Synthesis and study of Pt(II)-nitrile complexes. Multinuclear NMR spectra and crystal structures of compounds of the types [Pt(R-CN)Cl₃]⁻ and *cis* and *trans*-Pt(R-CN)₂Cl₂

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Abstract: Complexes of the type [Pt(R-CN)Cl₃]⁻ were synthesized and studied by ¹H, ¹³C, and ¹⁹⁵Pt NMR spectroscopies. The $^{2}J(^{195}\text{Pt-}^{13}\text{C})$ coupling constants are about 240 Hz. The signals due to the cyano carbon atoms of the coordinated ligands were observed at higher fields than those of the free ligands. The shielding on the cyano carbon increases as the alkyl chain lengthens and also when the branching increases. The 195 Pt signals of all the complexes were observed around -2000 ppm. The crystal structures of $(NMe_4)[Pt(C_3H_7-CN)Cl_3]$ (1) and $(NMe_4)[Pt(p-HO-C_6H_4-CN)Cl_3]$ (2) were determined. Compound 1 is monoclinic, $P2_1/c$, a = 8.384(5), b = 15.336(19), c = 11.759(9) Å, $\beta = 99.52(6)^\circ$, Z = 4, R = 0.054, and wR = 0.051. Crystal **2** is tetragonal with a = 16.222(6), c = 12.052(5) Å, Z = 8, R = 0.059, and wR = 0.044. The Pt—Cl bond *trans* to the nitrile ligand is shorter than normal (2.276(3) Å for 1 and 2.264(7) Å for 2) while the two other bonds are normal (2.293(4), 2.287(3) Å for 1 and2.320(7), 2.275(8) Å for 2). The Pt-N bonds are 1.97(1) Å (1) and 1.92(2) Å (2) and the segments Pt-N=C-C are linear. Disubstituted compounds were also synthesized and studied by multinuclear NMR. The ¹⁹⁵Pt signals of the cis isomers were observed at lower fields than those of the *trans* isomers ($\Delta \approx 65$ ppm), while the ¹³C signals of the cyano carbons of the *trans* isomers were observed at lower fields than those of the *cis* compounds ($\Delta \approx 0.6$ ppm). The *cis* complexes isomerize to the *trans* compounds upon heating. The crystal structures of cis-(3) and trans-Pt(C₂H₅-CN)₂Cl₂ (4) and also of cis-Pt(p-HO-C₆H₄- CN_2Cl_2 (5) were determined. Crystal 3 is monoclinic, $P2_1/c$, a = 7.506(5), b = 9.539(5), c = 14.823(7) Å, $\beta = 92.31(4)^\circ$, Z = 4, R = 0.050, and wR = 0.042. The trans isomer 4 is monoclinic with the Pt atom on an inversion centre, $P2_1/c$, a = 5.149(4), b = 5.149(4), b = 1.042. 9.394(8), c = 10.944(10) Å, $\beta = 97.84(7)^{\circ}$, Z = 4, R = 0.017 and wR = 0.020. Finally, compound 5 is triclinic, P-1, a = 7.464(3), b = 10.712(6), c = 12.291(5) Å, $\alpha = 75.63(4)^{\circ}, \beta = 75.63(4)^{\circ}, \gamma = 80.32(4)^{\circ}, Z = 2, R = 0.045, and wR = 0.056$. The Pt—Cl bond distances for the cis isomers are 2.269(5), 2.270(4) Å for 3 and 2.274(2), 2.279(3) Å for 5 while they are 2.289(3) Å for the trans isomer (4). The Pt-N bonds are 1.962(14), 1.988(11) Å (3), 1.972(7), 1.976(7) Å (5) and 1.969(5) Å for 4.

Key words: platinum, nitrile, NMR, isomerization, crystal structure.

Résumé: Des complexes de type $[Pt(R-CN)Cl_3]^-$ ont été synthétisés et étudiés par résonance magnétique nucléaire protonique, carbon-13 et platine-195. Les constantes de couplage ²J(¹⁹⁵Pt-¹³C) sont environ 240 Hz. La résonance des carbones cyano des ligands coordinés a été observée à un champ plus fort que celle des ligands libres. Ce blindage augmente lorsque la chaîne alkyle s'allonge et aussi lorsque le branchement augmente. Les signaux ¹⁹⁵Pt de tous les complexes ont été observés autour de -2000 ppm. Les structures cristallines des composés (NMe₄)[Pt(C₃H₇-CN)Cl₃] (1) et (NMe₄)[Pt(p-HO-C₆H₄-CN)Cl₃] (2) ont été déterminées. Le composé 1 est monoclinique, $P2_1/c$, a = 8,384(5), b = 15,336(19), c = 11,759(9) Å, $\beta = 99,52(6)^\circ$, Z = 4, R = 0.054 et wR = 0.051. Le cristal **2** est tétragonal avec a = 16,222(6), c = 12,052(5) Å. Z = 8, R = 0.059 et wR = 0.044. Le lien Pt-Cl en position trans du ligand nitrile est plus court qu'un lien normal (2,276(3) pour 1 et 2,264(7) Å pour 2) tandis que les deux autres liens sont normaux (2,293(4), 2,287(3) Å pour 1 et 2,320(7), 2,275(8) Å pour 2). Les liaisons Pt-N sont 1,97(1) Å (1) et 1.92(2) Å (2) et le segment Pt-N=C-C est linéaire. Des complexes disubstitués ont également été synthétisés et étudiés par résonance magnétique multinucléaire. Les signaux ¹⁹⁵Pt des isomères cis ont été observés à des champs plus faibles que ceux des complexes trans ($\Delta \approx 65$ ppm), tandis que les résonances des carbones cyano des isomères *cis* ont été observées à des champs plus forts que celles des composés *trans* ($\Delta \approx 0.6$ ppm). Les complexes *cis* s'isomèrisent en isomères *trans* sous l'effet de la chaleur. Les structures cristallines de cis-(3) et trans-Pt(C₂H₅-CN)₂Cl₂ (4) et de cis-Pt(p-HO-C₆H₄-CN)₂Cl₂ (5) ont été déterminées. Le crystal **3** est monoclinique, $P2_1/c$, a = 7,506(5), b = 9,539(5), c = 14,823(7) Å, $\beta = 92,31(4)^\circ$, Z = 4, R = 0,050et wR = 0.042. L'isomère trans (4) est monoclinique avec l'atome de Pt sur un centre d'inversion, $P2_1/c$, a = 5.149(4), b = 1000

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¹ Author to whom correspondence may be addressed. Telephone: (514) 987-4896. Fax: (514) 987-4054. E-mail: rochon.fernande@uqam.ca 9,394(8), c = 10,944(10) Å, $\beta = 97,84(7)^{\circ}$, Z = 4, R = 0,017 et wR = 0,020. Finalement, le composé **5** est triclinique, P-1, a = 7,464(3), b = 10,712(6), c = 12,291(5) Å, $\alpha = 75,63(4)^{\circ}$, $\beta = 75,63(4)^{\circ}$, $\gamma = 80,32(4)^{\circ}$, Z = 2, R = 0,045 et wR = 0,056. Les liens Pt—Cl des isomères *cis* sont 2,269(5), 2,270(4) Å (**3**) et 2,274(2), 2,279(3) Å (**5**), et 2,289(3) Å pour l'isomère *trans* (**4**). Les liaisons Pt—N sont 1,962(14), 1,988(11) Å (**3**), 1,972(7), 1,976(7) Å (**5**) et 1,969(5) Å (**4**).

