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Synthesis and spectroscopic investigation of *cis* and *trans* isomers of bis(nitrile)dichloroplatinum(II) complexes

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Abstract

A series of bis(nitrile) complexes *cis*- and *trans*-$Cl_2Pt(NCR)_2$ ($R=C_6H_5$, p-$CH_3C_6H_4$, p-$CF_3C_6H_4$, o-$CH_3C_6H_4$, CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $(CH_3)_3C$) has been prepared by either one of the two methods, $K_2PtCl_4/H_2O/RCN$(excess) or $PtCl_2/RCN$(neat), both of which usually yield the nitrile complexes as a mixture of *cis* and *trans* isomers in different ratios depending on the experimental conditions such as the reaction temperature and the reaction time. The separation of the stereoisomers of each bis(nitrile) compound could be achieved by fractional crystallization by taking advantage of the generally higher solubility of the *trans* species in non-polar solvents. The complexes were characterized by IR, ^1H and ^{13}C NMR spectroscopies. Some general trends of $\nu(C{\equiv}N)$ and $\nu(Pt{-}Cl)$ stretching frequencies as well as of the $^2J(PtC)$ values have been found to be useful in determining the stereogeometry of the *cis* and *trans* isomers of the $Cl_2Pt(NCR)_2$ complexes.

Introduction

The nitrile complexes $Cl_2Pt(NCR)_2$ ($R=CH_3$, C_6H_5) are widely used as precursors for other coordination and organometallic compounds [1]. Their synthesis may be accomplished by either one of the two methods, $K_2PtCl_4/H_2O/RCN$(excess) [2–4] or $PtCl_2/RCN$(neat) [5, 6], both of which usually yield the bis(nitrile) complexes as a mixture of *cis* and *trans* isomers in different ratios depending on the experimental conditions such as the reaction temperature and the reaction time. Although the separation of the stereoisomers is often unnecessary when the $Cl_2Pt(NCR)_2$ complexes are used in nitrile ligand metathesis reactions, this is however important when the reactivity involves the coordinated nitriles [4, 7, 8].

We have recently reported that acetonitrile and benzonitrile ligands in *cis*- and *trans*-$Cl_2Pt(NCR)_2$ complexes are converted to the corresponding 2-oxazoline derivatives *cis*- and *trans*-$Cl_2Pt[\overline{N{=}C(R)OCH_2CH_2}]_2$ by reaction with $HOCH_2CH_2Cl$/base or $\overline{OCH_2CH_2}/Cl^-$ systems [8]. In contrast to the organic synthetic procedure, which occurs in strongly acidic media [9], the Pt(II)-promoted nitrile to 2-oxazoline conversion proceeds under basic conditions.

In order to explore the generality of these latter reactions as a function of the nature of the metal-coordinated nitrile ligands [10], we set out to prepare a series of *cis*- and *trans*-$Cl_2Pt(NCR)_2$ ($R=C_6H_5$, p-$CH_3C_6H_4$, p-$CF_3C_6H_4$, o-$CH_3C_6H_4$, CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $(CH_3)_3C$) complexes, in which the electronic and steric properties of the R groups have been varied over a wide range. Except for the C_6H_5CN [3] and CH_3CN [4] derivatives, a detailed spectroscopic investigation of other bis(nitrile)dichloroplatinum(II) complexes is lacking. In the present work, we report the full spectroscopic characterization of the bis(nitrile) complexes based on IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopies; some general trends of $\nu(C{\equiv}N)$ and $\nu(Pt{-}Cl)$ stretching frequencies as well as of the $^2J(PtC)$ values appear to be useful in determining the stereogeometry of the *cis* and *trans* isomers of the $Cl_2Pt(NCR)_2$ complexes.

Experimental

Starting materials and general procedures

Commercially available $PtCl_2$ was used. Potassium tetrachloroplatinate, K_2PtCl_4, was prepared as described

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in ref. 11. All the solvents, except tetrahydrofuran (THF) which was distilled over sodium and benzophenone, and all the organonitriles used in this work were of reagent grade purity and used as received. IR spectra in the region 4000–400 cm^{-1} were taken on a Perkin-Elmer 983 spectrophotometer; FT-IR spectra in the range 400–100 cm^{-1} were taken on a Bruker IFS 113V instrument. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 spectrometer. The microanalyses were carried out by the Department of Analytical Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected.

The nitrile complexes were usually obtained as a mixture of *cis* and *trans* isomers in variable proportions depending on the experimental method used for their preparation and, for each method, also on the experimental conditions, as summarized in Table 1 (see 'Results and discussion'). In particular, the mixtures obtained from the reactions with alkylnitriles were analyzed by HPLC with a Perkin-Elmer series 2 instrument on a C_8 column using acetonitrile as eluant; it was observed that both isomers were present and the *cis* one was eluted first. However, we found that a complete and quantitative separation of the stereoisomers of each bis(nitrile) compound could be achieved by fractional crystallization by taking advantage of the generally higher solubility of the *trans* species in non-polar solvents as described below; the purity of the isomers so obtained was checked by IR and ^{13}C NMR spectroscopies.

