Conversion of Nitriles into Δ^2-1,3-Oxazolines in Platinum(II) Complexes. Crystal Structure of *trans*-$[PtCl_2\{\overline{N{=}C(Bu^t)OCH_2C}H_2\}_2]$†

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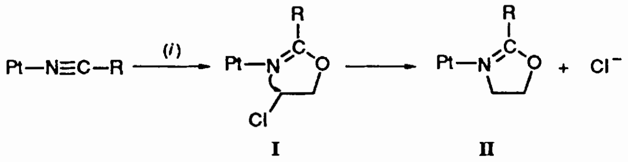
The reactions of *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = *p*-MeC_6H_4, *p*-$CF_3C_6H_4$, *o*-MeC_6H_4, Et, Pr^n, Pr^i or Bu^t) complexes with 2 equivalents of $^-OCH_2CH_2Cl$, generated by deprotonation of $HOCH_2CH_2Cl$ with $LiBu^n$, afford in high yield the bis(Δ^2-1,3-oxazoline) derivatives *cis*-and *trans*-$[PtCl_2\{\overline{N{=}C(R)OCH_2C}H_2\}_2]$. The complexes have been characterized by their elemental analyses, IR, ^1H NMR, ^{13}C-$\{^1H\}$ NMR and FAB mass spectra. The structure of *trans*-$[PtCl_2\{\overline{N{=}C(Bu^t)OCH_2C}H_2\}_2]$ was established also by X-ray crystallography: monoclinic, space group $P2_1/n$, $a = 11.233(2)$, $b = 8.741(2)$, $c = 9.394(2)$ Å, $\beta = 101.61(3)°$ and $Z = 2$; $R = 0.038$ ($R' = 0.042$) for 2514 measured reflections with $I \geqslant 3\sigma(I)$. The N–C(R) and (R)C–O bond distances of 1.284(5) and 1.335(5) Å suggest that there is extensive electron delocalization within the N–C(R)–O system. The co-ordination geometry around Pt^{II} is planar and the oxazoline rings are only slightly twisted. The formation of Δ^2-1,3-oxazolines from platinum(II)-co-ordinated nitriles has also been examined using $HOCH_2CH_2Cl$ in the presence of the weak base NEt_3. These reactions proceed through the initial formation of the bis(imido ester) complexes $[PtCl_2\{NH{=}C(R)OCH_2CH_2Cl\}_2]$, present as their (*Z,Z*), (*E,E*) and (*E,Z*) conformers, which slowly convert to the final cyclic Δ^2-1,3-oxazoline derivatives.

Δ^2-1,3-Oxazolines (or 4,5-dihydro-1,3-oxazoles) are five-membered cyclic imido esters having several properties which make them of interest in different fields of application.[1] There are many ways in which they may be formed,[1,2] but herein will be briefly examined, also for the purpose of this work, those involving nitriles. Reactions of equimolar amounts of RCN and 2-aminoalcohols at 130 °C in the presence of catalysts such as zinc chloride or cadmium acetate afford Δ^2-1,3-oxazolines in 62–96% yield.[2] They are prepared under milder conditions from the reactions of nitriles with several epoxides in the presence of the boron trifluoride–ether complex at room temperature, in 45–86% yield,[2,3] which is higher than that achieved when similar reactions are carried out in the presence of either concentrated sulfuric acid (not above 25%)[4] or tin(IV) chloride (10–40%).[5] Finally, they result when acyclic imido esters, $RC({=}NH)OR'$, or their salts, $RC({=}NH_2Cl)OR'$ (R, R′ = alkyl, aryl), are heated mainly with 2-aminoalcohols or, in a few cases, with β-chloroalcohols in the presence of ammonia solutions.[6] As for this method, it is worthwhile noting that imido esters are prepared by the Pinner synthesis, which consists in condensing a nitrile (either alkyl or aryl) and an alcohol under anhydrous conditions at low temperature (0–5 °C) in the presence of hydrogen chloride or bromide. These conditions must be strictly adhered to because of the thermal instability of the initially formed imido ester salt and its ready hydrolysis by even traces of moisture. The Pinner synthesis is subject to steric hindrance and fails with tertiary alcohols and hindered nitriles (*e.g. o*-toluonitrile); moreover, although it can be applied to certain functionalized nitriles (*e.g.* cyanohydrins) it fails, owing to the spontaneous instability of the imido ester products, in the case of electron-deficient nitriles (*e.g.* trichloroacetonitrile). Alcohol addition to nitriles to give imido esters can also be achieved under basic conditions using a sodium alkoxide in the corresponding alcohol at 25 °C. Yields are poor for simple aliphatic and aromatic nitriles but are excellent for electron-deficient nitriles (*e.g.* trichloroacetonitrile, *p*-nitrobenzonitrile), which are exactly those nitriles which fail to give imido esters by the Pinner synthesis. Like the latter reaction, the base-catalysed addition of alcohols to nitriles is subject to steric hindrance.