Mots clés : platine, nitrile, RMN, isomérisation, structure cristalline.

Introduction

Although several disubstituted nitrile-Pt(II) complexes, mostly with acetonitrile and benzonitrile, have been reported (1-7), few mononitrile complexes have been studied (8-10). The synthesis of these compounds is important as starting material for the preparation of mixed-ligand complexes.

The nature of the Pt-nitrile bond is not very well known. IR data and X-ray diffraction of a few acetonitrile complexes have shown that CH_3CN is bonded through its lone pair of electrons on the nitrogen atom (2, 8, 10, 11) and the segment Pt-N=C-C is linear. Acetonitrile is expected to accept electron density from the metal, much like CO, because of its empty π^* orbitals. Therefore it was expected that its *trans* effect should be fairly large but this hypothesis has not been confirmed.

Disubstituted nitrile compounds are usually the cis isomers. It was expected that the trans isomers would be formed first and would then isomerize to the *cis* compounds, similarly to the sulfoxide complexes (12-15). In the latter compounds, the $(d-d)\pi$ bonding is much more efficient in the *cis* configuration than in the trans isomers. But recent studies on disubstituted complexes with acetonitrile, and dibenzonitrile seem to indicate that the cis compound is the first product formed, and isomerization then occurs (3, 16). The nature of the backdonation in Pt-nitrile compounds $(d-\pi^*)$ is quite different from that in Pt-sulfoxide (d-d) complexes. Bond lengths usually give information on the presence of multiple bonding but this is not always obvious. Multinuclear NMR spectroscopy can also give some indication on the strength of the Pt-ligand bond. The σ bond will cause a deshielding effect on the ligand and a shielding effect on the metal, while back-donation from the metal to the ligand should produce the opposite effect. We have measured the proton, carbon-13, and platinum-195 NMR spectra of several complexes of the types [Pt(R-CN)Cl₃]⁻ and Pt(R-CN)₂Cl₂ in order to obtain information about the Ptnitrile bond. To study disubstituted compounds, it is important to know exactly the nature of these compounds. A study was undertaken to determine the configuration of such compounds, which were also studied by IR spectroscopy and a few by Xray diffraction. The potassium mononitrile complexes are not very stable and decompose quite readily. To stabilize the compounds, a larger cation was used. The tetramethylammonium salts proved much more stable and several complexes of the type $N(CH_3)_4[Pt(nitrile)Cl_3]$ were isolated and characterized. The compounds with butyronitrile and *p*-hydroxybenzonitrile gave crystals suitable for X-ray diffraction and their structures were determined. The crystal structures of the disubstituted complexes with propionitrile (cis and trans) and p-hydroxybenzonitrile were also studied. trans-Pt(C₂H₅CN)₂Cl₂ is the first example of this type of compound to be analyzed by Xray diffraction methods. The results of these studies are described below.

Experimental

The ¹⁹⁵Pt NMR spectra were measured either on a Bruker WH-400 (85.83 MHz) or a Varian-300 (64.507 MHz) spectrometer. The proton and ¹³C NMR spectra were obtained on the same instruments and occasionally (for ¹H) on a EM-360L (60 MHz) equipped with a signal averager (Varian V-2048) in order to measure the $J(^{195}Pt-^{1}H)$ couplings. The monosubstituted complexes were measured in D₂O, while the disubstituted complexes were measured in CDCl₃. The comparison with the free ligands is made with identical solvents, unless another solvent is specified. The external standard for the ¹⁹⁵Pt spectra was $[Pt(H_2O)_6]^{4+}$ ($\delta = 0$ ppm). The IR spectra were measured on either a FTIR Bio-Rad 600 (resolution 1 cm⁻¹) or a P.E. 783. The decomposition points were measured on a Fisher-Johns instrument. The ligands were obtained from Aldrich and K₂PtCl₄ from Johnson Matthey and Co. The latter was recrystallized from water before use.

 $(N(CH_3)_4)_2[PtCl_4]$ was prepared either by passing an aqueous solution of K_2PtCl_4 through a cation $(N(CH_3)_4^+)$ exchange resin or by mixing directly an aqueous solution of K_2PtCl_4 with tetramethylammonium chloride. The yield is quantitative; mp 260–262°C (dec.); IR: ν (Pt–Cl): 318 and 303 cm⁻¹; ¹H NMR in D₂O, δ : 3.2 ppm.

