{195}Pt chemical shifts are given relative to $Na_2[PtCl_6]$ (by using aq. $K_2[PtCl_4] = -1630$ ppm as a standard). The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected. The amines were purchased from Aldrich and were used as received.

The complexes *cis*- and *trans*-[$PtCl_2(NCPh)_2$] were prepared according to a reported procedure [13].

2.2. Reactions of *cis*-[$PtCl_2(NCPh)_2$] with primary amines

2.2.1. Reaction with $MeNH_2$. Synthesis of *cis*-[$PtCl_2${N(H)=C(NHMe)Ph}$_2$] (*1*)

A suspension of *cis*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) in CH_2Cl_2 (30 ml) was treated at −10 °C with a fivefold excess of $MeNH_2$ (1.6 ml of a 2 M THF solution, 3.2 mmol). The suspension turned to a yellow solution after a few minutes. The reaction mixture was stirred for 30 min at the low temperature and then the solvent was removed under reduced pressure to approximately 10 ml. Addition of Et_2O (40 ml) at the low temperature gave a pale yellow solid, which was stirred for an additional 60 min. It was then filtered off at room temperature (r.t.) and washed with Et_2O (3 × 5 ml). It

was recrystallized from CH_2Cl_2/Et_2O. Yield: 266 mg, 78.5%. *Anal*. Calc. for $C_{16}H_{20}N_4Cl_2Pt$: C, 35.96; H, 3.74; N, 10.49. Found: C, 34.39; H, 3.63; N, 10.20%. IR (Nujol mull): ν(NH) 3300, 3530, 3350 (m); ν(C=N) 1620 (s); ν(PtCl) 310, 320 (m, br). ^{1}H NMR (CD_2Cl_2, 270 K): δ 2.84, 2.38, 3.03 (d, C=N–CH_3); 6.61, 6.07 (br, PtNH); 7.67 (br, NH); 8.18–8.23 (m, Ph); 6.94–6.98 (m, Ph); 7.3–7.6 (m, Ph). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 170.97, 170.50, 166.48 (C=N); 132–126 (Ph); 31.65, 31.76 (s, CH$_3$). ^{195}Pt NMR (CD_2Cl_2): δ −2039.

2.2.2. Reaction with $EtNH_2$. Synthesis of cis-[$PtCl_2${N(H)=C(NHEt)Ph}$_2$] (2)

A suspension of *cis*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) in CH_2Cl_2 (30 ml) was treated at −10 °C with a fivefold excess of $EtNH_2$ (1.6 ml of a 2 M THF solution, 3.2 mmol). The suspension became a yellow solution after some minutes. The reaction mixture was stirred for 7 h at the low temperature and then the solvent was removed under reduced pressure to approximately 10 ml. Addition of Et_2O (40 ml) at the low temperature gave a pale yellow solid, which was stirred for an additional 60 min. It was then filtered off at r.t. and washed with Et_2O (3 × 5 ml). It was recrystallized from CH_2Cl_2/Et_2O and identified as **2**. Yield: 310 mg, 86.9%. *Anal*. Calc. for $C_{18}H_{24}N_4Cl_2Pt$: C, 38.43; H, 4.27; N, 9.96. Found: C, 39.07; H, 4.37; N, 9.73%. IR (Nujol mull): ν(NH) 3280 (m); ν(C=N) 1624 (s); ν(PtCl) 310 (m, br). ^{1}H NMR (CD_2Cl_2): δ 1.29, 1.15, 0.95 (t, CH_3); 3.35, 3.15, 2.75 (m, N–CH_2); 5.52, 6.25, 6.63 (br, PtNH); δ masked (NH); 7.56–7.38 (m, Ph); 8.20 (m, Ph); 6.98 (m, Ph). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 169.80 (s, C=N); 131–127 (m, Ph); 40.03 (s, CH$_2$), 16.05 (s, CH$_3$).

2.2.3. Reaction with Pr^iNH_2. Synthesis of cis-[$PtCl_2${N(H)=C(NHPr^i)Ph}$_2$] (3)

A suspension of *cis*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) in CH_2Cl_2 (30 ml) was treated at −10 °C with a fivefold excess of Pr^iNH_2 (270 μl, 3.17 mmol). The suspension turned to a yellow solution after a few minutes. The reaction mixture was stirred for 7 h at the low temperature and then the solvent was removed under reduced pressure to approximately 10 ml. Addition of Et_2O (40 ml) at the low temperature gave a pale yellow solid, which was stirred for an additional 60 min. It was then filtered off at r.t. and washed with Et_2O (3 × 5 ml). It was recrystallized from CH_2Cl_2/Et_2O. Yield: 240 mg, 63.8%. *Anal*. Calc. for $C_{20}H_{28}N_4Cl_2Pt$: C, 40.68; H, 4.75; N, 9.49. Found: C, 41.30; H, 5.20; N, 9.04%. IR (Nujol mull): ν(NH) 3280 (m-s); ν(C=N) 1624 (s); ν(PtCl) 330, 317 (m, br). ^{1}H NMR (CD_2Cl_2): δ 1.20, 0.95 (d, CHCH_3); 3.47, 3.20, 3.95 (m, C=N–CH); 5.95 (br, PtNH); δ masked (br, NH); 8.13 (m, Ph); 7.31–7.58 (m, Ph); 7.06–7.02 (m, Ph). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 168.97, 167.54 (C=N); 133–127 (Ph); 47.19, 46.77 (CH); 23.96, 23.63, 22.64 (CH$_3$).

2.2.4. Reaction with Bu^tNH_2. Synthesis of trans-[$PtCl_2${N(H)=C(NHBu^t)Ph}$_2$] (4)

A suspension of *cis*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) in CH_2Cl_2 (30 ml) was treated at −10 °C with an approximately fivefold excess of Bu^tNH_2 (334 μl, 3.17 mmol). On stirring for 1 h a yellow solution was obtained. The solvent was removed under reduced pressure to approximately 10 ml. Addition of Et_2O (40 ml) at the low temperature gave a pale yellow solid, which was stirred for an additional 60 min. It was then filtered off at r.t. and washed with Et_2O (3 × 5 ml). It was recrystallized from CH_2Cl_2/Et_2O. Yield: 284 mg, 72.4%. *Anal*. Calc. for $C_{22}H_{32}N_4Cl_2Pt$: C, 42.72; H, 5.18; N, 9.06. Found: C, 41.93; H, 5.17; N, 8.94%. IR (KBr): ν(NH) 3260, 3280 (m); ν(C=N) 1610 (s). IR (PE): ν(PtCl) 338, 317 (m). ^{1}H NMR (CD_2Cl_2, 290 K): δ 1.43, 1.15, 0.96 (s, NC(CH_3)$_3$); 5.6, 6.05 (br, PtNH); 7.68, 6.78 (s, NH); 7.49–7.33 (m, Ph); 6.6–7.0 (m, Ph); 8.1–8.2 (m, Ph). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 170.56 (s, N=C); 135–126 (Ph); 51.62 (s, N–C(CH$_3$)$_3$); 31.34 (s, N–C(CH$_3$)$_3$).

2.3. Reactions of trans-[$PtCl_2(NCPh)_2$] with primary amines

2.3.1. Reaction of trans-[$PtCl_2(NCPh)_2$] with $MeNH_2$. Synthesis of trans-[$PtCl_2${N(H)=C(NHMe)Ph}$_2$] (5)

The reaction has been performed as for **1**, starting from *trans*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) and $MeNH_2$ (1.6 ml of a 2 M THF solution, 3.2 mmol). Yield: 226 mg, 66.7%. *Anal*. Calc. for $C_{16}H_{20}N_4Cl_2Pt$: C, 35.96; H, 3.74; N, 10.49. Found: C, 34.33; H, 3.80; N, 10.49%. IR (KBr): ν(NH) 3340, 3234 (m); ν(C=N) 1603 (s). IR (PE): ν(PtCl) 322 (m). ^{1}H NMR (CD_2Cl_2, 270 K): δ 2.92, 2.78, 2.47 (d, NCH_3); 5.81, 5.50 (br, PtNH); 8.48, 7.66 (br, NH); 7.3–7.6 (m, Ph). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 165.99, 165.10 (s, N=C); 131–128 (m, Ph); 42.0, 37.5 (br, CH$_3$).