Scheme 1 (*i*) (*a*) $HO(CH_2)_2Cl$-$LiBu^n$, $-BuH$, 0–25 °C or (*b*) $\overline{CH_2CH_2O}$–Cl^-, 25 °C

By taking advantage of the ability of platinum(II)-co-ordinated nitriles to undergo nucleophilic attack by alcohols[7] to give platinum(II) imidates, we have recently reported[8] the conversion in 54–73% yield under mild conditions of both benzonitrile and acetonitrile ligands in *cis*- or *trans*-$[PtCl_2(NCR)_2]$ complexes into Δ^2-1,3-oxazolines according to Scheme 1. These reactions have been proposed to proceed by

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nucleophilic attack of $^{-}OCH_2CH_2Cl$, generated either by deprotonation of $HOCH_2CH_2Cl$ with $LiBu^n$ or by ring opening of OCH_2CH_2 by Cl^- ions, on the nitrile carbon to give the intermediate acyclic imino species **I**, which is converted into the oxazoline product **II** by intramolecular cyclization.

In order to explore the generality of Scheme 1 as a function of the nature of the metal-co-ordinated nitrile ligands, we report herein the reactions of $ClCH_2CH_2OH$ under basic conditions with a series of *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = *p*-MeC_6H_4, *p*-$CF_3C_6H_4$, *o*-MeC_6H_4, Et, Pr^n, Pr^i or Bu^t) complexes[9] in which the electronic and steric properties of the R groups have been varied over a wide range, to afford 2-R-oxazolines. The influence of the base in such conversions as well as the spectroscopic and structural characterization of the new complexes prepared are described.

Experimental

All reactions were carried out under a dinitrogen atmosphere, but work-up of the reaction products was performed in air. Tetrahydrofuran (thf) was distilled from sodium diphenylketyl; all the other solvents were of reagent grade used without further purification. Infrared spectra were recorded on a Perkin Elmer 983 spectrophotometer, ^1H and ^{13}C NMR spectra on Bruker AM-400 and AC-200 spectrometers, and fast atom bombardment (FAB) mass spectra using nitrobenzyl alcohol as a matrix on a VG ZAB 2F instrument operating with a Xe-atom beam energy of 8 keV (*ca.* 1.3×10^{-15} J). The elemental analyses were performed by the Department of Analytical Chemistry of the University of Padova. The melting points were taken on a hot-plate apparatus and are uncorrected.

The complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = *p*-MeC_6H_4, *p*-$CF_3C_6H_4$, *o*-MeC_6H_4, Et, Pr^n, Pr^i or Bu^t) were prepared according to ref. 9.

Reactions with $HOCH_2CH_2Cl$–$LiBu^n$.—*Synthesis of cis*-$[PtCl_2[\{N{=}C(C_6H_4Me\text{-}o)OCH_2CH_2\}_2]$ **1a**. A solution of $ClCH_2CH_2OH$ (0.50 cm^3, 7.46 mmol) in thf (40 cm^3) at 0 °C was treated with a 1.6 mol dm^{-3} hexane solution of $LiBu^n$ (0.68 cm^3, 1.1 mmol). Then, solid *cis*-$[PtCl_2(NCC_6H_4Me\text{-}o)_2]$ (0.250 g, 0.499 mmol) was added to give a suspension. After 5 min a pale yellow clear solution formed, which was stirred for 10 min. Then the ice–water bath was removed and the reaction mixture allowed to reach room temperature (10 min). An IR spectrum of the solution showed $\nu(C{=}N)$ at 1639 cm^{-1} and did not reveal any $\nu(C{\equiv}N)$ stretching at 2277 cm^{-1} of the starting nitrile complex. The solution was taken to dryness under reduced pressure and the yellow solid was treated with MeOH (2 cm^3). The solid residue was filtered off, washed with Et_2O (3×2 cm^3) and dried under vacuum. Yield 0.245 g (84%); m.p. 219–220 °C (Found: C, 40.00; H, 3.55; Cl, 12.30; N, 4.40. Calc. for $C_{20}H_{22}Cl_2N_2O_2Pt$: C, 40.80; H, 3.75; Cl, 12.05; N, 4.75%).

trans-$[PtCl_2\{N{=}C(C_6H_4Me\text{-}o)OCH_2CH_2\}_2]$ **1b**. A solution of $ClCH_2CH_2OH$ (1.00 cm^3, 14.92 mmol) in thf (10 cm^3) at 0 °C was treated with a 1.6 mol dm^{-3} hexane solution of Bu^n (0.95 cm^3, 1.52 mmol). Then, solid *trans*-$[PtCl_2(NCC_6H_4Me\text{-}o)_2]$ (0.346 g, 0.690 mmol) was added to give a clear solution. An IR spectrum of the solution showed $\nu(C{=}N)$ at 1641 cm^{-1} and did not reveal any $\nu(C{\equiv}N)$ stretching at 2287 cm^{-1} of the starting nitrile complex. After 10 min a pale yellow precipitate formed. The ice-bath was removed, the reaction mixture allowed to reach room temperature and stirred for an additional 3 h. The solid was filtered off, washed with MeOH (3×5 cm^3), then Et_2O (3×5 cm^3) and dried under vacuum. Yield 0.275 g (68%), m.p. 237–238 °C (decomp.) (Found: C, 40.15; H, 3.70; Cl, 12.25; N, 4.55. Calc. for $C_{20}H_{22}Cl_2N_2O_2Pt$: C, 40.80; H, 3.75; Cl, 12.05; N, 4.75%).