$(N(CH_3)_4)[Pt(R-CN)Cl_3]$

The nitrile (1 mmol) was added to 5 mL of an aqueous solution containing 1 mmol of $(N(CH_3)_4)_2[PtCl_4]$. The solution was stirred until it became yellow (about 10 days). The mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved in a small quantity of acetone and the mixture was filtered to remove KCl and unreacted K₂PtCl₄. The filtrate was evaporated to dryness and dried under vacuum. (N(CH₃)₄)[Pt(CH₃CN)Cl₃]: Yield: quantitative; mp 150–158°C (dec.); IR (cm⁻¹): 2300 ν (C=N), 2333 (δ (CH₃) + ν (C-C)), 345, 332, 310 (ν (Pt-Cl)); ¹H NMR, δ (ppm): 3.19 $((CH_3)_4N^+)$, 2.54s + d (CH₃), and ${}^4J({}^{195}Pt^{-1}H) = 14.5$ Hz. (N(CH₃)₄)[Pt(C₂H₅CN)Cl₃]: Yield: 40%; dec. mp 167-185°C (dec.); IR (cm⁻¹): 2295 ν (C=N), 333, 323, 318 (ν (Pt-Cl)); ¹H NMR, $\delta(ppm)$: 3.19 ((CH₃)₄N⁺), 1.41t(CH₃), 2.80q(CH₂), and ${}^{4}J({}^{195}Pt-{}^{1}H) = 14$ Hz. $(N(CH_{3})_{4})$ $[Pt(C_{3}H_{7}CN)Cl_{3}]$: Yield: 40%; mp 172-180°C (dec.); IR (cm⁻¹): 2290 $\nu(C = N)$, 2342 ($\delta(CH_3)$ + $\nu(C-C)$), 345, 333, 318 $(\nu(\text{Pt-Cl})); {}^{1}\text{H} \text{ NMR}, \delta(\text{ppm}): 3.20 ((CH_{3})_{4}\text{N}^{+}), 1.03t(CH_{3}),$ 1.78m(CH₂), 2.97t(CH₂), and ${}^{4}J({}^{195}\text{Pt}^{-1}\text{H}) = 15$ Hz. (N(CH₃)₄)[Pt(PhCN)Cl₃]: Yield: 20%; mp 165–172°C (dec.); IR (cm⁻¹): 2285 ν(C=N), 345, 339, 321 (ν(Pt-Cl)); ¹H NMR, $\delta(\text{ppm})$: 3.19 ((CH₃)₄N⁺), 7.75m (Ph).

K[Pt(R-CN)Cl₃]

The CH_3CN complex was prepared as already reported (8). The other complexes were synthesized in a similar way. The reaction time varied from 1 day to 1 week depending on the

ligand. The mixture was stirred on a cooling plate and evaporation was done below 30°C to avoid decomposition. K[Pt(CH₃CN)Cl₃: ¹³C NMR, δ(ppm): 3.84, 117.39 (ligand: 1.72, 119.81). K[Pt(C₂H₅CN)Cl₃: IR (cm⁻¹): 2310 ν (C=N) (ligand 2250), 342, 338, 333 ν(Pt-Cl). NMR, δ(ppm): ¹H, 1.27t, 2.90q (ligand: 1.22t, 2.44q); 13C, 9.87, 12.99, 121.16 (ligand: 10.45, 11.10, 123.83). $K[Pt(C_3H_7CN)Cl_3: IR (cm^{-1}):$ 2303 ν (C=N) (ligand 2250), 328 (br) ν (Pt-Cl). NMR δ (ppm): ¹H, 1.02t, 1.72m, 2.90t (ligand: 1.01t, 1.66m, 2.44t); ¹³C, 13.38, 19.05, 20.75, 120.21 (ligand: 13.38, 19.08, 19.27, 122.99). K[Pt(C₄H₉CN)Cl₃: IR (cm⁻¹): 2310 (ligand 2250) ν (C=N), 345, 338, 325 ν (Pt-Cl). K[Pt(CH₃)₂CHCN)Cl₃: ¹³C NMR, δ(ppm): 19.21, 22.11, 123.65 (ligand: 19.75, 20.29, 126.68). K[Pt((CH₃)₃CCN)Cl₃: IR (cm⁻¹): 2300 ν (C=N) (ligand 2235), 343, 328, 310 ν(Pt-Cl). NMR δ(ppm): ¹H, 1.43s (ligand, neat: 1.39s); ¹³C, 27.75, 30.77, 125.36 (ligand: 28.11, 28.84, 128.71). K[Pt(PhCN)Cl₃: IR (cm⁻¹): 2285 ν (C=N) (ligand 2230), 355, 348, 335 ν(Pt-Cl). NMR δ(ppm): ¹H, 7.75m (ligand, 7.69d); ¹³C, 117.24, 109.85, 134.68, 130.14, 135.99 (ligand: 119.26, 112.65, 132.48, 129.63, 133.27). $K[Pt(p-CH_3O-C_6H_4-CN)CI_3: IR (cm^{-1}): 2280 \nu(C=N), 352,$ 328, 310 ν(Pt-Cl). NMR δ(ppm): ¹H, 3.98s, 7.29d, 7.95d (ligand neat, 3.90s, 7.05d, 7.64d); ¹³C, 56.73, 117.76, 101.12, 136.66, 116.02, 165.10 (ligand in CDCl₃: 55.5, 119.1, 103.9, 133.9, 114.9, 163.0). $K[Pt(p-HO-C_6H_4-CN)Cl_3: IR (cm^{-1})$ 2290 ν (C=N), 340, 335, 320 ν (Pt-Cl). NMR δ (ppm): ¹H, 7.90, 7.48 (ligand neat, 7.60, 7.00); ¹³C, 117.96, 100.35, 136.90, 117.33, 162.73 (ligand in CDCl₃: 119.6, 101.9, 134.0, 116.5, 161.4).

$Pt(R-CN)_2Cl_2$

These complexes can be prepared from the aqueous reaction of K₂PtCl₄ with an excess of the nitrile at room temperature as already reported for acetonitrile (1). $(N(CH_3)_4)_2[PtCl_4]$ can also be used as starting material and the yields are quantitative. Pt(C₂H₅CN)₂Cl₂: Yield: 85%; mp 155–163°C (dec.); IR $(cm^{-1}): 2315 \nu(\bar{C}=N), 351, 345 (\nu(Pt-Cl)); {}^{1}H NMR, \delta(ppm):$ 1.42t (CH₃), 2.92q (CH₂), and ${}^{4}J({}^{19}\text{Pt}^{-1}\text{H}) = 14$ Hz. Pt(C₃H₇CN)₂Cl₂: Yield: 85%; mp 215-250°C (dec.); IR $(cm^{-1}): 2304 \nu(C = N), 2343 \delta(CH_3) + \nu(C-C), 355, 348 (\nu(Pt-C)))$ Cl)); ¹H NMR, δ (ppm): 1.12t (CH₃), 2.95t (CH₂), 1.87m (CH₂), and ${}^{4}J({}^{195}Pt-{}^{1}H) = 15$ Hz. $Pt(C_{4}H_{9}CN)_{2}Cl_{2}$: Yield: 80%; IR (cm⁻¹): 2309 ν (C \equiv N), 359, 348 (ν (Pt-Cl)). Pt(CH(CH₃)₂CN)₂Cl₂: Yield: 80%; IR (cm⁻¹): 2303 ν (C=N), 358, 352 (ν (Pt-Cl)). Pt(C(CH₃)₃CN)₂Cl₂: Yield: 80%; IR $(cm^{-1}): 2301 \nu(C=N), 353(br) (\nu(Pt-Cl)); {}^{1}H NMR, \delta(ppm):$ 1.43s. Pt(PhCN)₂Cl₂: Yield: 85%; mp 210–218°C (dec.); IR $(cm^{-1}): 2290 \nu(C = N), 360, 345 (\nu(Pt-Cl)); {}^{1}H NMR, \delta(ppm):$ 7.75m (Ph). $Pt(p-OH-C_6H_4-CN)_2Cl_2$: Yield: 75%; IR (cm⁻¹): 2290 ν (C=N), 353, 340 (ν (Pt-Cl)). Pt(p-CH₃O-C₆H₄- $CN_{2}Cl_{2}$: Yield: 75%; IR (cm⁻¹): 2280 ν (C=N), 352 (br) (ν(Pt-Cl)); ¹H NMR, δ(ppm): 3.92s (CH₃), 7.65d, 7.06d.