2.3.2. Reaction with $EtNH_2$. Synthesis of trans-[$PtCl_2${N(H)=C(NHEt)Ph}$_2$] (6)

Compound **6** was prepared under experimental conditions similar to those described for the synthesis of **2** starting from *cis*-[$PtCl_2(NCPh)_2$] (200 mg, 0.423 mmol) and $EtNH_2$ (1.05 ml of a 2 M THF solution, 2.10 mmol). The reaction mixture was stirred for 15 h at the low temperature and then the solvent was removed under reduced pressure to approximately 10 ml. Addition of Et_2O (40 ml) at the low temperature gave a pale yellow solid, which was stirred for an additional 60 min. It was then filtered off at r.t. and washed with Et_2O (3 × 5 ml). It was recrystallized from CH_2Cl_2/Et_2O and identified as **6**. Yield: 154 mg, 65.5%. *Anal*. Calc. for $C_{18}H_{24}N_4Cl_2Pt$: C, 38.43; H, 4.27; N, 9.96. Found: C, 37.95; H, 4.34; N, 9.78%. IR (Nujol mull): ν(NH) 3350, 3194 (m); ν(C=N) 1609 (s); ν(PtCl) 322 (m, br). ^{1}H

NMR (CD_2Cl_2): δ 3.21, 3.09, 2.65 (q, N–CH_2); 1.11, 1.16, 1.13 (t, CH_3); 5.43, 6.05, 6.75 (br, PtN*H*); 9.31 (t, $^3J_{HH}$ 6.15, N*H*); 7.60–7.20 (m, Ph); 7.72 (m, Ph); 6.97 (m, Ph); 8.11 (m, Ph). ^{13}C {^1H} NMR (CD_2Cl_2): δ 170.11 (s, *C*=N); 131–127 (m, Ph); 40.08 (s, CH_2); 16.28, 15.89 (s, CH_3).

2.3.3. Reaction with Pr^iNH_2. Synthesis of trans-[$PtCl_2${N(H)=C(NHPr^i)Ph}$_2$] (7) and trans-[$Pt(Pr^iNH_2)_2${N(H)=C(NHPr^i)Ph}$_2$][Cl]$_2$ (8)

The reaction of *trans*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) in CH_2Cl_2 (30 ml) with a fivefold excess of Pr^iNH_2 (270 μl, 3.17 mmol) at −10 °C for 3 h gave a mixture of **7** and **8** (in about 2:1 ratio) which could not be separated by fractional crystallization, but they were identified by ^1H NMR spectroscopy. **7**. IR (Nujol mull): ν(NH) 3349, 3308, 3190 (m); ν(C=N) 1618 (s); ν(PtCl) 321(m, br). ^1H NMR (CD_2Cl_2): δ 1.22, 1.15 (d, NCHCH_3); 3.53, 3.41 (m, NC*H*CH$_3$); 6.18 (br, PtN*H*); 6.95 (br, N*H*); 7.40–7.50 (m, Ph); 7.64 (m, Ph).

On the other hand, the same reaction carried out with a 50-fold molar excess of the amine gave **8**. Yield: 378 mg, 84.3%. *Anal*. Calc. for $C_{26}H_{44}N_6Cl_2Pt$: C, 44.19; H, 6.23; N, 11.90. Found: C, 43.75; H, 6.60; N, 11.33%. IR (KBr): ν(NH) 3344, 3165 (m); ν(C=N) 1629 (s). ^1H NMR (CD_2Cl_2): δ 1.32 (d, =C–NHCH(CH_3)$_2$); 1.33 (d, H_2NCH(CH_3)$_2$); 2.90 (m, H_2NC*H*(CH$_3$)$_2$); 3.40 (m, =C–NC*H*(CH$_3$)$_2$; 5.27 (br, $^3J_{HPt}$ 59.8, PtNH_{amine}); 6.75 (br, PtN$H_{amidine}$); 9.34 (d, $^3J_{HH}$ 10.4, =C–N*H*CH(CH_3)$_2$); 7.43–7.41 (m, Ph). ^{13}C {^1H} NMR (CD_2Cl_2): δ 168.89 (s, N=*C*); 133–127 (m, Ph); 48.30 and 48.25 (s, =C–NH*C*H(CH$_3$)$_2$ and NH$_2$*C*H(CH$_3$)$_2$); 23.32 (s, =C–NHCH(*C*H$_3$)$_2$); 24.10 (s, NH$_2$CH(*C*H$_3$)$_2$.

2.3.4. Reaction with Bu^tNH_2. Synthesis of trans-[$PtCl_2(NCPh)${N(H)=C(NHBu^t)Ph}] (9)

Compound **9** was prepared by reaction of a suspension of *trans*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) in CH_2Cl_2 (30 ml) with an equimolar amount of Bu^tNH_2 (334 μl, 3.17 mmol). The reaction mixture was stirred at −10 °C for 3 h. The reaction mixture appeared to be a suspension also after further addition of other 5 equiv. (331 μl) of amine. The unreacted starting material was filtered off and the remaining yellow solution was reduced to 10 ml under vacuum. Addition of n-C_6H_{14} (40 ml) at the low temperature gave a pale yellow solid, which was stirred for an additional 30 min. It was then filtered off and washed with n-C_6H_{14} (3 × 15 ml). The solid residue was analyzed as **9**. Yield: 264 mg, 76.2%. *Anal*. Calc. for $C_{18}H_{21}N_3Cl_2Pt$: C, 39.85; H, 3.87; N, 7.75. Found: C, 40.96; H, 4.82; N, 8.43%. IR (KBr): ν(NH) 3340, 3240 (m); ν(C≡N) not observed; ν(C=N) 1621 (s). IR (PE): ν(PtCl) 320, 340 (m). ^1H NMR (CD_2Cl_2): δ 1.48, 2.17, 1.16, 1.14 (s, NC(CH_3)$_3$); 6.79, 7.80 (br, PtN*H*); 8.07–7.25 (m, Ph). ^{13}C {^1H} NMR ($CDCl_3$): δ 170.38, 169.68, 170.21 (s, N=*C*); 109.71, 117.88, 116.37, 110.07 (s, N≡*C*–Ph); 56.83, 56.93, 55.24, 53.45 (s, N*C*(CH$_3$)$_3$); 31.17, 31.30, 30.35, 30.15 (s, NC(*C*H$_3$)$_3$).

2.4. Reactions of cis-[$PtCl_2(NCPh)_2$] with secondary amines

2.4.1. Reaction with Me_2NH. Synthesis of cis-[$PtCl_2${N(H)=C(NMe$_2$)Ph}$_2$] (10)

Compound **10** was prepared as described previously for **1** starting from *cis*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) and a 5 M excess of Me_2NH (1.6 ml of a 2 M solution in THF, 3.2 mmol). Yield: 291 mg, 81.5%. *Anal*. Calc. for $C_{18}H_{24}N_4Cl_2Pt$: C, 38.43; H, 4.27; N, 9.96. Found: C, 37.16; H, 4.12; N, 9.48%. IR (KBr): ν(NH) 3480, 3265, 3240 (m); ν(C=N) 1590 (s). IR (PE): ν(PtCl) 330, 323 (m). ^1H NMR (CD_2Cl_2, 260 K): δ 2.38 and 2.70, 3.06 and 2.88, 3.10 and 2.58 (s, CH_3); 4.98, 5.95, 6.65 (br, N*H*); 7.76–7.10 (m, Ph). ^{13}C {^1H} NMR ($CDCl_3$): δ 166.01, 165.28 (s, C=*N*); 134–121 (m, Ph); 40.77, 42.64 (br, *C*H$_3$).