cis-$[PtCl_2\{N{=}C(C_6H_4Me\text{-}p)OCH_2CH_2\}_2]$ **2a**. This compound was prepared as described for **1a** starting from $ClCH_2CH_2OH$ (0.50 cm^3, 7.46 mmol) in thf (30 cm^3), $LiBu^n$ (0.82 cm^3, 1.32 mmol) and *cis*-$[PtCl_2(NCC_6H_4Me\text{-}p)_2]$ (0.30 g, 0.60 mmol). After a few minutes compound **2a** started to precipitate, and the solution was warmed to room temperature and stirred for 1 h. The solvent was removed and the solid was treated with MeOH (5 cm^3). The solid residue was filtered off, washed with Et_2O (3×5 cm^3) and dried under vacuum. Yield 0.20 g (57%), m.p. 264–265 °C (decomp.) (Found: C, 40.80; H, 3.80; Cl, 12.00; N, 4.70. Calc. for $C_{20}H_{22}Cl_2N_2O_2Pt$: C, 40.80; H, 3.75; Cl, 12.05; N, 4.75%).

$[PtCl_2\{N{=}C(C_6H_4CF_3\text{-}p)OCH_2CH_2\}_2]$ **3**. This complex was prepared as for **2a** starting from $ClCH_2CH_2OH$ (0.50 cm^3, 7.46 mmol) in thf (20 cm^3), $LiBu^n$ (0.50 cm^3, 0.79 mmol) and $[PtCl_2(NCC_6H_4CF_3\text{-}p)_2]$ (0.23 g, 0.38 mmol), which was present as a mixture of *cis* and *trans* isomers. The reaction appears to be immediate as inferred by an IR spectrum of the solution which showed $\nu(C{=}N)$ at 1639 cm^{-1} and did not reveal any $\nu(C{\equiv}N)$ stretching at 2293 cm^{-1} of the starting nitrile complex. After a few minutes at 0 °C a pale yellow solid was formed. The reaction mixture was warmed to room temperature and stirred for 3 h. Work-up as for **2a** gave **3**. Yield 0.21 g (80%), m.p. 252–253 °C (decomp.) (Found: C, 36.65; H, 2.40; Cl, 10.95; N, 4.05. Calc. for $C_{20}H_{16}Cl_2F_3N_2O_2Pt$: C, 37.40; H, 2.50; Cl, 11.05; N, 4.35%).

cis-$[PtCl_2\{N{=}C(Et)OCH_2CH_2\}_2]$ **4a**. This complex was prepared as described for **2a** starting from $ClCH_2CH_2OH$ (0.50 cm^3, 7.46 mmol) in thf (20 cm^3) at 0 °C, $LiBu^n$ (1.32 cm^3, 2.12 mmol) and *cis*-$[PtCl_2(NCEt)_2]$ (0.38 g, 1.01 mmol). After a few minutes complex **4a** precipitated, and the solution was warmed to room temperature and stirred for 1 h. Removal of the solvent and work-up as for **2a** gave complex **4a**. Yield 0.36 g (76%), m.p. 223–224 °C (decomp.) (Found: C, 24.85; H, 3.80; Cl, 15.10; N, 5.95. Calc. for $C_{10}H_{18}Cl_2N_2O_2Pt$: C, 25.85; H, 3.90; Cl, 15.25; N, 6.05%).

trans-$[PtCl_2\{N{=}C(Et)OCH_2CH_2\}_2]$ **4b**. This complex was prepared as for **2a** starting from $ClCH_2CH_2OH$ (0.50 cm^3, 7.46 mmol) in thf (20 cm^3), $LiBu^n$ (1.32 cm^3, 2.12 mmol) and *cis*-$[PtCl_2(NCEt)_2]$ (0.38 g, 1.01 mmol). After stirring for 1 h at room temperature, work-up as for **2a** gave complex **4b**. Yield 0.30 g (63%), m.p. 194–195 °C (decomp.) (Found: C, 25.75; H, 3.80; Cl, 15.20; N, 6.00. Calc. for $C_{10}H_{18}Cl_2N_2O_2Pt$: C, 25.85; H, 3.90; Cl, 15.25; N, 6.05%).

cis-$[PtCl_2\{N{=}C(Pr^n)OCH_2CH_2\}_2]$ **5a**. This complex was prepared as described for **4a** starting from *cis*-$[PtCl_2(NCPr^n)_2]$ (0.41 g, 1.00 mmol). Yield 0.22 (45%), m.p. 180–181 °C (decomp.) (Found: C, 29.30; H, 4.50; Cl, 14.30; N, 5.65. Calc. for $C_{12}H_{22}Cl_2N_2O_2Pt$: C, 29.20; H, 4.50; Cl, 14.40; N, 5.70%).

trans-$[PtCl_2\{N{=}C(Pr^n)OCH_2CH_2\}_2]$ **5b**. This complex was prepared as described for **4a** starting from *trans*-$[PtCl_2(NCPr^n)_2]$ (0.30 g, 0.74 mmol). Yield 0.20 g (55%), m.p. 160–162 °C (decomp.) (Found: C, 29.20; H, 4.35; Cl, 14.30; N, 5.50. Calc. for $C_{12}H_{22}Cl_2N_2O_2Pt$: C, 29.20; H, 4.50; Cl, 14.40; N, 5.70%).