The data collections $(2\theta/\theta)$ were made at room temperature, either on a Syntex PI diffractometer (1, 5) or a Siemens P4 (2, 3, 4), with graphite-monochromatized MoK α radiation (0.71069 Å). The cell parameters were calculated from the refined angles of 15–30 centered reflections. The experimental details of the crystallographic studies are shown in Table 1. The scan rate varied between 1° and 29° min⁻¹. An absorption correction based on the equations of the crystal faces was applied and the data were corrected for Lorenz and polarization effects. The calculations were done on a Siemens SHELXTL system, PC-plus version.

Results and discussion

[Pt(R-CN)Cl₃]⁻ complexes

The complexes K[Pt(R-CN)Cl₃] were synthesized from the aqueous reaction of K₂PtCl₄ with the nitrile in a mole to mole ratio of 1:1.5. In a 1:2 proportion, only the disubstituted compound is formed, while in a 1:1 ratio the reaction is slow and decomposition can occur. The monoacetonitrile compound is fairly stable and can be obtained overnight, but the complexes with other ligands are more slowly formed (1 day to 1 week) and are less stable. It is therefore important to cool the reaction medium during their synthesis. The crystals were too unstable in air for X-ray diffraction studies. Therefore the larger cation N(CH₃)₄⁺ was used. The complexes were prepared from the aqueous reaction of (N(CH₃)₄)₂[PtCl₄] with the nitrile (1:1 ratio) at room temperature. The reaction time was between 7 and 10 days. The compounds with butyronitrile and *p*-hydroxybenzonitrile were studied by X-ray diffraction.

The IR spectra of the N(CH₃)₄⁺ complexes have shown that the ν (C=N) vibration is observed at higher frequency in the coordinated ligand ($\Delta = 43-50 \text{ cm}^{-1}$), while Δ is slightly larger (55-65 cm⁻¹) for the K⁺ compounds. This absorption at higher energy than in the free ligands is well known and has been discussed in detail for *cis*-Pt(CH₃CN)₂Cl₂ (11). The spectra showed three ν (Pt-Cl) (2A₁ and B₂) expected for a C_{2v} symmetry, between 345 and 310 cm⁻¹. The ¹H NMR spectra, measured on a low-field instrument, showed ⁴J(¹⁹⁵Pt-¹H) coupling constants of 14-15 Hz.

The refined atomic parameters of the two complexes $N(CH_3)_4^+$ [Pt(R-CN)Cl₃] where $R = C_3H_7$ and p-OH-C₆H₄, are listed in Table 2. Labelled diagrams of the molecules are shown in Figs. 1 and 2. As expected, the coordination around Pt(II) is square planar and the angles around Pt are close to 90 and 180°. The nitrile ligand is bonded through its lone pair of electrons on the N atom.

Some selected bond distances and angles are listed in Table 3. For each structure, the Pt-Cl bond in trans position to the nitrile ligand is shorter (2.276(3) Å for 1 and 2.264(7) Å for 2)than the other two Pt—Cl bonds, which are normal (2.293(4), 2.287(3) Å for 1 and 2.320(7), 2.275(8) Å for 2). Shorter Pt-Cl bonds located in trans position to CH₃CN (2.263(3)-2.277(5) Å) (11) and 2.266(2) Å (10)) have also been reported. The differences are not very large, but they are very consistent. The trans influence of nitriles seems therefore to be smaller than that of sulfoxides, halides, and amines. The short bond distances might also be due to the multiple nature of the Pt---N bonds located in trans position to the short Pt-Cl bonds. These results have shown that Pt-Cl bonds located in trans positions to nitrile ligands are definitely shorter than normal, and we suggest that the presence of multiple bonding in the trans bond is responsible for the bond shortening.

The Pt—N bonds are 1.97(1) Å for 1 and 1.92(2) Å for 2. These values are similar to the reported values (10, 11), and are shorter than those observed for Pt-amine or Pt-pyridine bonds. The shortening might be ascribed to the presence of electron back-donation from the metal to the ligand. The segment Pt-N=C-C is linear with angles Pt-N-C = $174(1)^{\circ}$, $171(2)^{\circ}$ and N-C-C = $178(1)^{\circ}$, $176(3)^{\circ}$ and