2.4.2. Reaction with Et_2NH. Synthesis of cis-[$PtCl_2(NCPh)${N(H)=C(NEt$_2$)Ph}] (11)

Compound **11** was prepared as described previously for **1** starting from *cis*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) and a 5 M excess of Et_2NH (329 μl, 3.17 mmol). Yield: 213 mg, 61.5%. *Anal*. Calc. for $C_{18}H_{21}N_3Cl_2Pt$: C, 39.63; H, 3.85; N, 7.71. Found: C, 38.37; H, 3.68; N, 7.39%. IR (KBr): ν(NH) 3365, 3272 (m); ν(C≡N) 2280; ν(C=N) 1582 (s). IR (PE): ν(PtCl) 345, 321 (m). ^1H NMR (CD_2Cl_2, 280 K): δ 1.47, 1.34, 1.19 (t, CH_3); 3.35, 3.62, 3.82 (q, CH_2); 6.0, 5.75 (br, PtN*H*); 8.32, 7.0 (br, N*H*); 7.07–7.89 (m, Ph). ^{13}C {^1H} NMR (CD_2Cl_2): δ 165.99 (s, *C*=N); 134–123 (m, Ph); 115.60 (s, N≡*C*–Ph); 47.71, 45.04, 44.51 (s, *C*H$_2$); 13.85, 13.06, 11.72 (s, *C*H$_3$). ^{195}Pt NMR: δ −2101.

2.4.3. Reaction with $MeBu^tNH$. Synthesis of cis-[$PtCl_2(NCPh)${N(H)=C(NMeBu^t)Ph}] (12)

Compound **12** was prepared reacting *cis*-[$PtCl_2(NCPh)_2$] (200 mg, 0.423 mmol) with a 5 M excess of $MeBu^tNH$ (254 μl, 2.12 mmol) at r.t. for 3 h. Yield: 130 mg, 55.0%. *Anal*. Calc. for $C_{19}H_{23}N_3Cl_2Pt$: C, 40.79; H, 4.11; N, 7.51. Found: C, 38.78; H, 3.99; N, 7.51%. IR (KBr): ν(NH) 3300, 3194 (m); ν(C≡N) 2284 (w); ν(C=N) 1592 (s). IR (PE): ν(PtCl) 348, 358 (m). ^1H NMR (CD_2Cl_2): δ 1.45, 1.48 (s, C(CH_3)$_3$); 3.24, 2.75 (s, CH_3); 6.10 (br, PtN*H*); 7.26–7.95 (m, Ph). ^{13}C {^1H} NMR (CD_2Cl_2): δ 165.12 (s, *C*=N); 135–127 (Ph); 60.78 (s, N–*C*(CH$_3$)$_3$); 37.50 (s, N–*C*H$_3$); 28.18, 26.13 (s, N–C(*C*H$_3$)$_3$); the signal of the benzonitrile carbon (N≡*C*–Ph) was of too low intensity to be observed.

2.5. Reactions of trans-[$PtCl_2(NCPh)_2$] with secondary amines

2.5.1. Reaction of trans-[$PtCl_2(NCPh)_2$] with Me_2NH. Synthesis of trans-[$PtCl_2\{N(H)=C(NMe_2)Ph\}_2$] (**13**) and trans-[$PtCl_2(NCMe)\{N(H)=C(NMe_2)Ph\}$] (**14**)

A suspension of *cis*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) in CH_2Cl_2 (30 ml) was treated at −10 °C with a 20-fold excess of Me_2NH (6.4 ml of a 2 M THF solution, 12.8 mmol). The suspension became a yellow solution after some minutes. The reaction mixture was stirred for 7 h at the low temperature and then the solvent was removed under reduced pressure to approximately 10 ml. Addition of Et_2O (40 ml) at the low temperature gave a pale yellow solid, which was stirred for an additional 60 min. It was then filtered off at r.t. and washed with Et_2O (3 × 5 ml). It was recrystallized from CH_2Cl_2/Et_2O and identified as **13**. Yield: 300 mg, 84.0%. *Anal*. Calc. for $C_{18}H_{24}N_4Cl_2Pt$: C, 38.43; H, 4.27; N, 9.96. Found: C, 36.49; H, 3.94; N, 9.11%. IR (Nujol mull): ν(NH) 3280 (m); ν(C=N) 1595 (s); ν(PtCl) 320 (m, br). ^{1}H NMR (CD_2Cl_2, 250 K): δ 3.10 and 2.86, 3.05 and 2.81, 2.92 and 2.70, 2.86 and 2.62 (s, NCH_3); 5.12, 5.20, 5.45 (br, PtNH); δ masked (br, NH). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 169.13, 168.39, 167.84, 165.34 (s, C=N); 135–121 (Ph); 42.69, 41.50, 40.93, 40.77 (s, CH_3).

A suspension of *trans*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) in CH_2Cl_2 (30 ml) was treated at −10 °C with a twofold excess of Me_2NH (0.6 ml of a 2 M THF solution, 1.3 mmol). The suspension became a yellow solution after a few minutes. The reaction mixture was stirred for 3 h at the low temperature and then the solvent was removed under reduced pressure to approximately 10 ml. Addition of Et_2O (40 ml) at the low temperature gave a pale yellow solid, which was stirred for an additional 60 min. It was then filtered off at r.t. and washed with Et_2O (3 × 5 ml). It was recrystallized from CH_2Cl_2/Et_2O and identified as **14**. Yield: 230 mg, 70.0%. *Anal*. Calc. for $C_{16}H_{17}N_3Cl_2Pt$: C, 37.13; H, 3.29; N, 8.12. Found: C, 37.49; H, 3.36; N, 8.03%. IR (Nujol mull): ν(NH) 3276 (m); ν(C≡N) 2282 (m); ν(C=N) 1591 (s); ν(PtCl) 317 (m, br). ^{1}H NMR (CD_2Cl_2): δ 3.07, 2.87 (m, NCH_3); 4.20 (br, PtNH); 5.25 (br, NH); 7.40–7.75 (m, Ph). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 173.52 (s, C=N); 139–130 (m, Ph); 47.30, 42.80 (br, CH_3); the signal of the benzonitrile carbon (N≡C–Ph) was of too low intensity to be observed.

2.5.2. Reaction with Et_2NH. Synthesis of trans-[$PtCl_2(NCPh)\{N(H)=C(NEt_2)Ph\}$] (**15**)

Compound **15** was prepared as described previously for **1** starting from *cis*-[$PtCl_2(NCPh)_2$] (300 mg, 0.635 mmol) and a 5 M excess of Et_2NH (329 μl, 3.17 mmol). Yield: 213 mg, 61.5%. *Anal*. Calc. for $C_{18}H_{21}N_3Cl_2Pt$: C, 39.63; H, 3.85; N, 7.71. Found: C, 38.37; H, 3.92; N, 7.34%. IR (KBr): ν(NH) 3306 (m); ν(C≡N) 2270; ν(C=N) 1587 (s). IR (PE): ν(PtCl) 339, 300 (m). ^{1}H NMR (CD_2Cl_2, 260 K): δ 5.05, 3.41, 3.10, 3.06, 2.77, 2.48 (q, CH_2); 1.48, 1.30, 0.99 (t, CH_3); 5.20 (br, PtNH); δ masked (br, NH); δ 7.3–7.8 (m, Ph). ^{13}C {^{1}H} NMR (CD_3CN): δ 167.03 (s, C=N); 136–128 (Ph); 110.54 (s, N≡C–Ph); 47.63, 42.22 (br, CH_2); 13.66, 12.06 (br, CH_3). ^{195}Pt NMR: δ −2108.