cis-$[PtCl_2\{N{=}C(Pr^i)OCH_2CH_2\}_2]$ **6a**. Preparation as described for **4a**, starting from *cis*-$[PtCl_2(NCPr^i)_2]$ (0.40 g, 0.99 mmol). Yield 0.41 g (84%), m.p. 221–222 °C (decomp.) (Found: C, 29.15; H, 4.45; Cl, 14.40; N, 5.55. Calc. for $C_{12}H_{22}Cl_2N_2O_2Pt$: C, 29.20; H, 4.50; Cl, 14.40; N, 5.70%).

trans-$[PtCl_2\{N{=}C(Pr^i)OCH_2CH_2\}_2]$ **6b**. Preparation as described for **4a** starting from *trans*-$[PtCl_2(NCPr^i)_2]$ (0.50 g, 1.23 mmol). Yield 0.40 g (66%), m.p. 218–219 °C (decomp.) (Found: C, 29.30; H, 4.40; Cl, 14.35; N, 5.70. Calc. for $C_{12}H_{22}Cl_2N_2O_2Pt$: C, 29.20; H, 4.50; Cl, 14.40; N, 5.70%).

cis-$[PtCl_2\{N{=}C(Bu^t)OCH_2CH_2\}_2]$ **7a**. Preparation as described for **4a** starting from *cis*-$[PtCl_2(NCBu^t)_2]$ (0.15 g, 0.35 mmol). Yield 0.098 g (55%), m.p. 220–221 °C (decomp.) (Found: C, 31.95; H, 4.90; Cl, 13.45; N, 5.25. Calc. for $C_{14}H_{26}Cl_2N_2O_2Pt$: C, 32.30; H, 5.05; Cl, 13.60; N, 5.40%).

trans-[PtCl$_2${N=C(Bu^t)OCH$_2$CH$_2$}$_2$] **7b**. Preparation as described for **4a** starting from *trans*-[PtCl$_2$(NCBu^t)$_2$] (0.50 g, 1.15 mmol). Yield 0.55 (91%), m.p. 217–218 °C (decomp.) (Found: C, 31.95; H, 4.95; Cl, 13.50; N, 5.15. Calc. for C$_{14}$H$_{26}$Cl$_2$N$_2$O$_2$Pt: C, 32.30; H, 5.05; Cl, 13.60; N, 5.40%).

Reactions with HOCH$_2$CH$_2$Cl–NEt$_3$.—*trans*-[PtCl$_2$(NCPh)$_2$]. A solution of HOCH$_2$CH$_2$Cl (1.0 cm^3, 15 mmol) in 1,2-dichloroethane (20 cm^3) was treated with NEt$_3$ (0.5 cm^3, 3.58 mmol) at room temperature. Then, solid *trans*-[PtCl$_2$(NCPh)$_2$] (0.30 g, 0.63 mmol) was added to give a clear solution. The reaction course was followed by IR spectroscopy. After 40 min no ν(C≡N) at 2289 cm^{-1} of the starting nitrile was present, while ν(C=N) at 1628 cm^{-1} was observed. The reaction mixture was taken to dryness under reduced pressure to give a white solid, which was washed with MeOH (10 cm^3) and Et$_2$O (3 × 5 cm^3). Yield 0.170 g. IR (Nujol mull): ν(NH) 3239s, ν(C=N) 1625s, ν(C–Cl) 674m, ν(Pt–Cl) 332m, 302m cm^{-1}. The ^{1}H NMR spectrum (CD$_2$Cl$_2$) showed that the white solid is a mixture of products (relative amounts from integration data): *trans*-[PtCl$_2${N=C(Ph)OCH$_2$CH$_2$}$_2$][8] (16%); *Z,Z-trans*-[PtCl$_2${NH=C(Ph)OCH$_2$CH$_2$Cl}$_2$] (48%) [δ 6.12 (t, OCH$_2$), 4.09 (t, CH$_2$Cl), $^3J_{HH}$ 5.1, 8.32 (NH)]; *E,Z-trans*-[PtCl$_2${NH=C(Ph)OCH$_2$CH$_2$Cl}$_2$] (26%) [δ 5.89 (t, OCH$_2$), 3.78 (t, CH$_2$Cl), $^3J_{HH}$ 4.66; 4.53 (t, OCH$_2$), 3.82 (t, CH$_2$Cl), $^3J_{HH}$ 5.1; 8.90 (NH)]; *E,E-trans*-[PtCl$_2${NH=C(Ph)OCH$_2$CH$_2$Cl}$_2$] (10%) [δ 4.01 (t, OCH$_2$), 3.67 (t, CH$_2$Cl), $^3J_{HH}$ 4.3 Hz].