Synthesis of bis(nitrile)dichloroplatinum(II) complexes

Preparation of cis-$Cl_2Pt(NCCH_3)_2$ (1a)

Method (1). The compound *cis*-$Cl_2Pt(NCCH_3)_2$ was prepared by the standard procedure of Hoffman and Bugge [2] from potassium tetrachloroplatinate(II) and acetonitrile as recently described by Natile and coworkers [4]. K_2PtCl_4 (2.0 g, 4.82 mmol) and acetonitrile (3.8 ml, 73 mmol) were reacted in water (40 ml) at room temperature for 3 days. Compound **1a** together with the *trans* isomer **1b** (see below) was extracted from the reaction mixture with CH_2Cl_2 (3×20 ml). The organic solution was dried over anhydrous Na_2SO_4 for 3 h, then filtered off and taken to dryness. Addition of Et_2O (30 ml) gave a yellow solid, which was filtered off and treated with CH_3CN (3×5 ml) which caused only compound **1a** to dissolve, while solid **1b** was recovered from the glass frit after washing with Et_2O (3×3 ml). The combined ethereal–acetonitrile solution was evaporated under reduced pressure to 2 ml and by addition of Et_2O (10 ml) the light yellow product **1a** was precipitated. It was collected by filtration and dried under vacuum. Yield 1.35 g (81%), m.p. 202–204 °C.

Method (2). **1a** was prepared also by reacting solid $PtCl_2$ (1.0 g, 3.8 mmol) with neat CH_3CN (40 ml) at 90 °C until the solid dissolved (*c.* 1h). The hot solution was filtered off to remove traces of undissolved platinum species, allowed to reach room temperature and evaporated under reduced pressure to *c.* 15 ml. After filtration to remove the insoluble *trans* species **1b**, the solution was concentrated under reduced pressure to *c.* 5 ml and treated with Et_2O (20 ml) to give **1a** as a yellow precipitate. After filtration, **1a** was washed with Et_2O (2×5 ml) and dried under vacuum. Yield 1.03 g (78%).

Preparation of trans-$Cl_2Pt(NCCH_3)_2$ (1b)

This compound was obtained as a by-product in the synthesis of **1a** according to either method (1) or (2) (see above). Method (1): yield 0.250 g (15%); method (2): yield 0.265 g (20%), m.p. 198–200 °C.

Preparation of cis-$Cl_2Pt(NCC_6H_5)_2$ (2a)

Method (1). **2a** was prepared by reacting K_2PtCl_4 (3.40 g, 8.2 mmol) with benzonitrile (8.4 ml, 82 mmol) in water (40 ml) at 60 °C for 6 h. Then the reaction mixture was pumped to dryness and the solid residue was extracted with CH_2Cl_2 (3×20 ml). The combined dichloromethane extractant solutions were dried over anhydrous Na_2SO_4 for 2 h, then filtered off and taken to dryness under reduced pressure to give a solid residue. Treatment with hot benzene (2×10 ml) caused the *trans* isomer to dissolve. The insoluble *cis* isomer **2a** was filtered off, washed with petroleum ether (3×5 ml) and dried under vacuum. Yield 2.32 g (60%), m.p. 215–217 °C.

Method (2). The synthesis was carried out as reported in refs. 3 and 6, starting from solid $PtCl_2$ (1.40 g, 5.25 mmol) in benzonitrile (60 ml) for 1 h at 100 °C. After this time, the hot solution was filtered off and the filtrate was pumped to dryness and treated with hot benzene. Working up as described above by method (1) gave **2a**. Yield 1.98 g (80%).

Preparation of trans-$Cl_2Pt(NCC_6H_5)_2$ (2b)

Compound **2b** was obtained by pumping to dryness the benzene solution obtained as described above by either method (1) or (2) used for the synthesis of **2a**. Upon treatment of the solid residue with petroleum ether (10 ml), a light yellow solid was obtained, which was filtered off, washed with petroleum ether (2×5 ml) and dried under vacuum. Method (1): yield 1.24 g (32%); method (2): yield 0.37 g (15%), m.p. 208–210 °C.

Preparation of cis-$Cl_2Pt(NCC_6H_4$-p-$CH_3)_2$ (3a)

A solution of K_2PtCl_4 (3.04 g, 7.32 mmol) in water (10 ml) was reacted with an excess of *p*-tolunitrile (8.00 ml, 67 mmol) at 90 °C for 10 h. After cooling to room temperature, the reaction mixture was treated with CH_2Cl_2 (5×30 ml) and the combined extractant solutions were pumped to dryness. Upon treatment with n-hexane (500 ml) under vigorous stirring for *c.* 4 h in order to dissolve the unreacted free nitrile, **3a** was formed as a pale yellow solid. It was filtered off, washed with n-hexane (7×5 ml) and dried under vacuum. Yield 3.08 g (84%), m.p. 204–205 °C. *Anal.* Calc. for $C_{16}H_{14}N_2Cl_2Pt$: C, 38.41; H, 2.82; N, 5.69; Cl, 14.17. Found: C, 38.58; H, 2.70; N, 5.60; Cl, 14.00%. No *trans* isomer could be isolated either from this reaction or by reacting $PtCl_2$ with *p*-tolunitrile for 10 h in boiling 1,2-dichloroethane.

Preparation of cis-$Cl_2Pt(NCC_6H_4$-p-$CF_3)_2$ (4a)

A solution of K_2PtCl_4 (2.08 g, 5.00 mmol) in water (50 ml) was reacted with an excess of solid *p*-(trifluoromethyl)benzonitrile (8.56 g, 50.02 mmol) dissolved in 1,2-dichloroethane (10 ml) for 4 h at 65 °C and for an additional 10 h at 85 °C. The reaction mixture was treated with CH_2Cl_2 (5×30 ml) and the combined extractant solutions were taken to dryness under reduced pressure at 70 °C to dry off the free starting nitrile. A white solid was obtained, which was treated with n-hexane (30 ml), filtered off, washed with Et_2O (2×5 ml) and dried under vacuum. Yield 0.79 g (26%), m.p. 207–208 °C. *Anal.* Calc. for $C_{16}H_8N_2F_6Cl_2Pt$: C, 31.59; H, 1.32; N, 4.61; Cl, 11.66. Found: C, 31.14; H, 1.37; N, 4.63; Cl, 11.76%. From this reaction as well as by refluxing $PtCl_2$ with an excess of *p*-(trifluoromethyl)benzonitrile dissolved in 1,2-bis dichloroethane only the *cis* isomer could be isolated.