2.5.3. Reaction with $MeBu^tNH$. Synthesis of trans-[$PtCl_2(NCPh)\{N(H)=C(NMeBu^t)Ph\}$] (**16**)

Compound **16** was prepared reacting *trans*-[$PtCl_2(NCPh)_2$] (200 mg, 0.423 mmol) and a 5 M excess of $MeBu^tNH$ (254 μl, 2.12 mmol) at r.t. for 3 h. Yield: 150 mg, 63.4%. *Anal*. Calc. for $C_{19}H_{23}N_3Cl_2Pt$: C, 40.79; H, 4.11; N, 7.51. Found: C, 37.90; H, 4.25; N, 7.40%. IR (KBr): ν(NH) 3420, 3231 (m); ν(C≡N) 2287 (m); ν(C=N) 1591 (s). IR (PE): ν(PtCl) 321, 345 (m). ^{1}H NMR (CD_2Cl_2): δ 1.20, 1.49 (s, C(CH_3)$_3$); 2.76 (s, CH_3); 4.04 (s, $^5J_{HPt} < 0.1$, CH_3); 5.49 (br, PtNH); 7.37–7.83 (m, Ph). ^{13}C {^{1}H} NMR (CD_2Cl_2): δ 178.31 (s, C=N); 135–129 (m, Ph); 117.26 (s, N≡C–Ph); 56.44 (s, C(CH_3)$_3$); 37.53 (s, CH_3), 25.67, 26.41 (s, C(CH_3)$_3$).

2.6. X-ray measurements and structure determination

2.6.1. Crystal data for $C_{22}H_{32}N_4Cl_2Pt$ (**4**)

Mw = 394.4 triclinic, space group $P\bar{1}$, $a = 10.918(2)$, $b = 10.108(2)$, $c = 6.020(1)$ Å, $\alpha = 83.46(2)$, $\beta = 104.89(2)$, $\gamma = 108.99(2)°$; $V = 606.8(2)$ Å^3; $Z = 1$, $D_{calc} = 1.693$ g cm^{-3}; $F(000) = 304$; λ(Mo Kα) = 0.71073 Å; $\mu = 6.01$ mm^{-1}, $T = 293(2)$ K. A prismatic colorless crystal of dimensions 0.22 × 0.28 × 0.30 mm was centered on a four-circle Philips PW1100 (Febo System) [14] diffractometer operating in $\theta/2\theta$ scan mode with graphite-monochromated Mo Kα, following standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lp effects and for absorption, as described by North et al. [15]. The structure was solved by heavy atoms methods [16]. Refinement was carried out by full-matrix least-squares. The t-butyl group is found statistically distributed on two positions with occupancy factors of 0.6 and 0.4, respectively, the function minimized was $\Sigma\, w(F_o^2 - F_c^2)^2$, with weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0320P)^2 + 1.17P]$, where $P = \max(F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 U_{equiv} of the parent carbon atom). $wR = \{\Sigma\,[w(F_o^2 - F_c^2)^2]/\Sigma\,[w(F_o^2)^2]\}^{1/2} = 0.060$, $S = 1.065$, and conventional $R = 0.023$, based on the F values of 2898 reflections having $F_o^2 = 2\sigma(F_o^2)$.

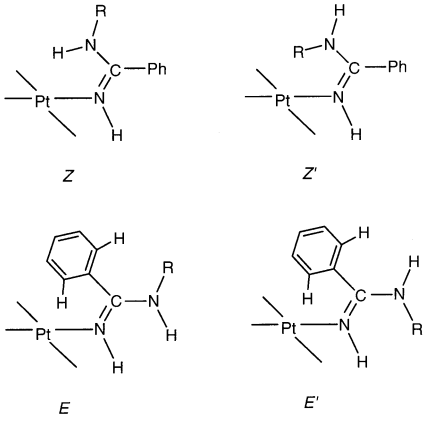
Structure refinement and final geometrical calculations were carried out with SHELXL-97 [16] program, drawings were produced using ORTEP II [17].

3. Results and discussion

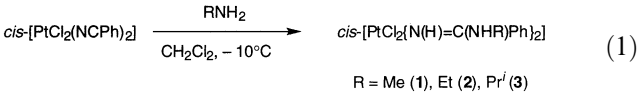
3.1. Reactions of cis- and trans-[$PtCl_2(NCPh)_2$] complexes with primary amines

In contrast with the reactions with the acetonitrile derivatives [11,12], the corresponding reactions of the benzonitrile complexes *cis*- and *trans*-[$PtCl_2(NCPh)_2$] with primary and secondary aliphatic amines afford, on the basis of ^{1}H NMR data, a complex mixture of isomers, which can be referred to the structures reported in Scheme 2. The *Z* and *Z′* isomers show the presence of the N–H and N–R groups, respectively, close to the metal center; thus, it is expected that they would experience a deshielding effect by the metal that will cause a downfield shift of the corresponding signals in the ^{1}H NMR spectra [3a]. It is also expected, as previously reported [11,12], that the *Z* configuration will likely predominate over *Z′* since the former will be stabilized by the formation of strong intramolecular N–H···Cl hydrogen bonds involving the NH amino proton and an adjacent chlorine atom bonded to the metal center. On the other hand, the presence of more downfield shifted signals in the region of the phenyl protons would suggest the presence of *E* and *E′* isomers, where the *ortho* protons of the phenyl ring are now close to the metal center [3a].

Thus, *cis*-[$PtCl_2(NCPh)_2$] reacts with an excess of the primary aliphatic amines RNH_2 (R = Me, Et, Pr^i) at −10 °C in CH_2Cl_2 to give in high yield the di-amidine derivatives *cis*-[$PtCl_2${N(H)=C(NHR)Ph}$_2$] (**1**–**3**) (Eq. (1)), where the amidine ligands are present in different configurations as summarized in Table 1. A typical example of the ^{1}H NMR spectrum of an amidine complex is reported in Fig. 1.

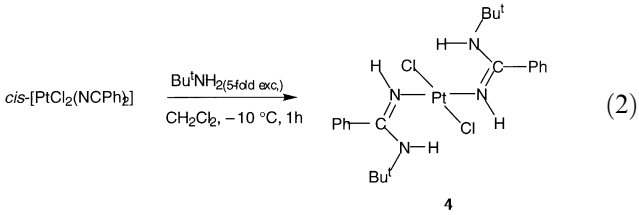


Scheme 2.



(1)

The analogous reaction of *cis*-[$PtCl_2(NCPh)_2$] with the sterically hindered Bu^tNH_2 proceeds with the inversion of the geometry at the metal center affording the di-amidine complex *trans*-[$PtCl_2${*Z*-N(H)=C(NHBu^t)Ph}$_2$] (**4**) (Eq. (2)), which has been characterized also by an X-ray diffraction analysis.



(2)

Such a *cis* to *trans* isomerization was not previously observed in the addition reactions of amines as well as of other nucleophiles [7,11] to the Pt(II) nitrile complexes *cis*-[$PtCl_2(NCR)_2$] (R = Me, Ph) and it is likely due to the sterical hindrance of the two amidines. Eq. (2) was also followed by ^{1}H NMR spectroscopy in CD_2Cl_2 at −10 °C using a fivefold molar excess of amine with respect to the metal complex. The immediate appearance of a singlet at 1.08 ppm was attributed to the t-butyl resonance of the amidine ligands in *cis*-[$PtCl_2${N(H)=C(NHBu^t)Ph}$_2$], which is initially formed. The intensity of the signal at 1.08 ppm was observed to slowly decrease with time (ca. 3 h), while a new resonance at 1.15 ppm formed, which corresponds to the t-butyl groups of the amidine ligands in the final complex **4**.