In a second experiment the same reaction was continued for 3 h and worked up as before. The ^{1}H NMR analysis showed the following relative amounts: *trans*-[PtCl$_2${N=C(Ph)OCH$_2$CH$_2$}$_2$][8] (35%); *Z,Z-trans*-[PtCl$_2${NH=C(Ph)OCH$_2$CH$_2$Cl}$_2$] (17%); *E,Z-trans*-[PtCl$_2${NH=C(Ph)OCH$_2$CH$_2$Cl}$_2$] (35%); *E,E-trans*-[PtCl$_2${NH=C(Ph)OCH$_2$CH$_2$Cl}$_2$] (17%). The mixture, treated again with an excess of NEt$_3$ in dichloromethane, gave after 2 d at room temperature the final bis(oxazoline) derivative as the main product.

cis-[PtCl$_2$(NCC$_6$H$_4$Me-*p*)$_2$]. The reaction was carried out as described above using 1,2-dichloroethane (30 cm^3), HOCH$_2$CH$_2$Cl (1.0 cm^3, 15 mmol) and NEt$_3$ (0.5 cm^3, 3.58 mmol) and the *cis*-[PtCl$_2$(NCC$_6$H$_4$Me-*p*)$_2$] (0.30 g, 0.60 mmol) to give a clear solution. After 1 h a white solid began to precipitate. The reaction mixture was stirred for 24 h. Then, the solid was filtered off, washed with Et$_2$O (3 × 5 cm^3) and dried under vacuum. Yield 0.24 g. IR (Nujol mull): ν(NH) 3230s, ν(C=N) 1620s, ν(C–Cl) 674m, ν(Pt–Cl) 326 (br) cm^{-1}. The ^{1}H NMR spectrum (CD$_2$Cl$_2$) showed that the solid is a mixture of products (relative amounts from integration data): *cis*-[PtCl$_2${N=C(C$_6$H$_4$Me-*p*)OCH$_2$CH$_2$}$_2$] (52%) (see Table 2); *Z,Z-cis*-[PtCl$_2${NH=C(C$_6$H$_4$Me-*p*)OCH$_2$CH$_2$Cl}$_2$] (36%) [δ 6.11 (t, OCH$_2$), δ 4.08 (t, CH$_2$Cl), $^3J_{HH}$ 5.3, 2.41 (s, CH$_3$)]; *E,Z-cis*-[PtCl$_2${NH=C(C$_6$H$_4$Me-*p*)OCH$_2$CH$_2$Cl}$_2$] (8%) [δ 4.43 (t, OCH$_2$), 3.88 (t, CH$_2$Cl), $^3J_{HH}$ 5.3, 2.69 (s, CH$_3$); 5.94 (t, OCH$_2$), 3.83 (t, CH$_2$Cl), $^3J_{HH}$ 5.2, 2.42 (s, CH$_3$)]; *E,E-cis*-[PtCl$_2${NH=C(C$_6$H$_4$Me-*p*)OCH$_2$CH$_2$Cl}$_2$] (4%) [δ 3.97 (t, OCH$_2$), 3.65 (t, CH$_2$Cl), $^3J_{HH}$ 4.97 Hz, 2.41 (s, CH$_3$)].

cis-[PtCl$_2$(NCMe)$_2$]. The reaction was carried out in CH$_2$Cl$_2$ (10 cm^3) at room temperature using HOCH$_2$CH$_2$Cl (1.0 cm^3, 15 mmol), NEt$_3$ (0.5 cm^3, 3.58 mmol) and *cis*-[PtCl$_2$(NCMe)$_2$] (0.20 g, 0.57 mmol) to give a yellowish suspension. After 2 h the reaction mixture was taken to dryness to give a whitish solid, which was treated with MeOH (20 cm^3) and then filtered off and washed with Et$_2$O (3 × 5 cm^3). Yield 0.208 g. IR (Nujol mull): ν(NH) 3300s, ν(C=N) 1641s, ν(C–Cl) 669m, ν(Pt–Cl) 324 (br), 352 (br) cm^{-1}. The ^{1}H NMR spectrum [(CD$_3$)$_2$SO] showed that the solid consists mainly of the isomer *E,E-cis*-[PtCl$_2${NH=C(Me)OCH$_2$CH$_2$Cl}$_2$] [δ 4.64 (t, OCH$_2$), 3.9 (t, CH$_2$Cl), $^3J_{HH}$ 5.17 Hz, 2.33 (s, CH$_3$); 9.09 (br, NH)] together with a small amount of the starting nitrile complex (*ca.* 10%). The yellow methanolic solution was taken to dryness to give a yellow solid, taken up with CH$_2$Cl$_2$ and, after filtration, the dichloromethane solution was taken to dryness. The ^{1}H NMR spectrum (CD$_2$Cl$_2$) showed that the solid is a mixture of products (relative amounts from integration data): *cis*-[PtCl$_2${N=C(Me)OCH$_2$CH$_2$}$_2$][8] (46%); *Z,Z-cis*-[PtCl$_2${NH=C(Me)OCH$_2$CH$_2$Cl}$_2$] (21%) [δ 5.92 (t, OCH$_2$), 3.97 (t, CH$_2$Cl), $^3J_{HH}$ 5.88, 2.64 (s, CH$_3$), 8.53 (br, NH)]; *E,Z-cis*-[PtCl$_2${NH=C(Me)OCH$_2$CH$_2$Cl}$_2$] (18%) [δ 5.84 (t, OCH$_2$), 3.92 (t, CH$_2$Cl), $^3J_{HH}$ 4.93, 2.61 (s, CH$_3$); 4.92 (t, OCH$_2$), 3.90 (t, CH$_2$Cl), $^3J_{HH}$ 4.99 Hz, 2.22 (s, CH$_3$)]; *E,E-cis*-[PtCl$_2${NH=C(Me)OCH$_2$CH$_2$Cl}$_2$] (15%) (see above).