	1	2	3	4	5
Formula	$C_8H_{19}N_2Cl_3Pt$	$C_{11}H_{17}N_2OCl_3Pt$	$C_6H_{10}N_2Cl_2Pt$	$C_6H_{10}N_2Cl_2Pt$	C ₁₄ H ₁₀ N ₂ O ₂ Cl ₂ Pt
fw	404.24	494.72	376.15	376.15	504.24
Space group	$P2_1/c$	P42bc	$P2_1/c$	$P2_1/c$	<i>P</i> -1
a (Å)	8.384(5)	16.222(6)	7.506(5)	5.149(4)	7.464(3)
b (Å)	15.336(19)		9.539(5)	9.394(8)	10.712(6)
c (Å)	11.759(9)	12.052(5)	14.823(7)	10.944(10)	12.291(5)
α (°)	90.	90.	90.	90.	75.63(4)
β (°)	99.52(6)	90.	92.31(4)	97.84(6)	75.48(4)
γ (°)	90.	90.	90.	90.	80.32(4)
Volume (Å ³)	1491(2)	3172(3)	1061(1)	524.3(8)	915.7(8)
Ζ	4	8	4	2	2
<i>F</i> (000)	840	1872	688	344	472
ρ_{calcd} (Mg m ⁻³)	1.854	2.072	2.356	2.382	1.828
μ(MoKα) (mm)	10.025	9.34	13.83	13.834	8.036
Crystal faces and	12 Faces with dimen-	(100) (-100) 0.048	(100) (-100) 0.22	(0-11) (01-1) 0.048	(010) (0-10) 0.063
distance from center	sions 0.18×0.35	(010) (0-10) 0.029	(010) (0-10) 0.058	(011) (0-1-1) 0.067	(001) (00-1) 0.106
(mm)	× 0.71	(001) (00-1) 0.120	(001) (00-1) 0.011	(-114) (11-2)0.15	(110) (-1-10) 0.221
Transm. factor range	0.032-0.222	0.421-0.595	0.212-0.723	0.189-0.318	0.191-0.418
2θ max (°)	58	57	55	55	60
h, k, l	0→11, 0→20,	$-1 \rightarrow 21, -1 \rightarrow 21,$	0→9, 0→12,	0→6, 0→12,	0→9, -14→15,
	–16→15	-1→16	-19→19	-14→14	− 16→17
Independent reflens.	3975	2285	2754	1215	5149
Observed reflcns.	2246 $(F > 2.5\sigma(I))$	1034 $(F > 4\sigma(F))$	1447 $(F > 5.5\sigma(F))$	863 $(F > 4.0\sigma(F))$	3928 $(I > 2.5\sigma(I))$
w^{-1}	$\sigma^2(F)$	$\sigma^2(F) + 0.0001(F^2)$	$\sigma^2(F) + 0.0001(F^2)$	$\sigma^2(F) + 0.0001(F^2)$	$\sigma^2(F)$
R	0.054	0.059	0.050	0.017	0.045
wR	0.051	0.044	0.042	0.020	0.056
S	1.63	1.14	1.88	1.3	1.58
$(\Delta/\sigma)_{max}$	0.08	0.06	0.08	0.000	0.07
$(\Delta^{p})_{max}$ (e Å ³)	1.3 (close to Pt)	1.8 (close to Pt)	1.7 (close to Pt)	0.49 (close to Pt)	1.9

Fig. 1. Labelled diagram of $N(CH_3)_4[Pt(C_3H_7-CN)Cl_3]$ (1).



the N=C bond distances are 1.13(2) and 1.13(4) Å for 1 and 2, respectively.

The crystal N(CH₃)₄[Pt(p-OH-C₆H₄-CN)Cl₃] is stabilized by intermolecular hydrogen bonding between the hydroxy group and Cl(3), located in *trans* position to the nitrile ligand. This hydrogen bond does not seem to affect the Pt—Cl(3) bond length. The distance O···Cl(3) is 3.271 Å. A packing diaFig. 2. Labelled diagram of the ion $[Pt(p-OH-C_6H_4-CN)Cl_3]^-$ (2).



gram of the molecules has been prepared and is part of the supplementary material.²

² The following tables and figures have been deposited: anisotropic thermal factors (S1), H coordinates (S2), bond distances and angles (S3), weighted best planes (S4), and packing diagrams of crystal 2 (Fig. S1) and of crystal 5 (Fig. S2). This material may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada K1A 0R6. With the exception of Tables S1 and S4, the above have also been deposited with the Cambridge Crystallographic Data Centre, and can be obtained on request from The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Table 2. Positional parameters (×10⁴) with their e.s.d.'s and temperature factors (10³). $U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$

		1 ,			
Atom	x	у	Z	$U_{ m eq}$ (Å)	
$\frac{1}{N(CH_{3})_{4}[Pt(C_{3}H_{7}-CN)Cl_{3}]} (1)$					
Pt	2265.2(5)	754.6(3)	-1968.1(3)	50.2	
Cl(1)	3952(4)	126(3)	-3082(3)	90.3	
Cl(2)	1490(4)	1775(2)	-3354(2)	69.6	
C1(3)	576(4)	1358(2)	-843(2)	83.5	
N(1)	2880(12)	-176(7)	-827(7)	72	
N(2)	1700(10)	4109(5)	-1684(6)	54	
$\Gamma(2)$	3182(14)	-762(9)	-243(10)	71	
C(2)	3545(17)	-1542(10)	-2+5(10) 475(11)	80	
C(2)	3104(20)	-1342(10) -2342(11)	-234(14)	115	
C(3)	3104(20) 3875(27)	-2.542(11)	-2.34(14) 1320(14)	172	
C(4)	3873(27)	-2552(14)	-1320(14)	50	
C(3)	1744(17)	3322(8)	-1108(8)	J9 02	
C(0)	1744(17)	4247(9)	-2973(8)	74	
C(7)	107(13)	5010(9)	-1330(9)	74	
C(8)	1801(18)	5010(8)	-1093(10)	91	
N(CH ₃) ₄	$Pt(p-OH-C_6H_4$	CN)Cl ₃] (2)			
Pt	7566(1)	1128(1)	3000	38(1)	
Cl(1)	6275(4)	545(4)	3265(8)	56(2)	
Cl(2)	8809(5)	1754(5)	2765(9)	75(3)	
C1(3)	7290(5)	1319(6)	1178(6)	59(2)	
ο	9024(15)	941(15)	9888(17)	69(4)	
N(1)	7890(16)	922(16)	4506(17)	49(4)	
N(2)	3693(16)	1240(18)	370(17)	39(4)	
Cù	8074(18)	916(16)	5408(25)	44(4)	
C(2)	4414(19)	1189(19)	1405(28)	55(4)	
C(3)	3622(22)	425(26)	-118(30)	71(4)	
C(4)	3017(16)	1317(21)	1346(28)	56(4)	
C(5)	3813(29)	2186(24)	-15(38)	109(4)	
C(11)	8335(17)	848(14)	6596(23)	28(4)	
C(12)	7787(18)	972(19)	7373(22)	29(4)	
C(13)	7980(20)	933(21)	8469(22)	45(4)	
C(14)	8757(20)	945(16)	8758(24)	46(4)	
C(15)	9364(13)	879(12)	7926(30)	34(4)	
C(16)	9100(17)	846(15)	6873(21)	29(4)	
cis-Pt(C ₂ H ₅ -CN) ₂ Cl ₂ (3)					
Dt	2117 2(8)	6185 3(6)	5033 0(4)	20 8(2)	
	2117.2(0) 2149(7)	6680(5)	5055.9(4)	72(1)	
C(1)	5140(7)	0009(J) 8421(4)	4931(3)	72(1) 55(1)	
CI(2)	1182(0)	6451(4)	4031(3) 5202(8)	49(2)	
N(1)	2823(15)	4191(12)	3202(8)	48(2) 54(2)	
N(2)	1255(15)	5789(11)	5793(9)	34(2)	
C(1)	3331(13)	5154(10)	3294(11)	40(Z)	
C(2)	729(19)	3033(13)	5005(11)	57(2)	
C(3)	3833(19)	1651(14)	5464(12)	03(2) 50(2)	
C(4)	12(19)	5451(16)	2160(11)	59(Z)	
C(5)	4431(20)	1326(17)	6394(12)	80(2)	
C(6)	-1518(20)	0303(18)	1978(12)	82(2)	