The molecular structure of **4** shows a perfect *trans* orientation of the ligands with the metal ion lying in an inversion center due to the crystallographic imposed C_i symmetry. A view of the molecule with the atom numbering scheme is shown in Fig. 2, while significant bond distances and angles are reported in Table 2. The molecules in the crystal cell are separated only by Van der Waals contacts as shown in Fig. 3. The square planar coordination geometry around Pt is characterized by the values of the Pt–N and Pt–Cl bond distances of 2.015(3) and 2.306(1) Å, respectively, in agreement with literature data [11,12] for similar Pt(II) derivatives with coordinated amidine ligands. The amidine ligands are shown to be in the *Z* configuration. The molecular structure is characterized by two strong intramolecular hydrogen bonds involving the N(2)–H proton and the chlorine atom (Cl′) (′ at $-x$, $-y$, $-z$) as well as the centrosymmetrically related part of the molecule. The N(2)···Cl′ separation is 3.094(4) Å, while the N(2)–H(2)···Cl′ contact is 2.17(7) Å with a N(2)–H(2)···Cl′ angle of 175°. It is likely that this interaction, coupled with the steric hindrance of the t-butyl group, may

Table 1
Selected ^{1}H NMR data for compounds **1**–**9**

Compound	R group	*Z* (%)	*Z′* (%)	*E*, *E′* (%)
1	CH_3	2.84 d (60), $^3J_{HH}$ 5.10	3.03 d (20), $^3J_{HH}$ 4.50	2.38 d (20), $^3J_{HH}$ 4.45, Ph: 8.20 m, 6.96 m
2	CH_2CH_3	3.15 m (60)	3.35 m (20)	2.75 m (20)
	CH_2CH_3	1.15 t (60), $^3J_{HH}$ 7.10	0.95 t (20), $^3J_{HH}$ 7.02	1.29 t (60), $^3J_{HH}$ 7.20, Ph: 8.20 m, 6.98 m
3	$CH(CH_3)_2$	3.47 m (90)	3.95 m (5)	3.20 m (5), Ph: 8.13 m, 7.00 m
4	$C(CH_3)_3$	1.15 s (90)	1.43 s (5)	0.96 s (5), Ph: 8.15 m, 7.00 m
5	CH_3	2.78 d (85), $^3J_{HH}$ 4.00	2.92 d (15), $^3J_{HH}$ 4.60	
6	CH_2CH_3	3.09 q (40)	3.21 q (40)	2.65 m (20)
	CH_2CH_3	1.13 t (40), $^3J_{HH}$ 7.22	1.17 t (40), $^3J_{HH}$ 7.00	1.11 t (20), $^3J_{HH}$ 7.05, Ph: 6.97 m, 7.72 m, 8.11 m
7	$CH(CH_3)_2$	1.15 d (68), $^3J_{HH}$ 6.30	1.22 d (30), $^3J_{HH}$ 6.31	1.01 d (2), $^3J_{HH}$ 6.02, Ph: 7.64 m
9	$C(CH_3)_3$	1.48 s (28)	2.17 s (8)	1.16 s (32), 1.14 s (32), Ph: 8.07 m, 7.25 m

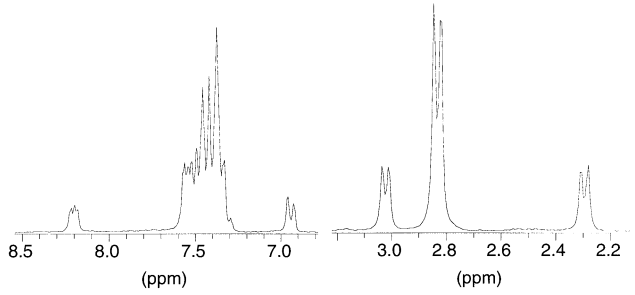


Fig. 1. ^{1}H NMR spectrum at 270 K (CD_2Cl_2) of complex **1**.

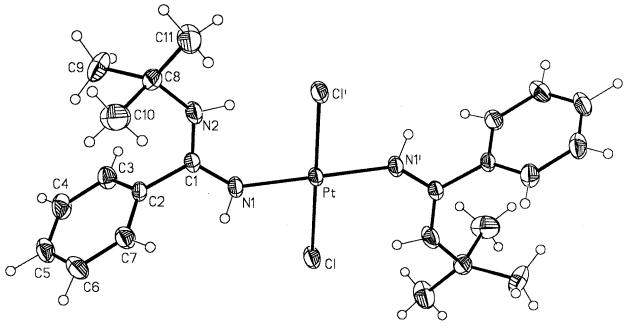


Fig. 2. ORTEP view of the molecule *trans*-[$PtCl_2${*Z*-N(H)=C(NHBu^t)Ph}$_2$] (**4**) (ellipsoids are at 40% probability); the t-butyl positions are those with the higher occupancy factor.

Table 2
Relevant bond distances (Å) and angles (°) for *trans*-[$PtCl_2${*Z*-N(H)=C(NHBu^t)Ph}$_2$] (**4**)

Bond lengths			
Pt–Cl	2.306(1)	Pt–N(1)	2.015(3)
N(1)–C(1)	1.304(4)	N(2)–C(1)	1.321(5)
N(2)–C(8)	1.485(5)	C(1)–C(2)	1.497(4)
Bond angles			
Cl–Pt–N(1)	82.3(1)	Pt–N(1)–C(1)	138.7(3)
C(1)–N(2)–C(8)	131.7(4)	N(1)–C(1)–N(2)	121.5(3)
N(2)–C(1)–C(2)	122.0(3)	N(1)–C(1)–C(2)	116.4(3)
N(2)–C(8)–C(10)	113.1(7)	N(2)–C(8)–C(9)	114.0(8)

determine a wider opening of the angle Pt–N(1)–C(1) (138.7(3)°) with respect to that found in the corresponding methyl derivative *trans*-[$PtCl_2${*Z*-N(H)=C(NHMe)Me}$_2$] [11a] of 131.9(7)°. Short contacts Cl···H–N of the order of 2.16 Å have been found in both derivatives [($C_6H_4CH_2NHMe_2$–C^2)PdCl(MDMPP-*P*,*OMe*)](PF_6) and [($C_6H_4CH_2NHMe_2$–C^2)-PdCl(TDMPP-*P*,*OMe*)](PF_6) [18]. The six-membered ring involving Pt, N(1), C(1), N(2), H(2), Cl′ is about planar, the deviations from least-square plane ranging from −0.029(3) to 0.020(2) Å.

The N(1)–C(1) bond distance of 1.304(4) Å is of the same order of magnitude of the C(1)–N(2) bond length of 1.321(5) Å, suggesting an extensive electron delocalization along the N(1)–C(1)–N(2) system from which the phenyl group is rotated by 105.3(2)°. Similar values for the same type of distances have been found in the previously quoted derivative *trans*-[$PtCl_2${*Z*-N(H)=C(NHMe)Me}$_2$] [11a], which shows equal N(1)–C(1) and C(1)–N(2) values of 1.32(1) Å, even though in the presence of a longer intramolecular interaction of 2.61 Å (with a N(2)–H···Cl′ angle of 127°) between the N(2)–H proton and the adjacent chlorine atom, with respect to that found in the present derivative (see above).

The results reported here seem to suggest that the electron delocalization is peculiar of this type of ligands, as shown by the reported examples, where the N–C(R)–N system is about planar in analogy with the same evidence reported for the imino ether moiety in the free ligand [19].