Preparation of cis-$Cl_2Pt(NCC_6H_4$-o-$CH_3)_2$ (5a)

A solution of K_2PtCl_4 (1.40 g, 3.37 mmol) in water (10 ml) was reacted with an excess of *o*-tolunitrile (4.27 ml, 36.12 mmol) for 6 h at 60 °C. After cooling to room temperature, the reaction mixture was treated with CH_2Cl_2 (5×30 ml) and the combined extractant solutions were pumped to dryness. The solid residue was treated with hot benzene (80 ml) which caused the *trans* isomer **5b** (see below) to solubilize. The insoluble **5a** was filtered off, washed with Et_2O (2×5 ml) and dried under vacuum. Yield 0.71 g (42%), m.p. 215–216 °C. *Anal.* Calc. for $C_{16}H_{14}N_2Cl_2Pt$: C, 38.41; H, 2.82; N, 5.60; Cl, 14.17. Found: C, 38.17; H, 2.83; N, 5.64; Cl, 14.02%.

Preparation of trans-$Cl_2Pt(NCC_6H_4$-o-$CH_3)_2$ (5b)

The benzene solution from the synthesis of **5a** was evaporated to dryness under reduced pressure to give a solid residue. Upon treatment with petroleum ether (5 ml), a pale yellow solid was obtained which was filtered off, washed with Et_2O (2×5 ml) and dried under vacuum. Yield 0.39 g (23%), m.p. 210–211 °C. *Anal.* Calc. for $C_{16}H_{14}N_2Cl_2Pt$: C, 38.41; H, 2.82; N, 5.60; Cl, 14.17. Found: C, 38.21; H, 2.85; N, 5.62; Cl, 14.20%.

Preparation of cis-$Cl_2Pt(NCCH_2CH_3)_2$ (6a)

The reaction was carried out as reported for **5a** starting from K_2PtCl_4 (2.00 g, 4.82 mmol) and an excess of propionitrile (5.5 ml, 77 mmol) in water (15 ml) for 2 h at 65 °C. After cooling to room temperature, the reaction mixture was treated with CH_2Cl_2 (5×30 ml). The combined extractant solutions were pumped to dryness. The residue was treated with petroleum ether (5 ml) to give a solid which was filtered off, washed with petroleum ether (2×5 ml) and dissolved in THF (30 ml). Upon addition of n-hexane (10 ml) a pale yellow precipitate was formed, which was filtered off and dried under vacuum. Yield 0.87 g (48%), m.p. 100–111 °C. *Anal.* Calc. for $C_6H_{10}N_2Cl_2Pt$: C, 19.16; H, 2.68; N, 7.45; Cl, 18.85. Found: C, 18.93; H, 2.59; N, 7.54; Cl, 18.50%. The same reaction was carried out also at room temperature for 80 h and **6a** was isolated as described above. Yield 1.02 g (56%).

Preparation of trans-$Cl_2Pt(NCCH_2CH_3)_2$ (6b)

The THF/n-hexane solution from the synthesis of **6a** was pumped to dryness and treated with n-hexane (10 ml) to give a yellow solid, which was filtered, washed with n-hexane (2×2 ml) and dried under vacuum. The yield was 0.29 g (16%) from the reaction at high temperature and 0.27 g (15%) from that at room temperature. m.p. 175–176 °C.

Preparation of cis-$Cl_2Pt(NCCH_2CH_2CH_3)_2$ (7a)

The reaction was carried out as reported for **6a** starting from K_2PtCl_4 (1.50 g, 3.61 mmol) and an excess of n-butyronitrile (5 ml, 57.8 mmol) in water (10 ml) for 1 h at 90 °C. The *cis* isomer was obtained on addition of n-hexane (10 ml) to a THF solution of the isolated reaction mixture. Yield 1.00 g (68%). m.p. 85–86 °C. *Anal.* Calc. for $C_8H_{14}N_2Cl_2Pt$: C, 23.77; H, 3.49; N, 6.93; Cl, 17.54. Found: C, 23.22; H, 3.36; N, 6.88; Cl, 17.44%. The same reaction was carried out also at room temperature for 90 h and worked up as described for **6a**. Yield 0.80 g (55%).

Preparation of trans-$Cl_2Pt(NCCH_2CH_2CH_3)_2$ (7b)

The THF/n-hexane solution obtained in the synthesis of **7a** was pumped to dryness and then treated with Et_2O (10 ml). A yellow solid product was obtained, which was filtered off, washed with Et_2O (2×2 ml) and dried under vacuum. The yield was 0.30 g (20%)

when the reaction was carried out at high temperature and 0.20 g (14%) when it was performed at room temperature. m.p. 190–191 °C.

Preparation of cis-$Cl_2Pt[NCCH(CH_3)_2]_2$ (8a)

The reaction was carried out as reported for **6a** starting from K_2PtCl_4 (1.50 g, 3.61 mmol) and isobutyronitrile (5.30 ml, 58.3 mmol) either for 3 h at 75 °C or for 48 h at room temperature. The pale yellow solid **8a** was isolated by addition of Et_2O (10 ml) to a THF solution (30 ml) of the reaction mixture. The yields were 1.00 g (68%) and 1.02 g (70%), respectively. m.p. 145–146 °C. *Anal.* Calc. for $C_{18}H_{14}N_2Cl_2Pt$: C, 23.77; H, 3.49; N, 6.93; Cl, 17.54. Found: C, 23.95; H, 3.51; N, 6.90; Cl, 17.32%.