The ¹⁹⁵Pt NMR spectra of the complexes were measured in D_2O and the results are shown in Table 4. The signals were observed between -1997 and -2020 ppm. The chemical shifts seem almost independent of the R substituent on the

Table 2 (concluded).					
Atom	x	у	Z	$U_{ m eq}$ (Å)	
trans-Pt	$(C_2H_5-CN)_2Cl_2$ (4)			
Pt	5000	0	5000	37(1)	
C1	4394(3)	2391(2)	5249(1)	61(1)	
Ν	7345(8)	404(4)	3764(4)	44(1)	
C(1)	8672(9)	647(5)	3057(4)	42(1)	
C(2)	10370(10)	909(5)	2138(4)	47(1)	
C(3)	11447(13)	-459(6)	1637(6)	56(2)	
cis-Pt(p	-OH-C ₆ H ₄ -CN) ₂	$\operatorname{Cl}_2(5)$			
Pt	1868.3(5)	955.4(3)	4261.5(3)	354	
Cl(1)	538(3)	2918(2)	4652(2)	536	
Cl(2)	1369(4)	1663(3)	2447(2)	631	
O(1)	7043(11)	-6646(7)	3207(7)	705	
O(2)	2847(11)	-799(8)	11359(5)	721	
N(1)	2968(10)	-761(7)	3937(6)	439	
N(2)	2262(10)	399(7)	5846(6)	460	
C(1)	3570(12)	-1787(9)	3780(7)	439	
C(2)	4451(12)	-3025(8)	3596(7)	440	
C(3)	3622(14)	-3809(10)	3158(8)	518	
C(4)	4527(15)	-5021(10)	3028(8)	567	
C(5)	6247(14)	-5443(9)	3319(8)	518	
C(6)	7039(14)	-4650(10)	3741(8)	584	
C(7)	6130(13)	-3465(9)	3892(8)	508	
C(8)	2425(13)	140(9)	6786(7)	450	
C(9)	2573(12)	-109(9)	7946(6)	456	
C(10)	3277(16)	-1279(10)	8472(8)	595	
C(11)	3313(18)	-1523(10)	9660(9)	696	
C(12)	2747(13)	-536(10)	10236(7)	529	
C(13)	2072(15)	693(10)	9676(7)	550	
C(14)	2003(14)	901(10)	8537(8)	558	

ligand. Pregosin (17) had observed a downfield shift when the ligand became sterically larger. Due to the linear nature of the Pt-N=C-C segment, the binding site in nitriles is far from the R substituent, resulting in almost constant chemical shifts. The signals are observed at higher fields than those reported for $[Pt(amine)Cl_3]^-$ (-1822 to -1865 in DMF, -1855 to -1875 ppm in acetone (18)) and for $[Pt(pyridine)Cl_3]^-$ complexes (-1763 to -1897 ppm in D₂O (19)). The shielding observed for the mononitrile complexes (compared to amine complexes) might be attributed to the special nature of the Pt-nitrile bond. Nitrile ligands might be good π -donors in addition to their σ -donor ability.

The ¹³C NMR spectra of the complexes were also measured in D₂O. The positions of the cyano carbons are listed in Table 4, along with Δ (complex–ligand) in order to evaluate the influence of the R substituents. The two ligands *p*-CH₃O-C₆H₄-CN and *p*-HO-C₆H₄-CN are not soluble in water, therefore their spectra were measured in CDCl₃. For comparison, Ph-CN was also measured in CDCl₃. The chemical shifts of the cyano carbon atoms are shifted towards higher field upon coordination. Most of the other C atoms are deshielded when compared to those of the ligands. The substituent effects on the ¹³C chemical shifts in free nitriles were studied and it was found that the cyano carbon resonance shifts to higher field

Table 3. Selected bond distances (Å) and angles (°).

Bond	Distance	Bonds	Angle		
$\frac{1}{N(CH_{3})_{4}[Pt(C_{3}H_{7}-CN)Cl_{3}] (1)}$					
Pt—Cl(1) Pt—Cl(2) Pt—Cl(3) Pt—N(1) N(1)-C(1) C(1)-C(2)	2.293(4) 2.276(3) 2.287(3) 1.97(1) 1.13(2) 1.47(2)	Cl(1)-Pt-Cl(2) Cl(1)-Pt-Cl(3) Cl(1)-Pt-N(1) Cl(2)-Pt-Cl(3) Cl(2)-Pt-N(1) Cl(3)-Pt-N(1) Pt-N(1)-C(1) N(1)-C(1)-C(2)	90.6(1) 179.0(1) 88.2(3) 90.3(1) 177.0(3) 90.9(3) 174(1) 178(1)		
$N(CH_3)_4[Pt(p-$	OH-C ₆ H₄-CN)Cl	₃] (2)			
Pt—Cl(1) Pt—Cl(2) Pt—Cl(3) Pt—N(1) N(1)-C(1)	2.320(7) 2.275(8) 2.264(7) 1.92(2) 1.13(4)	Cl(1)-Pt-Cl(2) Cl(1)-Pt-Cl(3) Cl(1)-Pt-N(1) Cl(2)-Pt-Cl(3) Cl(2)-Pt-N(1) Cl(3)-Pt-N(1) Pt-N(1)-C(1) N(1)-C(1)-C(11)	177.5(3) 90.6(3) 92.6(8) 89.6(4) 87.3(8) 174.9(8) 171(2) 176(3)		
cis-Pt(C ₂ H ₅ -Cl	$N)_2Cl_2(3)$				
Pt—Cl(1) Pt—Cl(2) Pt—N(1) Pt—N(2) N(1)-C(1) N(2)-C(2) C(1)-C(3) C(2)-C(4)	2.269(5) 2.270(4) 1.988(11) 1.962(14) 1.09(2) 1.14(2) 1.48(2) 1.44(2)	Cl(1)-Pt-Cl(2) Cl(1)-Pt-N(1) Cl(1)-Pt-N(2) Cl(2)-Pt-N(1) Cl(2)-Pt-N(2) N(1)-Pt-N(2) Pt-N(1)-C(1) Pt-N(2)-C(2) N(1)-C(1)-C(3) N(2)-C(2)-C(4)	90.9(2) 90.4(4) 178.7(3) 177.4(4) 88.2(3) 90.5(5) 175(1) 176(1) 174(1) 178(1)		
<i>trans</i> -Pt(C_2H_5 -CN) ₂ Cl ₂ (4)					
Pt—Cl(1) Pt—N(1) N(1)-C(1)	2.289(3) 1.969(5) 1.124(7)	Cl(1)-Pt-N(1) Cl(1)-Pt-N(1a) Pt-N(1)-C(1) N(1)-C(1)-C(2)	89.9(1) 90.1(1) 179.3(4) 178.1(5)		
cis-Pt(p -OH-C ₆ H ₄ -CN) ₂ Cl ₂ (5)					
Pt - Cl(1) Pt - Cl(2) Pt - N(1) Pt - N(2) O(1)-C(5) O(2)-C(12) N(1)-C(1) N(2)-C(8) C(1)-C(2) C(8)-C(9)	2.279(3) $2.274(2)$ $1.976(7)$ $1.972(7)$ $1.35(1)$ $1.36(1)$ $1.16(1)$ $1.15(1)$ $1.42(1)$ $1.41(1)$	Cl(1)-Pt-Cl(2) Cl(1)-Pt-N(1) Cl(1)-Pt-N(2) Cl(2)-Pt-N(1) Cl(2)-Pt-N(2) N(1)-Pt-N(2) Pt-N(1)-C(1) Pt-N(2)-C(8) N(1)-C(1)-C(2) N(2)-C(8)-C(9)	89.2(1) 178.7(2) 88.9(2) 90.9(2) 178.1(2) 91.1(3) 177.7(7) 175.9(7) 175.3(9) 177(1)		