The nitrile complex *trans*-[$PtCl_2(NCPh)_2$], under experimental conditions analogous to those used for the reactions of the parent *cis* complex, reacts with a fivefold excess of RNH_2 (R = Me, Et) to give the di-amidine derivatives *trans*-[$PtCl_2${N(H)=C(NHR)Ph}$_2$] (R = Me, **5**; Et = **6**) (Scheme 3), for which the ^{1}H NMR spectra showed the formation of *Z* and *Z′* isomers (Table 1). On the other hand, the corresponding reaction with Pr^iNH_2 gives different products depending on the amine concentration. Thus, with a fivefold excess of the amine, a mixture of the di-amidine derivative

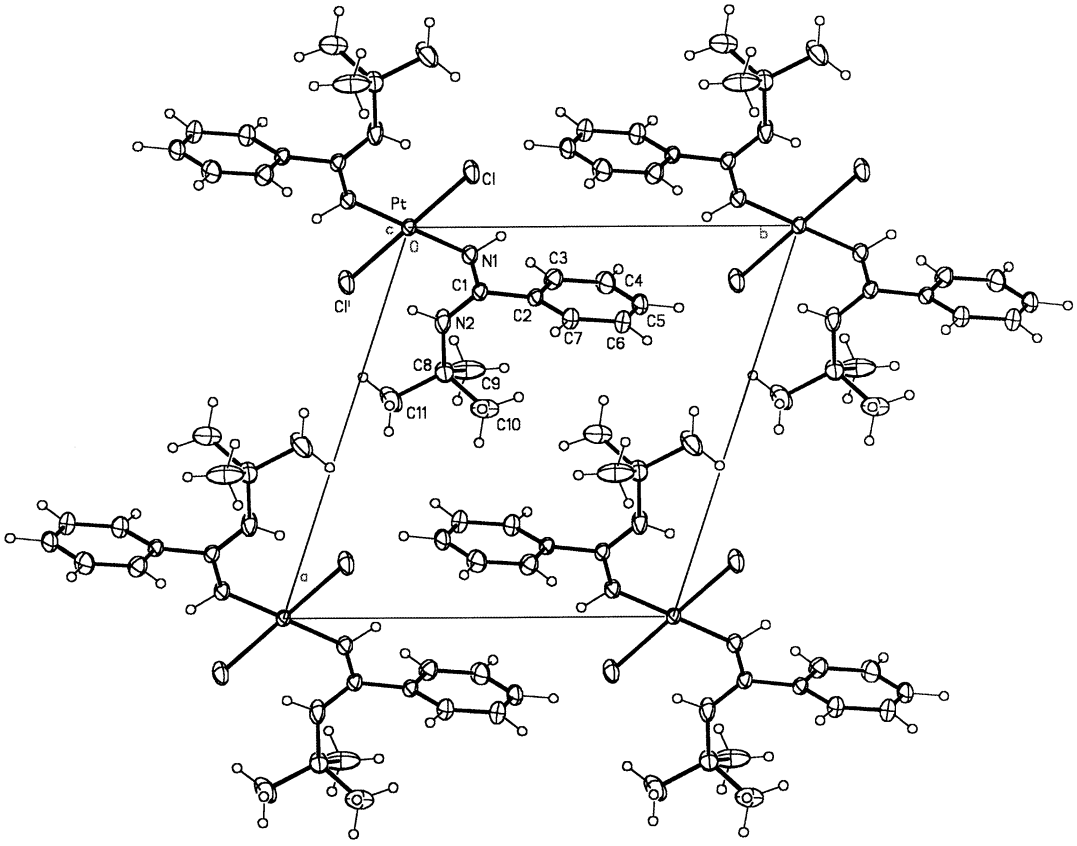
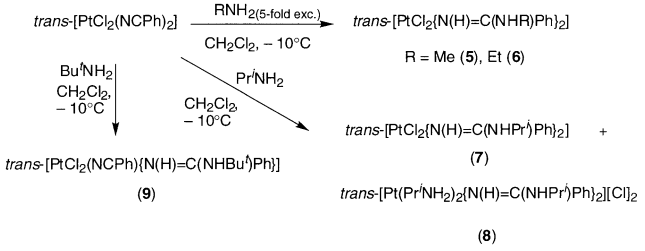


Fig. 3. Packing diagram for *trans*-[$PtCl_2${*Z*-N(H)=C(NHBu^t)Ph}$_2$] (**4**) viewed down the *c*-axis.



Scheme 3.

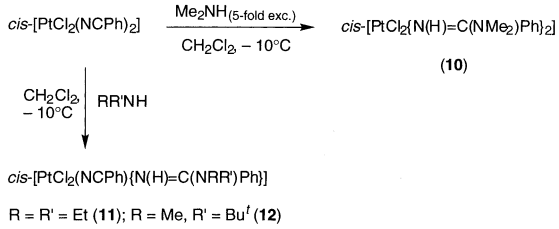
trans-[$PtCl_2${N(H)=C(NHPr^i)Ph}$_2$] (**7**) with the dicationic complex *trans*-[$Pt(Pr^iNH_2)_2${N(H)=C(NHPr^i)Ph}$_2$][Cl]$_2$ (**8**), having two coordinated amine molecules, was formed (Scheme 3). This latter complex could be obtained in a pure form by reaction of the *trans* dinitrile derivative with a 50-fold excess of the amine. An analogous behavior was previously observed in the reaction of *trans*-[$PtCl_2(NCMe)_2$] with Pr^iNH_2 [11b].

The reaction of *trans*-[$PtCl_2(NCPh)_2$] with Bu^tNH_2, even in the presence of a large excess of the amine, gave the mono-amidine derivative *trans*-[$PtCl_2$(NCPh)-{N(H)=C(NHPr^i)Ph}] (**9**), whose ^{1}H NMR spectrum shows the simultaneous presence of the *Z*, *Z*′, *E* and *E*′ isomers almost in the same amounts (Table 1).

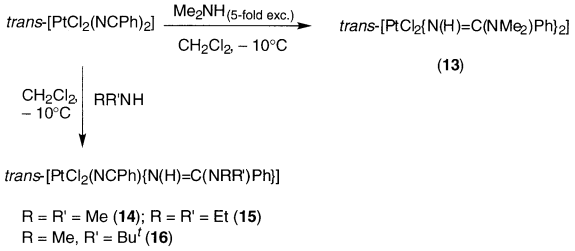
Complexes **1**–**9** have been characterized by microanalysis, IR, ^{1}H and ^{13}C {^{1}H} NMR (see Section 2). In the ^{195}Pt {^{1}H} NMR spectrum of **1**, the observed broad resonance (δ −2039) lies within the range (δ from −2028 to −2091) [20] exhibited by related neutral dichloroplatinum(II) complexes with imine ligands formed upon nucleophilic addition of oximes to ligated nitriles. The IR spectra (KBr pellets or Nujol mulls) show the N–H vibrations of the amidine ligands in the range 3530–3190 cm^{-1}, while the C=N absorption appears in the range 1624–1603 cm^{-1} and the Pt–Cl stretchings in the range 310–340 cm^{-1}.

3.2. Reactions of *cis*- and *trans*-[$PtCl_2(NCPh)_2$] complexes with secondary amines

The reaction at low temperature of *cis*-[$PtCl_2(NCPh)_2$] with a fivefold excess of Me_2NH leads to the formation of the di-amidine complex *cis*-[$PtCl_2${N(H)=C(NMe$_2$)Ph}$_2$] (**10**), which is present, according to ^{1}H NMR data, as a mixture of *E* and *Z* isomers (Scheme 4, Table 3). It is noteworthy that in the case of the reactions of *cis*-[$PtCl_2(NCMe)_2$] with Me_2NH, under the same experimental conditions, the di-amidine complex *cis*-[$PtCl_2${N(H)=C(NMe$_2$)Me}$_2$],



Scheme 4.