Preparation of trans-$Cl_2Pt[NCCH(CH_3)_2]_2$ (8b)

The THF/n-hexane solutions obtained from the two independent syntheses of **8a** were taken to dryness and each residue treated with Et_2O (20 ml) to give a yellow solid which was filtered off, washed with Et_2O (2×2 ml) and dried under vacuum. The yields were 0.30 g (20%) and 0.10 g (7%), respectively. m.p. 115–116 °C.

Preparation of cis-$Cl_2Pt[NCC(CH_3)_3]_2$ (9a)

Method (1). The reaction was carried out as described for **6a** starting from K_2PtCl_4 (2.08 g, 5.00 mmol) and trimethylacetonitrile (5.53 ml, 50 mmol) for 30 min at 80 °C and then for an additional 3 h at 65 °C. After cooling to room temperature, the reaction mixture was treated with CH_2Cl_2 (5×30 ml) and the combined dichloromethane extractant solutions were pumped to dryness. The pale yellow residue was treated with Et_2O (30 ml) and the suspension filtered. The insoluble material was found to be the *trans* isomer **10a** (see below). The ethereal solution was taken to dryness and a solid formed on adding petroleum ether (2×5 ml). It was filtered off, washed with petroleum ether (2×3 ml) and dried under vacuum. Yield 0.22 g (10%), m.p. 200–201 °C. *Anal.* Calc. for $C_{10}H_{18}N_2Cl_2Pt$: C, 27.78; H, 4.19; N, 6.84; Cl, 16.40. Found: C, 27.55; H, 4.20; N, 6.50; Cl, 16.48%.

Method (2). $PtCl_2$ (0.50 g, 1.88 mmol) was refluxed in trimethylacetonitrile (25 ml, 226 mmol) for 1.5 h at 95 °C. After cooling to room temperature, the reaction mixture was taken to dryness under reduced pressure and the solid residue worked up as reported above in method (1). Yield 0.29 g (35%).

Preparation of trans-$Cl_2Pt[NCC(CH_3)_3]_2$ (9b)

The solids obtained by filtration of the ethereal solution in the above reported syntheses of **9a** were washed with petroleum ether (2×2 ml) and dried under vacuum. The yields were 1.24 g (57%) (method (1)) and 0.42 g (52%) (method 2)). m.p. 193–194 °C. The yield of **9b** could be significantly increased to 80% using method (1) described above for **9a** by reacting K_2PtCl_4 and trimethylacetonitrile in water at room temperature for 4 days.

Results and discussion

The bis(nitrile)dichloroplatinum(II) complexes **1–9** were prepared according to the following general reactions (1) and (2), which refer to methods (1) and (2), respectively, reported in 'Experimental'.

$$K_2PtCl_4 + RCN(\text{excess}) \xrightarrow{H_2O} \textit{cis-} \text{ and } \textit{trans-}Cl_2Pt(NCR)_2 \tag{1}$$

$$PtCl_2 + RCN(\text{neat}) \longrightarrow \textit{cis-} \text{ and } \textit{trans-}Cl_2Pt(NCR)_2 \tag{2}$$

In reaction (1), each nitrile ligand was added in large excess (*c.* 100-fold or more with respect to Pt) to an aqueous solution of K_2PtCl_4 and the reaction mixture stirred until the initial red color of the solution turned yellow. This occurred in a few hours on heating at *c.* 60–90 °C or in a few days on running the reaction at room temperature. Reaction (2) was carried out by refluxing solid $PtCl_2$ and neat RCN (except for R = *p*-$C_6H_4CF_3$ and *p*-$C_6H_4CH_3$) for a few hours until dissolution of $PtCl_2$ was complete.

From both reactions (1) and (2) each nitrile complex was generally obtained as a mixture of *cis* and *trans* isomers, in variable proportions depending upon the experimental conditions used as summarized in Table 1. From these data it is observed that the *cis* isomer is usually formed to a greater extent compared to the corresponding *trans* species. These results parallel those previously reported for the CH_3CN reactions [4], which show that the *cis* isomer is kinetically favoured, but then it isomerizes to the *trans* species on heating or on a prolonged stirring at room temperature. As for *p*-tolunitrile and *p*-(trifluoromethyl)benzonitrile complexes **3a** and **4a**, they were isolated only as *cis* forms; furthermore, the low yield of **4a** may be explained by either the low solubility of the nitrile in the reaction medium or the low nucleophilicity of the nitrogen atom owing to the presence of the strong electron-withdrawing–CF_3 group on the aryl ring.

The *cis* and *trans* isomers for each bis(nitrile) complex were separated by fractional crystallization by taking advantage of their different solubilities, the *cis* form generally being less soluble in non or slightly polar solvents as reported for the benzonitrile [3] and acetonitrile [4] complexes. In particular, we found that the less polar *trans* arylnitrile derivatives are better

TABLE 1. Yields of isolated products and experimental conditions used for the synthesis of *cis* and *trans* isomers of bis(nitrile)dichloroplatinum(II) complexes