trans-[PtCl$_2$(NCMe)$_2$]. The reaction was carried out in CH$_2$Cl$_2$ (10 cm^3) at room temperature using HOCH$_2$CH$_2$Cl (1.0 cm^3, 15 mmol), NEt$_3$ (0.5 cm^3, 3.58 mmol) and *trans*-[PtCl$_2$(NCMe)$_2$] (0.20 g, 0.57 mmol) to give a whitish suspension. After 8 h the reaction mixture was filtered and the solution was taken to dryness to give a whitish solid, which was treated with water (10 cm^3) and CH$_2$Cl$_2$ (70 cm^3). The organic solution was collected, treated with Na$_2$SO$_4$, filtered off and taken to dryness. On addition of hexane (20 cm^3) a whitish precipitate was obtained. Yield 0.18 g. IR (Nujol mull): ν(NH) 3297s, ν(C=N) 1631s, ν(C–Cl) 666m, ν(Pt–Cl) 303 (br), 348 (br) cm^{-1}. The ^{1}H NMR spectrum (CD$_2$Cl$_2$) showed that the solid was a mixture of products (relative amounts from integration data): *trans*-[PtCl$_2${N=C(Me)OCH$_2$CH$_2$}$_2$][8] (11%); *Z,Z-trans*-[PtCl$_2${NH=C(Me)OCH$_2$CH$_2$Cl}$_2$] (16%) [δ 5.96 (t, OCH$_2$), 3.94 (t, CH$_2$Cl), $^3J_{HH}$ 5.0, 2.29 (s, CH$_3$) 8.63 (br, NH)]; *E,Z-cis*-[PtCl$_2${NH=C(Me)OCH$_2$CH$_2$Cl}$_2$] (29%) [δ 5.58 (t, OCH$_2$), 3.89 (t, CH$_2$Cl), $^3J_{HH}$ 5.1, 2.20 (s, CH$_3$), 8.43 (NH); 4.24 (t, OCH$_2$), 3.71 (t, CH$_2$Cl), $^3J_{HH}$ 5.39, 2.60 (s, CH$_3$)]; *E,E-cis*-[PtCl$_2${NH=C(Me)OCH$_2$CH$_2$Cl}$_2$] (44%) [δ 4.28 (t, OCH$_2$), 3.73 (t, CH$_2$Cl), $^3J_{HH}$ 4.8 Hz, 2.49 (s, CH$_3$) 7.26 (br, NH)].

cis-[PtCl$_2$(NCBu^t)$_2$]. The reaction was carried out in 1,2-dichloroethane (15 cm^3) at room temperature using HOCH$_2$CH$_2$Cl (1.0 cm^3, 15 mmol), NEt$_3$ (0.5 cm^3, 3.58 mmol) and *cis*-[PtCl$_2$(NCBu^t)$_2$] (0.21 g, 0.48 mmol) to give a clear solution. It was followed by IR spectroscopy observing the disappearance of ν(C≡N) at 2301 cm^{-1} and the appearance of ν(C=N) at 1634 cm^{-1}. After 2 h no residual ν(C≡N) was present and the reaction mixture was taken to dryness to give a yellow oil, which was dissolved in CH$_2$Cl$_2$ (3 cm^3) and filtered off. The mother-liquor was taken to dryness to give a yellow solid. Yield 0.180 g. IR (Nujol mull): ν(NH) 3269s, ν(C=N) 1628s, ν(C–Cl) 672m, ν(Pt–Cl) 333 (br), 350 (br) cm^{-1}. The ^{1}H NMR spectrum (CD$_2$Cl$_2$) showed that the solid is a mixture of products (relative amounts from integration data): *cis*-[PtCl$_2${N=C(Bu^t)OCH$_2$CH$_2$}$_2$] (40%) (see Table 2); *Z,Z-cis*-[PtCl$_2${NH=C(Bu^t)OCH$_2$CH$_2$Cl}$_2$] (50%) [δ 6.02 (t, OCH$_2$), 3.94 (t, CH$_2$Cl), $^3J_{HH}$ 4.85, 1.60 (s, CH$_3$)]; *E,Z-cis*-[PtCl$_2${NH=C(Bu^t)OCH$_2$CH$_2$Cl}$_2$] (10%) [δ 6.23 (t, OCH$_2$), 3.70 (t, CH$_2$Cl), $^3J_{HH}$ 5.14, 1.67 (s, CH$_3$); OCH$_2$ masked by other signals, 3.56 (t, CH$_2$Cl), $^3J_{HH}$ 5.0 Hz, 1.65 (s, CH$_3$)]; the signals due to *E,E-cis*-[PtCl$_2${NH=C(Bu^t)OCH$_2$CH$_2$Cl}$_2$] could not be safely assigned due to its very low concentration.