Scheme 5.

having both the amidine ligands only in the *E* configuration, was formed [11b].

The reactions of *cis*-$[PtCl_2(NCPh)_2]$ with the more hindered amines Et_2NH and $MeBu^tNH$ afforded only the mono-amidine derivatives *cis*-$[PtCl_2(NCPh)\{N(H)=C(NRR')Ph\}]$ [R = R′ = Et, **11**; R = Me, R′ = Bu^t, **12**], even in the presence of a large excess of the amine (Scheme 4).

The reactions of *trans*-$[PtCl_2(NCPh)_2]$ with twenty- or twofold of Me_2NH yields the di-amidine complex *trans*-$[PtCl_2\{N(H)=C(NMe_2)Ph\}_2]$ (**13**) or the mono-amidine derivative *trans*-$[PtCl_2(NCPh)\{N(H)=C(NMe_2)Ph\}]$ (**14**), respectively, as illustrated in Scheme 5. Similar type of complexes, i.e. **15** and **16**, were obtained (see Scheme 5) also by reaction with the more sterically hindered amines Et_2NH and $MeBu^tNH$, respectively.

Complexes **10**–**16** have been characterized by microanalysis, IR, ^1H and ^{13}C $\{^1H\}$ NMR (see Section 2). The ^{195}Pt $\{^1H\}$ NMR spectra of **11** and **15** display broad resonances at δ −2101 and −2108, respectively, which are only very slightly higher field than that of **1** (see above), approaching those reported (δ from −2104 to −2210) [21] for neutral dichloroplatinum(II) complexes with Δ^4-1,2,4-oxadiazoline ligands derived from cycloaddition of nitrones to coordinated nitriles. The IR spectra show the N–H vibrations of the amidine ligands in the range 3480–3194 cm^{-1}, while the C=N absorption appears in the range 1590–1582 cm^{-1} and the Pt–Cl stretchings in the range 300–358 cm^{-1}.

4. Concluding remarks

The results reported above show that the addition reactions of primary and secondary aliphatic amines to the C≡N triple bond of the benzonitrile ligands in *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ complexes afford the corresponding amidine derivatives thus paralleling the observed reactivity of the acetonitrile ligands in *cis*- and *trans*-$[PtCl_2(NCMe)_2]$. However, while the reactions of the latter complexes with primary or secondary amines afford amidine complexes *exclusively* with *Z* or *E* configuration, respectively, those with the benzonitrile ligands *always* afford a mixture of *Z* and *E* isomers as reported in Scheme 2 and Tables 1 and 3. This observation is in agreement with previous studies performed on the reactions of *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ complexes with MeOH under basic conditions to yield the imino ether complexes *cis*- and *trans*-$[PtCl_2\{N(H)=C(OMe)Ph\}_2]$ [3a], where the observed *Z* to *E* isomerization takes place about the C=N double bond being promoted by MeO^- ions. However, no evidence of such isomerization has been obtained by NMR studies in the corresponding reactions with amines. It is noteworthy to mention that different isomers have been also obtained in the reactions of *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ with aziridine [5g].

The addition reactions described in this paper confirm previous studies [11,12] that the dinitrile complexes of *cis* geometry are more reactive (under analogous

Table 3
Selected ^1H NMR data for compounds **10**–**16**

Compound	R and R′ groups	*E*, *E*′ (%)	*Z*, *Z*′ (%)
10	R = R′ = CH_3	2.38 s and 2.70 s (33)	3.06 s and 2.88 s (33), 3.10 s and 2.58 s (33)
11	R = R′ = CH_2CH_3	3.35 q, 3.21 q (60)	3.82 q (40)
	R = R′ = CH_2CH_3	1.47 t, $^3J_{HH}$ 7.30; 1.17 t, $^3J_{HH}$ 7.10 (60)	1.19 t, $^3J_{HH}$ 7.14 (40)
12	R = CH_3	2.75 s (70)	3.24 s (30)
	R′ = Bu^t	1.45 s (70)	1.48 s (30)
13	R = R′ = CH_3	2.92 s and 2.70 s, 2.86 s and 2.62 s (70)	3.10 s and 2.86 s, 3.05 s and 2.81 s (30)
14	R = R′ = CH_3	2.87 s (70)	3.09 s (30)
15	R = R′ = CH_2CH_3	3.06 q, 3.41 q (80)	3.10 q, 5.05 q (20)
	R = R′ = CH_2CH_3	1.30 t, $^3J_{HH}$ 7.20; 0.99 t, $^3J_{HH}$ 7.13 (80)	1.48 t, $^3J_{HH}$ 7.00; 1.30 t, $^3J_{HH}$ 7.13 (20)
16	R = CH_3	2.76 s (70)	4.04 s, $^5J_{HPt}$ 0.06 (30)
	R′ = Bu^t	1.49 s (70)	1.20 s (30)

experimental conditions) than the corresponding *trans* isomers. Finally, it is also observed that the addition reactions are influenced both by the sterical hindrance of the R group(s) of the entering amine and the nature (primary or secondary) of the amine.

5. Supplementary material

Tables of additional material, including atomic coordinates, full listing of bond lengths/angles and anisotropic thermal parameters are available from the Cambridge Crystallographic Data Centre, CCDC No. 178619 for compound **4**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

R.A.M thanks MURST Cofin-99 and the University of Padova for financial support.

References

[1] (a) R.A. Michelin, M. Mozzon, R. Bertani, Coord. Chem. Rev. 147 (1996) 299;
(b) Yu.N. Kukushkin, Koord. Hhim. 7 (1981) 323;
(c) B.N. Storhoff, H.C. Lewis, Jr., Coord. Chem. Rev. 23 (1977) 1;
(d) V.Yu. Kukushkin, A.J.L. Pombeiro, Chem. Rev., in press.

[2] (a) T. Yoshida, T. Matsuda, T. Okano, T. Kitani, S. Otsuda, J. Am. Chem. Soc. 101 (1979) 2027;
(b) D.P. Arnold, M.A. Bennett, J. Organomet. Chem. 199 (1980) 119;
(c) C.M. Jensen, W.C. Trogler, J. Am. Chem. Soc. 108 (1986) 723.

[3] (a) F.P. Fanizzi, F.P. Intini, G. Natile, J. Chem. Soc., Dalton Trans. (1989) 947;
(b) R. Cini, P.A. Caputo, F.P. Intini, G. Natile, Inorg. Chem. 34 (1995) 1130.

[4] (a) C.M.P. Ferreira, M.F.C. Guedes da Silva, J.J.R. Frausto da Silva, A.J.L. Pombeiro, V.Yu. Kukushkin, R.A. Michelin, Inorg. Chem. 40 (2001) 1134;
(b) M. Kopylovich, V.Yu. Kukushkin, M.F.C. Guedes da Silva, M. Haukka, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, J. Chem. Soc., Dalton Trans. (2001) 1569;
(c) M.L. Kuznetsov, N.A. Bokach, V.Yu. Kukushkin, T. Pakkanen, G. Wagner, A.J.L. Pombeiro, J. Chem. Soc., Dalton Trans. (2000) 4683;
(d) V.Yu. Kukushkin, I.V. Ilichev, M.A. Zhdanova, G. Wagner, A.J.L. Pombeiro, J. Chem. Soc., Dalton Trans. (2000) 1567;
(e) V.Yu. Kukushkin, T.B. Pakhomova, N.A. Bokach, G. Wagner, M.L. Kuznetsov, M. Galanski, A.J.L. Pombeiro, Inorg. Chem. 39 (2000) 216;
(f) D.A. Garnovskii, M.F.C. Guedes da Silva, T.B. Pakhomova, G. Wagner, M.T. Duarte, J.J.R. Frausto da Silva, A.J.L. Pombeiro, V.Yu. Kukushkin, Inorg. Chim. Acta 300–302 (2000) 499;
(g) G. Wagner, A.J.L. Pombeiro, N.A. Bokach, V.Yu. Kukushkin, J. Chem. Soc., Dalton Trans. (1999) 4083;
(h) G. Wagner, A.J.L. Pombeiro, Y.N. Kukushkin, T.B. Pakhomova, A.D. Ryabov, V.Yu. Kukushkin, Inorg. Chim. Acta 292 (1999) 272;
(i) V.Yu. Kukushkin, I.V. Ilichev, G. Wagner, J.J.R. Frausto da Silva, A.J.L. Pombeiro, J. Chem. Soc., Dalton Trans. (1999) 3047;
(j) V.Yu. Kukushkin, T.B. Pakhomova, Yu.N. Kukushkin, H. Hermann, G. Wagner, A.J.L. Pombeiro, Inorg. Chem. 37 (1998) 6511.