Method (1)					
$K_2PtCl_4 \xrightarrow{H_2O, RCN} cis\text{-}Cl_2Pt(NCR)_2 + trans\text{-}Cl_2Pt(NCR)_2$					
$R = CH_3$	**1a**	(81%)	**1b**	(15%)	r.t., 3 days
$R = CH_3$	**1a**	(30%)	**1b**	(66%)	75 °C, 3 h
$R = C_6H_5$	**2a**	(60%)	**2b**	(32%)	60 °C, 6 h
$R = C_6H_4\text{-}p\text{-}CH_3$	**3a**	(84%)			90 °C, 10 h
$R = C_6H_4\text{-}p\text{-}CF_3$	**4a**	(26%)			65 °C, 4 h + 85 °C, 10 h
$R = C_6H_4\text{-}o\text{-}CH_3$	**5a**	(42%)	**5b**	(23%)	60 °C, 6 h
$R = CH_2CH_3$	**6a**	(48%)	**6b**	(16%)	65 °C, 2 h
$R = CH_2CH_3$	**6a**	(56%)	**6b**	(15%)	r.t., 80 h
$R = CH_2CH_2CH_3$	**7a**	(68%)	**7b**	(20%)	90 °C, 1 h
$R = CH_2CH_2CH_3$	**7a**	(55%)	**7b**	(14%)	r.t., 90 h
$R = CH(CH_3)_2$	**8a**	(68%)	**8b**	(20%)	75 °C, 3 h
$R = CH(CH_3)_2$	**8a**	(70%)	**8b**	(7%)	r.t., 48 h
$R = C(CH_3)_3$	**9a**	(10%)	**9b**	(57%)	80 °C, 30 min + 65 °C, 3 h
$R = C(CH_3)_3$	**9a**	(<5%)	**9b**	(80%)	r.t., 4 days
Method (2)					
$PtCl_2 \xrightarrow{RCN} cis\text{-}Cl_2Pt(NCR)_2 + trans\text{-}Cl_2Pt(NCR)_2$					
$R = CH_3$	**1a**	(78%)	**1b**	(20%)	90 °C, 1 h
$R = C_6H_5$	**2a**	(80%)	**2b**	(15%)	100 °C, 1 h
$R = C(CH_3)_3$	**9a**	(35%)	**9b**	(52%)	95 °C, 1.5 h

solubilized in hot benzene, while the corresponding alkylnitriles in tetrahydrofuran.

The characterization of the isomers was carried out by IR, ^1H and ^{13}C NMR spectroscopies. As expected for Pt(II) coordination [12], the IR spectra (nujol mulls) of **1**–**9** (Table 2) show the $\nu(C{\equiv}N)$ stretching in the range 2272–2317 cm^{-1} as a medium to strong absorption about 50 cm^{-1} at higher wavenumbers with respect to the corresponding free nitriles.

The two homologous series of *trans* and *cis* isomers **1**–**9** display similar $\nu(C{\equiv}N)$ values, which always appear at slightly higher wavenumbers (*c.* 5–10 cm^{-1}) for the *trans* with respect to the *cis* species. This spectroscopic feature may be related to a slightly higher σ-donor ability of Cl^- compared to RCN ligands. An X-ray study of *cis*- and *trans*-$Cl_2Pt(NCC_6H_5)_2$ derivatives shows that the Pt–N bond distances are very close in the two isomers [13].

The 800–600 cm^{-1} region has been investigated in detail by several authors [3, 13, 14] for *cis*- and *trans*-$Cl_2Pt(NCC_6H_5)_2$ derivatives. The *cis* form shows δ(CH) out-of-plane deformation vibrations as split bands at 680, 692 cm^{-1} and 754, 776 cm^{-1}, while the *trans* isomer shows only two strong single bands at 683 and 762 cm^{-1}. Although we observe a similar behaviour for **2a** and **2b**, the other arylnitrile derivatives **3a**, **4a** and **5a**, **5b** show only one single absorption in the above reported region, thus making these bands not of diagnostic use for the identification of these isomers.

The IR analysis reported for *cis*- and *trans*-$Cl_2Pt(NCCH_3)_2$ complexes showed that the band multiplicity does not significantly change for the two stereoisomers although their relative intensities did change [4]. The alkylnitrile derivatives **6**–**9** show very similar

TABLE 2. IR data for compounds **1**–**9**[a]

Compound	ν(CN)[b]	Pt–Cl region[c]	Other bands
1a	2302s[d] (2254s)	354s, 362s	1029s, 722w
1b	2307s[e]	348s	1021s, 722w
2a	2286m (2230s) 2286m[f]	348s, 359s	547s[g], 680s[g], 692s[g], 754s[g], 776s[g], 1967s[g], 1990s[g]
2b	2290m 2294m[f]	308m, 345s, 356s	550s[g], 535m[g], 683s[g], 762s[g], 1163s[g], 1177s[g], 1199s[g]
3a	2285m (2227s)[h]	335m, 348m	543s, 817s, 1181s
4a	2293w (2236s)[h] 2288m[f]	346m, 357m	836w, 849m, 1019m, 1065s, 1108s, 1133s, 1174s, 1321s[i]
5a	2272s (2225s)	351s, 361s	459s, 556w, 722w, 768s, 1217m
5b	2287s	306m, 327m, 350s	462s, 555m, 566m, 722s, 737s, 757s, 1044m, 1161m, 1217s
6a	2302m (2247s)	340m, 351m	722w, 783s, 1066s
6b	2317m	319m, 346s	722m, 783s, 1066m
7a	2311m (2249s)	349s, 357s	732s, 770m
7b	2313s	353s	732m, 772m
8a	2301m (2245s)	352s, 358s	943s, 1108s, 1169m[k]
8b	2308m	337s	721m, 913m, 939m, 1102s, 1167m[k]
9a	2299m (2234s)	298w, 352s, 358s	571m, 722s, 891m, 940m, 1209s, 1167m
9b	2304m	334s, 352m	722m, 871m, 1208m[l], 1238s[l]

[a] Nujol mull, ν in cm^{-1} (± cm^{-1}); abbreviations: s = strong, m = medium, w = weak. [b] In parentheses ν(CN) of the corresponding free nitriles (neat unless otherwise stated). [c] FT-IR, nujol mull (± cm^{-1}). [d] A combination band at 2330 cm^{-1} is also present, see ref. 14b. [e] Combination band at 2339 cm^{-1}. [f] CH_2Cl_2 solution. [g] For tentative assignment see ref. 13. [h] Nujol mull. [i] C–F stretching. [k] Iso-propyl skeletal vibrations. [l] t-Butyl skeletal vibrations.