Structure Determination.—The crystal and refinement data for *trans*-[PtCl$_2${NC(Bu^t)OCH$_2$CH$_2$}$_2$] **7b** are summarized in Table 5. A prismatic (pale yellow) crystal of dimensions 0.42 × 0.50 × 0.24 mm was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW 1100 diffractometer equipped with graphite-monochromated Mo-Kα radiation. The orientation matrix and preliminary unit-cell dimensions were determined from 25 reflections found by mounting the crystal at random and varying each of the orientation angles χ and φ over a range of 120°, with $7 \leqslant \theta \leqslant 9°$. For the determination of precise lattice parameters, 25 strong reflections with $10 \leqslant \theta \leqslant 13°$ were considered. Integrated intensities for reflections in the intervals $h = \pm 14$, $k = 0$–11, $l = 0$–12 were measured, and three standard

Table 1 Infrared data (cm^{-1}) for compounds **1**–**7**[a]

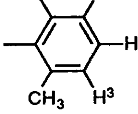
Compound	ν(C=N)	Pt–Cl region
1a *cis*-$[PtCl_2\{NC(C_6H_4Me\text{-}o)OCH_2CH_2\}_2]$	1629s	337s, 342s, 368m
1b *trans*-$[PtCl_2\{NC(C_6H_4Me\text{-}o)OCH_2CH_2\}_2]$	1652s	317vs, 342m, 367m
2a *cis*-$[PtCl_2\{NC(C_6H_4Me\text{-}p)OCH_2CH_2\}_2]$	1638s	326s, 335m
3 $[PtCl_2\{NC(C_6H_4CF_3\text{-}p)OCH_2CH_2\}_2]$[b]	1643s	344m
4a *cis*-$[PtCl_2\{NC(Et)OCH_2CH_2\}_2]$	1655s	330s, 336s
4b *trans*-$[PtCl_2\{NC(Et)OCH_2CH_2\}_2]$	1652s	297m, 322m, 334s, 347m
5a *cis*-$[PtCl_2\{NC(Pr^n)OCH_2CH_2\}_2]$	1646s	333s(br)
5b *trans*-$[PtCl_2\{NC(Pr^n)OCH_2CH_2\}_2]$	1650s	301w, 331s, 374m
6a *cis*-$[PtCl_2\{NC(Pr^i)OCH_2CH_2\}_2]$	1649s	330s, 336s
6b *trans*-$[PtCl_2\{NC(Pr^i)OCH_2CH_2\}_2]$	1651s	335s, 363m, 378m
7a *cis*-$[PtCl_2\{NC(Bu^t)OCH_2CH_2\}_2]$	1624s	327s, 352m, 365m
7b *trans*-$[PtCl_2\{NC(Bu^t)OCH_2CH_2\}_2]$	1621s	329s

[a] In Nujol mull. Abbreviations: s = strong, m = medium, br = broad. [b] This compound was found to be a mixture of *cis* and *trans* isomers, which could not be separated, but were identified by NMR data (see Table 2).

Table 2 Proton NMR data for compounds **1**–**7**[a]

Compound	δ(NCH_2)	δ(OCH_2)	$^3J_{HH}$/Hz	δ(other),[b] J/Hz
1a	3.17 (br)	4.24 (t)	9.8	2.58 (s, CH_3), 8.31 (dd, H^6), $^3J(H^5H^6)$ 7.5, 7.56 (td, H^4), 7.50 (td, H^5), $^4J(H^4H^6)$ 1.3, 7.40 (td, H^3), $^3J(H^3H^4)$ 7.6, $^4J(H^3H^5) < 1$
1b	4.11 (t)	4.59 (t)	9.9	2.33 (s, CH_3), 8.05 (dd, H^6), $^3J(H^5H^6)$ 7.6, $^4J(H^4H^6)$ 1.1, 7.43 (td, H^4), 7.17 (td, H^5), 7.22 (dd, H^3), $^3J(H^3H^4)$ 7.7, $^4J(H^3H^5) < 1$
2a	4.30 (t)	4.62 (t)	9.9	2.46 (s, CH_3), 8.59–8.55 and 7.43–7.39 (m, $C_6H_4CH_3$)
3a	3.84	4.34	9.7	8.96–8.92 and 7.84–7.83 (m, $C_6H_4CF_3$), 63.64 (CF_3)[c]
3b	4.34	4.70	10.0	8.96–8.92 and 7.76–7.52 (m, $C_6H_4CF_3$) 63.67 (CF_3)[c]
4a	3.92 (t)	4.50 (t)	9.8	1.28 (t, CH_3), 2.98 (q, CH_2), $^3J_{HH}$ 7.5
4b	3.90 (t)	4.44 (t)	9.9	1.30 (t, CH_3), 2.95 (q, CH_2), $^3J_{HH}$ 7.3
5a	3.92 (t)	4.49 (t)	9.8	1.04 (t, CH_3), $^3J_{HH}$ 7.4, 1.77 (spt, CH_2), 2.92 (t, CH_2), $^3J_{HH}$ 7.7
5b	3.94 (t)	4.44 (t)	10.0	1.06 (t, CH_3), $^3J_{HH}$ 7.3, 1.86 (spt, CH_2), 2.91 (t, CH_2), $^3J_{HH}$ 7.6
6a	3.91 (t)	4.49 (t)	9.8	1.26 (d, CH_3), 3.92 (spt, CH), $^3J_{HH}$ 6.9
6b	3.88 (t)	4.44 (t)	9.9	1.30 (d, CH_3), 3.86 (spt, CH), $^3J_{HH}$ 7.0
7a	3.82 (m), 4.28 (m)	4.39 (m), 4.35 (m)		1.65 (s, CH_3)
7b	4.07 (t)	4.36 (t)	9.9	1.69 (s, CH_3)