[5] (a) R. Ros, J. Renaud, R. Roulet, J. Organomet. Chem. 87 (1975) 379;
(b) L. Calligaro, R.A. Michelin, P. Uguagliati, Inorg. Chim. Acta 76 (1983) L83;
(c) P. Uguagliati, U. Belluco, R.A. Michelin, P. Guerriero, Inorg. Chim. Acta 81 (1984) 61;
(d) C.A. Amodio, K.B. Nolan, Inorg. Chim. Acta 113 (1986) 27;
(e) C.A. Amodio, D.J. Eastwood, Inorg. Chim. Acta 122 (1986) L3;
(f) L. Maresca, G. Natile, F.P. Intini, F. Gasparrini, A. Tiripicchio, M. Tiripicchio-Camellini, J. Am. Chem. Soc. 108 (1986) 1180;
(g) R.A. Michelin, M. Mozzon, R. Bertani, F. Benetollo, G. Bombieri, R.J. Angelici, Inorg. Chim. Acta 222 (1994) 327.

[6] D.A. Garnovskii, V.Yu. Kukushkin, M. Haukka, G. Wagner, A.J.L. Pombeiro, J. Chem. Soc., Dalton Trans. (2001) 560.

[7] (a) R.A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo, R.J. Angelici, Organometallics 10 (1991) 1751;
(b) R.A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo, R.J. Angelici, J. Chem. Soc., Dalton Trans. (1993) 959;
(c) R.A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri, R.J. Angelici, Organometallics 13 (1994) 1341;
(d) R.A. Michelin, U. Belluco, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri, R.J. Angelici, Inorg. Chim. Acta 220 (1994) 21;
(e) U. Belluco, R. Bertani, F. Meneghetti, R.A. Michelin, M. Mozzon, G. Bandoli, A. Dolmella, Inorg. Chim. Acta 300–302 (2000) 912.

[8] (a) G. Natile, M. Coluccia, Coord. Chem. Rev. 216–217 (2001) 383;
(b) Y. Liu, C. Pacifico, G. Natile, E. Sletten, Angew. Chem., Int. Ed. Engl. 40 (2001) 1226.

[9] (a) Y. Liu, M.F. Sivo, G. Natile, E. Sletten, Met.-Based Drugs 7 (2000) 169;
(b) M. Leng, D. Locker, M.-J. Giraud-Panis, A. Schwartz, F.P. Intini, G. Natile, C. Pisano, A. Boccarelli, D. Giordano, M. Coluccia, Mol. Pharmacol. 58 (2000) 1525;
(c) B. Andersen, N. Margiotta, M. Coluccia, G. Natile, E. Sletten, Met.-Based Drugs 7 (2000) 23;
(d) M. Coluccia, A. Nassi, A. Boccarelli, D. Giordano, N. Cardellicchio, F.P. Intini, G. Natile, A. Barletta, A. Paradiso, Int. J. Oncol. 15 (1999) 1039;
(e) A. Boccarelli, M. Coluccia, F.P. Intini, G. Natile, D. Locker, M. Leng, Anti-Cancer Drug Des. 14 (1999) 253.

[10] (a) A.J.L. Pombeiro, M.F.C. Guedes da Silva, D.L. Hughes, R.L. Richards, J. Organomet. Chem. 371 (1989) C45;
(b) M.F.N.N. Carvalho, A.J.L. Pombeiro, J. Organomet. Chem. 410 (1991) 347;
(c) M.F.N.N. Carvalho, A.J.L. Pombeiro, A. Hills, D.L. Hughes, R.L. Richards, J. Organomet. Chem. 469 (1993) 179;
(d) M.F.C. Guedes da Silva, E.M.P.R.P. Branco, Y. Wang, J.J.R. Frausto da Silva, A.J.L. Pombeiro, R. Bertani, R.A. Michelin, M. Mozzon, F. Benetollo, G. Bombieri, J. Organomet. Chem. 490 (1995) 89;
(e) M.F.C. Guedes da Silva, C.M.P. Ferreira, E.M.P.R.P. Branco, J.J.R. Frausto da Silva, A.J.L. Pombeiro, R.A. Michelin, U. Belluco, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo, V.Yu. Kukushkin, Inorg. Chim. Acta 265 (1997) 267;

(f) M.T.A.R.S. Costa, J.J.R. Frausto da Silva, A.J.L. Pombeiro, R.A. Michelin, G. Bombieri, F. Benetollo, Inorg. Chim. Acta 280 (1998) 308;
(g) L.M.D.R.S. Martins, J.J.R. Frausto da Silva, A.J.L. Pombeiro, R.A. Henderson, D.J. Evans, F. Benetollo, G. Bombieri, R.A. Michelin, Inorg. Chim. Acta 291 (1999) 39.

[11] (a) R. Bertani, D. Catanese, R.A. Michelin, M. Mozzon, G. Bandoli, A. Dolmella, Inorg. Chem. Commun. 3 (2000) 16;
(b) R.A. Michelin, R. Bertani, M. Mozzon, A. Sassi, F. Benetollo, G. Bombieri, A.J.L. Pombeiro, Inorg. Chem. Commun. 4 (2001) 275.

[12] U. Belluco, F. Benetollo, R. Bertani, G. Bombieri, R.A. Michelin, M. Mozzon, A.J.L. Pombeiro, M.F.C. Guedes da Silva, Inorg. Chim. Acta 330 (2002) 229.

[13] D. Fraccarollo, R. Bertani, M. Mozzon, U. Belluco, R.A. Michelin, Inorg. Chim. Acta 201 (1992) 15.

[14] D. Belletti, 'FEBO', A New Hardware and Software System for Controlling a Philips PW1100 Single Crystal Diffractometer, Internal report 1/93, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

[15] A.C.T. North, D.C. Philips, F.S. Mathews, Acta Crystallogr. 87 (1968) 902.

[16] G.M. Sheldrick, 'SHELXL-97', Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany.

[17] C.K. Johnson 'ORTEP II' report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1976.

[18] J.-F. Ma, Y. Kojima, Y. Yamamoto, J. Organomet. Chem. 616 (2000) 149.

[19] D. Mackay, D.D. McIntyre, N.J. Taylor, L.L. Wong, Can. J. Chem. 61 (1983) 1213.

[20] G. Wagner, T.B. Pakhomova, N.A. Bokach, J.J.R. Fraústo da Silva, J. Vicente, A.J.L. Pombeiro, V.Yu. Kukushkin, Inorg. Chem. 40 (2001) 1683.

[21] G. Wagner, M. Haukka, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, V.Yu. Kukushkin, Inorg. Chem. 40 (2001) 264.