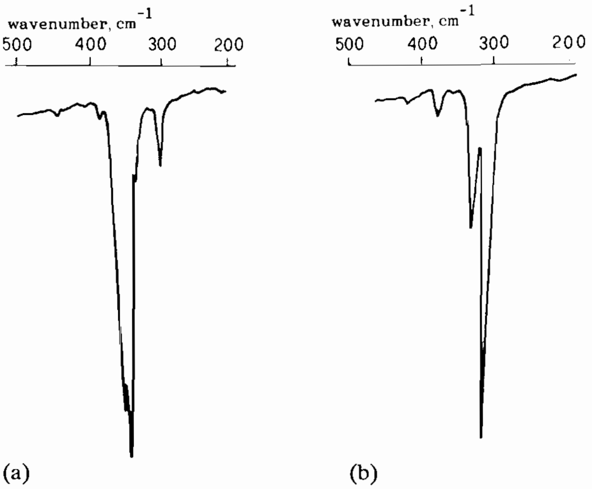


Fig. 1. Far-IR spectra in the region 500–200 cm^{-1} of the compounds cis-$\mathrm{Cl_2Pt(NCBu^t)_2}$ (a) and $trans$-$\mathrm{Cl_2Pt(NCBu^t)_2}$ (b).

TABLE 3. ^{1}H NMR data[a] for compounds **1–9** and the corresponding free nitriles

Compound	$\delta(R\mathrm{CN})_{\mathrm{coord}}$	$\delta(R\mathrm{CN})_{\mathrm{free}}$
1a	2.65s[b]	2.03s[b]
1b	2.75s[b]	
2a	7.84–7.53m[c]	7.69–7.44m[c]
2b	7.83–7.53m[c]	7.85–7.74m[c]
3a	2.47s[b], 7.69–7.35m[c]	2.40s[b], 7.55–7.25m[c]
4a[d]	7.83–8.03m[c]	7.85–7.74m[c]
5a	2.59s[b], 7.33–7.73m[c]	2.53s[b], 7.23–7.61m[c]
5b	2.60s[b], 7.36–7.72m[c]	
6a	1.37t[e], 2.84q[f]	1.23t[g], 2.32q[h]
6b	1.34t[i], 2.85q[j]	
7a	1.08t[k], 1.79m[l], 2.80t[m]	1.05t[n], 1.67m[o], 2.34t[p]
8a	1.40d[q], 3.18st[r]	1.29d[s], 2.69st[t]
8b	1.38d[u], 3.17st[v]	
9a	1.45s[z]	1.44s[z]
9b	1.43s[z]	

[a] The spectra were recorded in $\mathrm{CD_2Cl_2}$; proton chemical shifts are reported from $\mathrm{Me_4Si}$ by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm. J is given in Hz. Abbreviations: s = singlet, t = triplet, q = quartet, st = septet, m = multiplet. [b] $\mathrm{CH_3}$ protons. [c] $\mathrm{C_6H_5}$ protons. [d] ^{19}F NMR (referenced to internal $\mathrm{CFCl_3}$): $\delta(\mathrm{CF_3})$ −10.7s. [e] $\mathit{CH_3}\mathrm{CH_2}$ protons, ^3J(HH) = 7.97. [f] $\mathrm{CH_3}\mathit{CH_2}$ protons, ^3J(HH) = 7.97. [g] $\mathit{CH_3}\mathrm{CH_2}$ protons, ^3J(HH) = 7.59. [h] $\mathrm{CH_3}\mathit{CH_2}$ protons, ^3J(HH) = 7.59. [i] $\mathit{CH_3}\mathrm{CH_2}$ protons, ^3J(HH) = 7.58. [j] $\mathrm{CH_3}\mathit{CH_2}$ protons, ^3J(HH) = 7.58. [k] $\mathit{CH_3}\mathrm{CH_2CH_2}$ protons, ^3J(HH) = 7.35. [l] $\mathrm{CH_3}\mathit{CH_2}\mathrm{CH_2}$ protons. [m] $\mathrm{CH_3CH_2}\mathit{CH_2}$ protons, ^3J(HH) = 6.88. [n] $\mathit{CH_3}\mathrm{CH_2CH_2}$ protons, ^3J(HH) = 7.21. [o] $\mathrm{CH_3}\mathit{CH_2}\mathrm{CH_2}$ protons. [p] $\mathrm{CH_3CH_2}\mathit{CH_2}$ protons, ^3J(HH) = 6.99. [q] $(\mathit{CH_3})_2\mathrm{CH}$ protons, ^3J(HH) = 7.04. [r] $(\mathrm{CH_3})_2\mathit{CH}$ protons, ^3J(HH) = 7.04. [s] $(\mathit{CH_3})_2\mathrm{CH}$ protons, ^3J(HH) = 7.00. [t] $(\mathrm{CH_3})_2\mathit{CH}$ protons, ^3J(HH) = 7.00. [u] $(\mathit{CH_3})_2\mathrm{CH}$ protons, ^3J(HH) = 7.07. [v] $(\mathrm{CH_3})_2\mathit{CH}$ protons, ^3J(HH) = 7.07. [z] $(\mathit{CH_3})_3\mathrm{C}$ protons.

IR spectra in the finger print region but not with a regular trend in their intensities. Absorptions in the region 500–600 cm^{-1} are observed for most of the complexes reported in Table 2 and they have been tentatively assigned to ν(Pt–N) as reported in the literature [12, 14] for cis-$\mathrm{Cl_2Pt(NCC_6H_5)_2}$.