with increasing electronegativity of the substituent R (20). The correlation was explained in terms of the π -bond polarization, which is caused by the electric field of the substituent. The chemical shifts are linearly dependent on the π -electron density on the nucleus and a change on the cyano carbon atom is caused by the variation of the π -bond polarization (20). The complexation of the nitrile ligand to platinum will increase the polarization of the bond. It can be observed from Table 4 that, upon complexation, the cyano carbon atoms become more shielded as the number of methyl groups increase (Δ (complex-ligand) = -2.4 for R = CH₃ to -3.4 ppm for R = $C(CH_3)_3$). There are at least three factors that could affect the electron density on the complexed ligand: the π -bond polarization effect as discussed above, which should increase the electron density on the cyano carbons as the number of methyl groups in the substituent R increases, the σ -bond, which should reduce the electron density on the nitrile ligand; and finally the π -back-donation, which should increase the electronic density of the ligand. Therefore, it is not easy to interpret the results of such studies. When the alkyl groups on the nitriles are replaced by phenyl groups, the shielding on the cyano carbon is slightly reduced (Table 4). The formation of complexes with these derivatives is favored by the mesomeric effect on the ligand, which increases the polarization of the C \equiv N π -bond.

The ${}^{2}J({}^{195}Pt-{}^{13}C)$ were difficult to measure for several reasons: the low intensity of quaternary cyano carbon atoms, the high field of the instrument (a 400 MHz was used, since on lower field instruments, the compounds decomposed after several hours of accumulation) that causes low intensities for the satellites' couplings, and finally the close environment of a ${}^{14}N$ atom with a spin $I > \frac{1}{2}$ that increases the relaxation time of the cyano carbon atom. The ${}^{2}J$ couplings vary from 223 to 257 Hz, but the values are not very precise. The couplings are quite high because of the large *s* character of the cyano carbon atoms.

Pt(R-CN)₂Cl₂ complexes

Some of these complexes are known in the literature, but their ¹⁹⁵Pt NMR spectra and their crystal structures (except for cis- $Pt(CH_3CN)_2Cl_2$) have not been reported. When the reactions were done at room temperature, only cis-Pt(RCN)₂Cl₂ was formed (or >95%), since only one peak was observed in ¹⁹⁵Pt NMR spectroscopy. These results are different from those published by Fraccarollo et al. (7), who reported that most of their products at room temperature were cis-trans mixtures containing between 7 and 15% of trans compounds, except for trimethylacetonitrile, which produced 80% of trans isomers after 4 days. But their experimental procedures were different. They used a much larger excess of nitrile ligands. The mixture was treated with dichloromethane and the isomers were separated by crystallization in organic solvents such as hot benzene, n-hexane, ether, and petroleum ether. We believe that the trans isomers were probably formed when dichloromethane was added to the mixture to extract the complexes. The cis-trans isomerization of these complexes in chloroform is discussed below.

The ¹⁹⁵Pt signals for all the *cis* complexes (Table 5) were observed at very similar fields (-2276 to -2288 ppm) except for *cis*-Pt(*p*-CH₃O-C₆H₄-CN)₂Cl₂, which was observed at slightly lower field (-2239 ppm). These values are at a

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Fig. 3. Labelled diagram of cis-Pt(C₂H₅-CN)₂Cl₂ (**3**).



slightly higher field than those reported for the *cis* complexes of several primary amines (\approx -2230 ppm), and the corresponding complexes with secondary amines (\approx -2180 ppm) (18). These observations are in agreement with the results observed by Pregosin (17), who reported a ¹⁹⁵Pt downfield shift when the ligand became more sterically demanding close to the binding site. Nitriles are never bulky around the binding atom, resulting in slightly more shielded ¹⁹⁵Pt signals. As already mentioned for mononitrile complexes, nitriles might be good π -donors in addition to their σ -donor ability. The IR spectra of these complexes showed two ν (Pt-Cl) bands (or a large band) around 345 and 355 cm⁻¹ as expected for $C_{2\nu}$ symmetry and as already reported (2, 3, 7, 11).

The crystal structures of the *cis* complexes with C_2H_5 -CN (3) and *p*-HO-C₆H₄-CN (5) were determined. The refined

Fig. 4. Labelled diagram of cis-Pt(p-OH-C₆H₄-CN)₂Cl₂ (**5**).

atomic parameters of the complexes are listed in Table 2. Labelled diagrams of the molecules are shown in Figs. 3 and 4. Some selected bond distances and angles are listed in Table 3. The Pt—Cl bonds are again shorter than normal (2.269(5), 2.270(4) Å for 3 and 2.274(2), 2.279(3) Å for 5) as observed for the Pt(II)-mononitrile complexes discussed above and as reported for *cis*-Pt(CH₃CN)₂Cl₂ (11), confirming the small *trans* influence of nitriles. Again, we believe that the presence of multiple bonding in the *trans* bond is responsible for these bond shortenings.