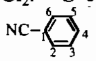
The *trans* or *cis* stereogeometry of dichloro complexes of Pt(II) can usually be deduced by the presence of one or two bands, respectively, in the Pt–Cl region [15]. This is found for all *cis* isomers **1–9**, but for the *trans* isomers only **1b**, **7b** and **8b** have one band, while all the others display two or even three bands in that region. This behavior was previously observed for the bis-nitrile complexes $trans$-$\mathrm{Cl_2Pt(NCC_6H_5)_2}$ [3, 7], the bis-imido ester compounds $trans$-$\mathrm{Cl_2Pt[N(H){=}C(OMe)C_6H_5]_2}$ [7a] and for the bis(2-oxazoline) derivatives $trans$-$\mathrm{Cl_2Pt[\overline{NC(R)OCH_2CH_2}]_2}$ ($\mathrm{R = CH_3, C_6H_5}$) [8, 10]. Although not perhaps of diagnostic use for the identification of the stereoisomers, we have observed that for each set of the bis(nitrile) isomers the difference between the frequencies of the two bands in the *cis* isomers is about 10 cm^{-1}, while the difference for the *trans* isomers is in a larger range (up to 50 cm^{-1}). As a typical example, the IR spectra of compounds **9a** and **9b** in the Pt–Cl region are reported in Fig. 1.

The ^{1}H NMR data for **1–9** are reported in Table 3. It is observed that for each couple of *cis* and *trans* isomers the ^{1}H NMR spectra are very similar, thus making their identification impossible. As for the alkylnitrile derivatives, coupling to ^{195}Pt is observed only for $\mathrm{R = CH_3}$ (**1a**: ^4J(HPt) 13.02 Hz; **1b**: ^4J(HPt) 15.10 Hz).

The ^{13}C NMR data of complexes **1–9** together with those of the corresponding free nitriles are reported in Table 4. Of particular significance for the characterization of the isomer stereogeometry are the ^2J(PtC) values, which fall in the range 218–234 Hz for all the *cis* species and in the range 273–298 Hz for the *trans* derivatives. This feature has been previously observed only for *cis*- and $trans$-$\mathrm{Cl_2Pt(NCC_6H_5)_2}$ isomers [3] and it was related to the higher *trans* influence of chlorine compared to the benzonitrile ligand. Although the *trans* influence estimate based on NMR data for ligands in platinum(II) complexes has been derived by examining the magnitude of the coupling constants of directly bonded nuclei (i.e. H, P, C, etc.) to ^{195}Pt [16, 17], it has been reported that Pt coupling over two bonds gave similar results. For instance, an NMR-based *trans* influence series derived from the magnitudes of ^1J(PtC), ^2J(PtC) and ^3J(PtC) coupling constants has been reported [18] for cationic complexes of the type $trans$-$\mathrm{[(R)Pt(L)_2X]^+}$ (L = tertiary phosphine or arsine; R = alkyl, aryl; X = neutral ligand) and it has been related to the σ-donor ability of the ligand X *trans* to the R group. As the σ-donor ability of X increases and, consequently, its *trans* influence, the ligand will compete more effectively for the Pt(6s) orbital thus leading to

TABLE 4. ^{13}C NMR data[a] for compounds **1–9** and the corresponding free nitril

Compound	Coordinated nitriles		Free nitriles	
	$\delta(CN)$	Other	$\delta(CN)$	Other
1a	[b]	[b]	117.7 ($^{2}J_{\mathrm{CH}}$ 9.9)	CH_3: 1.71 ($^{1}J_{\mathrm{CH}}$ 136.02)
1b	[b]	[b]		
2a	115.3 ($^{2}J_{\mathrm{PtC}}$ 234)	Ph[c]: C_1 109.1; $C_{2,6}$ 133.7; $C_{3,5}$ 129.6; C_4 135.2	119.27	Ph[c]: C_1 112.77 ($^{2}J_{\mathrm{CH}}$ 8.8); $C_{2,6}$ 132.53 ($^{1}J_{\mathrm{CH}}$ 165.4, $^{2}J_{\mathrm{CH}}$ 6.7); $C_{3,5}$ 129.67 ($^{1}J_{\mathrm{CH}}$ 164.7, $^{2}J_{\mathrm{CH}}$ 7.2); C_4 133.27 ($^{2}J_{\mathrm{CH}}$ 7.2, $^{1}J_{\mathrm{CH}}$ 163.3)
2b	116.8 ($^{2}J_{\mathrm{PtC}}$ 289)	Ph[c]: C_1 109.0 ($^{3}J_{\mathrm{PtC}}$ 20); $C_{2,6}$ 133.7; $C_{3,5}$ 129.5; C_4 135.4		
3a	118.1 ($^{2}J_{\mathrm{PtC}}$ 226)	Ph[c]: C_1 106.2; $C_{2,6}$ 134.0; $C_{3,5}$ 130.7; C_4 147.8; CH_3: 22.35	119.47	Ph[c]: C_1 109.67 ($^{2}J_{\mathrm{CH}}$ 8.6); $C_{2,6}$ 132.44 ($^{1}J_{\mathrm{CH}}$ 165.3, $^{3}J_{\mathrm{CH}}$ 6.4); $C_{3,5}$ 130.24 ($^{1}J_{\mathrm{CH}}$ 161.3, $^{3}J_{\mathrm{CH}}$ 5.4, $^{3}J_{\mathrm{C\text{-}Me}}$ 5.3); C_4 144.26 ($^{2}J_{\mathrm{C\text{-}Me}}$ 6.6); CH_3 21.95 ($^{1}J_{\mathrm{CH}}$ 126.90)
4a	116.17[d]	Ph[c]: C_1 109.93; $C_{2,6}$ 134.99; $C_{3,5}$ 127.09; C_4[e]	117.86	Ph[c]: C_1 116.56 ($^{2}J_{\mathrm{CH}}$ 8.00); $C_{2,6}$ 133.19 ($^{1}J_{\mathrm{CH}}$ 170.8, $^{2}J_{\mathrm{CH}}$ 5.4); $C_{3,5}$ 126.50 ($^{1}J_{\mathrm{CH}}$ 168.9, $^{2}J_{\mathrm{CH}}$ 3.8); C_4 134.22; CF_3 123.64 ($^{1}J_{\mathrm{CF}}$ 272.7)
5a	115.40 ($^{2}J_{\mathrm{PtC}}$ 231)	Ph[c]: C_1 110.13; C_2-CH_3 145.26; C_3 131.26; C_4 135.58; C_5 127.13 C_6 134.21; CH_3: 20.78		
5b	116.93 ($^{2}J_{\mathrm{PtC}}$ 298)	Ph[c]: C_1 109.79; C_2-CH_3 145.29 C_3 131.19; C_4 135.58; C_5 127.07 C_6 134.27: CH_3: 20.75	118.33	Ph[c]: C_1 113.09; C_2 142.20 ($^{2}J_{\mathrm{CH}}$ 6.2); C_3 130.6 ($^{1}J_{\mathrm{CH}}$ 161.4, $^{2}J_{\mathrm{CH}}$ 6.2); C_4 133.14 ($^{1}J_{\mathrm{CH}}$ 162.4, $^{2}J_{\mathrm{CH}}$ 7.9); C_5 126.7 ($^{1}J_{\mathrm{CH}}$ 165.2, $^{2}J_{\mathrm{CH}}$ 7.6); C_6 132.87 ($^{1}J_{\mathrm{CH}}$ 165.3, $^{2}J_{\mathrm{CH}}$ 8.0); CH_3 20.13 ($^{1}J_{\mathrm{CH}}$ 127.82, $^{2}J_{\mathrm{CH}}$ 4.02)
6a	118.80 ($^{2}J_{\mathrm{PtC}}$ 229)	CH_2: 13.26; CH_3: 9.93	120.8	CH_2: 10.8 CH_3: 10.6
6b	119.75 ($^{2}J_{\mathrm{PtC}}$ 277)	CH_2: 12.99; CH_3: 2.79		
7a	117.89 ($^{2}J_{\mathrm{PtC}}$ 229)	CH_2-CN: 20.96; CH_2: 20.14; CH_3: 13.39	119.8	CH_2CN: 19.3 CH_2: 19.0 CH_3: 13.4
7b	119.04 ($^{2}J_{\mathrm{PtC}}$ 282)	CH_2-CN: 20.87; CH_2: 20.14 CH_3: 13.32		
8a	121.40 ($^{2}J_{\mathrm{PtC}}$ 222)	CH: 22.05; CH_3: 19.38	123.7	CH: 19.8 CH_3: 19.9
8b	122.58 ($^{2}J_{\mathrm{PtC}}$ 275)	CH: 22.02 ($^{3}J_{\mathrm{PtC}}$ 13.8) CH_3: 19.39 ($^{4}J_{\mathrm{PtC}}$ 5.7)		
9a	123.22 ($^{2}J_{\mathrm{PtC}}$ 218)	C: 30.67 CH_3: 28.03	125.1	C: 28.1 CH_3: 28.5
9b	124.42 ($^{2}J_{\mathrm{PtC}}$ 273)	C: 30.44 CH_3: 27.87		

[a] The spectra were recorded in CD_2Cl_2. ^{13}C chemical shifts are reported from Me_4Si by taking the chemical shift of dichloromethane-d_2 as +53.80 ppm. J is given in Hz.
[b] Too insoluble. [c] Carbon labeling: 

[d] ^{195}Pt satellites too weak to be observed. [e] $^{3}J_{\mathrm{C\text{-}F}}$ 7.6. [f] Too weak to be observed.

a decrease of the J(PtC) magnitude, which depends predominantly on the s character of the platinum hybrid orbital used in the Pt–R bond. Should these considerations hold also for the ^2J(PtC) values of the Pt–NCR complexes **1–9**, one would conclude that chloride has a higher *trans* influence of either an alkyl- or arylnitrile.

It is also worthwhile noting that for each homologous series of *cis* and *trans* isomers the ^2J(PtC) values do not significantly change upon changing the electronic and steric factors of the nitrile, thus indicating that they are not influenced by the nature of the R group of the RCN ligand. This observation may be explained by assuming that the *trans* influence is dominated by the σ-bonding orbital of the Pt–NCR bond and that the electron-withdrawing and π-acceptor properties of the R group have a small effect on the *trans* bond.

The chemical shift of the nitrile carbon is only slightly shielded with respect to the corresponding free nitriles. Interestingly, however, it is found that the shielding for the *cis* isomers is always almost twice (*c.* 2 ppm) that found for the corresponding *trans* isomers (*c.* 1 ppm). This shielding together with the shift of $\nu(C{\equiv}N)$ to higher wavenumbers may be related to the susceptibility of the nitrile carbon atom towards nucleophilic attack [4, 6, 10, 12]; this is similar to what is found for other isoelectronic ligands such as CO [16]* and RNC** in certain carbonyl and isocyanide transition metal complexes, respectively.

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*In the ^{13}C NMR spectrum free CO appears at $\delta(CO)_{free}$ 182.2 [19], while $\delta(CO)_{coord}$ fall in the range 151–180 [20].

**In ^{13}C NMR spectra, $\delta(CNR)_{free}$ fall in the range 155–165 ppm [21], while $\delta(CNR)_{coord}$ appear in the range 124–105 ppm [22].

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