The Pt—N bonds are 1.962(14), 1.988(11) Å for 3 and 1.976(7), 1.972(7) Å for 5. These values are similar to those observed for cis-Pt(CH₃CN)₂Cl₂ (11), and are shorter than those usually reported for Pt-amine or Pt-pyridine bonds. The shortening might be due to the presence of electron backdonation from the metal to the ligand or (and) to the presence of π -donation from the ligand. The segments Pt-N=C-C are linear with angles Pt-N-C = $175(1)^{\circ}$, $176(1)^{\circ}$; $177.7(7)^{\circ}$. $175.9(7)^{\circ}$ and N-C-C = $174(1)^{\circ}$, $178(1)^{\circ}$; $175.3(9)^{\circ}$, $177(1)^{\circ}$ for 3 and 5, respectively. The nitrile bonds are 1.09(2), 1.14(2)Å for 3 and 1.15(1), 1.16(1) Å for 5. The crystal *cis*-Pt(*p*-OH- C_6H_4 -CN)₂Cl₂ is stabilized by intermolecular hydrogen bonds between the hydroxy groups and the chloro ligands. The distances $O(1) \cdots Cl(1)$ and $O(2) \cdots Cl(2)$ are 3.417(6) and 3.161(8) Å and the angles C-O \cdots Cl are reasonable, $101.5(6)^{\circ}$ and 111.3(6)°, respectively.

When the *cis* isomers were heated for a few hours at about 50°C in CHCl₃, they partly isomerized to the *trans* compounds. The ¹⁹⁵Pt NMR spectra showed a new signal at lower field than that of the *cis* isomers ($\Delta = 65$ Hz). The isomerization was not complete. For the complex Pt(C₂H₅CN)₂Cl₂, the proportion of each isomer was about 50%. The mixture was



Table 4. ¹³C (cyano carbon) and ¹⁹⁵Pt NMR spectra of K[Pt(R-CN)Cl₃] in D₂O.

R	$\delta(CN)$, ppm	Δ (complex–ligand)	$^{2}J(^{195}\text{Pt}-^{13}\text{C}), \text{Hz}$	δ(Pt), ppm
CH ₃	117.4	-2.4	228	-2000
C_2H_5	121.2	-2.7	257	-2002
$n-C_3H_7$	120.2	-2.8	244	-1997
iso-C ₃ H ₇	123.7	-3.0	223	
$t-C_4H_9$	125.4	-3.4	239	-2008
Ph	117.2	-2.0	244	-2020
		-1.6^{a}		
CH ₃ O-Ph	117.8	-1.3^{a}	n.o.	-2004
HO-C ₆ H ₄	118.0	-1.6^{a}	n.o.	-2003

"The ligands were measured in CDCl₃; n.o., not observed.

Table 5. 13 C (of the cyano C) and 195 Pt NMR signals of the Pt(R-CN)₂Cl₂ complexes (in CDCl₃).

	δ(¹³ C)		$^{2}J(^{195}\text{Pt}-^{13}\text{C})$ (Hz)		δ(¹⁹⁵ Pt) (ppm)	
R	cis	trans	cis	trans	cis trans	
$\overline{C_2H_5}$	118.4	119.0	231	283	-2280 -2344	
$n-C_3H_7$	117.4	118.2			-2277	
$n-C_4H_9$	117.4	118.4			-2276	
iso-C ₃ H ₇	120.8	121.8	228		-2283	
$t-C_4H_9$	122.6	123.8			-2288	
Ph	115.3	116.8	234	289	-2284 -2350	
p-CH ₃ O-C ₆ H ₄					-2239	

Fig. 5. Labelled diagram of $trans-Pt(C_2H_5-CN)_2Cl_2$ (4).



chromatographed on a silica gel column using CH₂Cl₂– CH₃OH as eluant. The separation was almost complete. The first compound to be eluted was the *trans* isomer, which was shown by ¹⁹⁵Pt NMR to contain about 5% of the *cis* isomer. The IR spectrum of the purified *trans* compound showed a single sharp ν (Pt-Cl) band at 347 cm⁻¹. These results are similar to those reported on *cis*-Pt(R-CN)₂Cl₂ (R = CH₃ and Ph), which were found to isomerize in the solid state, to the *trans* isomers with partial decomposition. In solution, a mixture of *cis* and *trans* isomers were obtained (4, 16).

These observations suggest that, at room temperature, the first compound formed in these reactions is the *cis* isomer, which then isomerizes to the *trans* compound upon heating. The *trans* effect of nitriles seems therefore to be smaller than that of chlorides. This result might appear surprising because of the presence of multiple bonding in the nitrile ligands. But

the nature of the Pt-nitrile bond is very different from that with ligands having a high *trans* effect. Ligands which have a high *trans* effect can form π -bonds with the metal either through a $(d-d)\pi$ bond like sulfoxides or phosphines, or through the multiple bond of the ligand as observed for alkenes or alkynes, where the multiple bond of the ligand is perpendicular to the platinum plane. With nitriles, the segment Pt-N=C-C is linear and therefore the triple bond of the nitrile is in the Pt square plane.

In ¹³C NMR spectroscopy, the cyano carbon atoms of the *cis* isomers are more shielded (0.6–1.5 ppm) than those of the *trans* compounds (Table 5). The ¹⁹⁵Pt NMR spectra have shown that the *trans* isomers are more shielded (\approx 65 ppm), as expected from the results of ¹³C NMR spectroscopy. The back-donation of electron density from the metal to the ligand is less effective in the *trans* isomer than in the *cis* isomer, which has very effective $\pi(d-\pi^*)$ bonding. The ²J(¹⁹⁵Pt-¹³C) coupling constants for the *trans* isomers (286 Hz) are larger than those for the *cis* compounds (231 Hz), as was observed by Fraccarollo et al. (7).

The crystal structure of $trans-Pt(C_2H_5CN)_2Cl_2$ (4) was determined. This is the first crystal structure report on a *trans* compound. The labelled diagram of the molecule is shown in Fig. 5. The Pt atom lies on an inversion centre. The Pt—Cl distances are 2.289(3) Å, very similar to the distances observed for the bonds located in *cis* positions to the nitrile in [Pt(R-CN)Cl_3]⁻, in agreement with the hypotheses described above regarding short Pt—Cl bonds located in *trans* positions to nitrile ligands. The Pt—N bonds are 1.969(5) Å, identical to the values obtained in the crystals described above. The N-C bond is 1.124(7) Å, and the Pt-N-C(1) and N-C(1)-C(2) angles are $179.3(4)^{\circ}$ and $178.1(5)^{\circ}$, respectively.

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