[a] Spectra recorded in CD_2Cl_2; proton chemical shifts are with reference to $SiMe_4$ by taking the chemical shift of CD_2Cl_2 as δ +5.32. Abbreviations: s = singlet, d = doublet, t = triplet, spt = septet, m = multiplet. [b]



[c] Fluorine chemical shifts referenced to internal $CFCl_3$.

reflections (2,1,3; −5,2,3 and −3,3,2) were measured every 180 min. There were no significant fluctuations in intensities other than those expected from Poisson statistics.

The intensity data were corrected for Lorenz-polarization effects and for absorption, by following the method of North *et al.*;[10] no correction was made for extinction. The structure was solved by three-dimensional Patterson and Fourier techniques and refined with full-matrix least-squares, anisotropic thermal parameters being assigned to all the non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions and allowed to ride on their associated carbon atoms during the least-squares refinement (d_{C-H} = 0.98 Å and U = 0.07 Å^2). The function minimized was $\Sigma w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$. Final R values were R = 0.038 and R' = 0.042. The largest peak in the final difference map (0.8 e Å^{-3}) was located near the platinum atom positions. Atomic scattering factors were taken from ref. 11. Data processing and computation were carried out by using the SHELX 76 program package[12] and ORTEP[13] for drawings. The atomic coordinates are reported in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results

Reactions with $HOCH_2CH_2Cl–LiBu^n$.—Following earlier work from our laboratory on the reactions of acetonitrile and benzonitrile ligands,[8] we have found that a wide series of nitriles in *cis*- or *trans*-$[PtCl_2(NCR)_2]$ complexes can be converted in good yield into 2-R-oxazolines by reaction with 2-chloroethanol in the presence of 2 equivalents of $LiBu^n$ as summarized in Scheme 2. Compounds **1**–**7** are pale yellow solids, which are air stable in the solid state and in solution, soluble in chlorinated solvents but insoluble in saturated hydrocarbons. They have been characterized by IR (Table 1), ^1H NMR (Table 2), ^{13}C NMR (Table 3) and FAB mass spectra (Table 4) and by an X-ray structural determination for **7b** (see below). The Nujol mull IR spectra show the ν(C=N) stretching of the oxazoline ring in the range 1621–1655 cm^{-1} with no significant differences between *trans* and *cis* isomers or also between aryl- and alkyl-substituted oxazolines, but similar to that observed for the analogous phenyl and methyl derivatives.[8] The platinum–chlorine stretching vibrations of **1**–**7** fall in the range 297–378 cm^{-1}, but more bands than those expected for a *cis*- or *trans*-Cl_2PtL_2 stereogeometry are present for several of these compounds. This phenomenon has been previously observed for the dichloro derivatives of the aforementioned phenyl- and methyl-oxazo-

Table 3 ^{13}C-{^1H} NMR data for compounds **1**–**7***

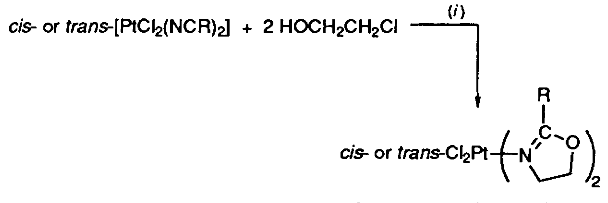
Compound	δ(C^2)	δ(NCH_2)	δ(OCH_2)	δ(other)
1a	169.05	55.07	69.55	20.81 (CH_3), 138.36–126.23 ($C_6H_4CH_3$)
1b	169.93	55.89	69.17	20.31 (CH_3), 138.22–125.69 ($C_6H_4CH_3$)
2a	167.82	56.66	68.58	21.95 (CH_3), 144.91–122.69 ($C_6H_4CH_3$)
3a	166.86	57.64	69.04	127.02 (CF_3), $^1J_{CF}$ 167.5; 134.86–129.64 ($C_6H_4CF_3$)
3b	166.86	57.49	69.09	125.53 (CF_3), $^1J_{CF}$ 164.9; 135.45–129.70 ($C_6H_4CF_3$)
4a	175.20	55.73	69.19	9.93 (CH_3), 23.21 (CH_2)
4b	174.15	54.83	68.97	10.15 (CH_3), 22.86 (CH_2)
5a	174.45	55.68	69.04	14.04 (CH_3), 19.37 (CH_2), 31.37 (CH_2)
5b	174.20	54.80	68.90	14.07 (CH_3), 19.60 (CH_2), 30.99 (CH_2)
6a	178.06	54.80	66.89	19.17 (CH_3), 30.14 (CH)
6b	176.55	55.64	69.06	19.09 (CH_3), 29.69 (CH)
7a	176.80	57.60	67.50	28.90 (CH_3), 34.27 (C)
7b	179.17	58.80	67.39	29.04 (CH_3), 34.98 (C)

* Spectra recorded in CD_2Cl_2; carbon chemical shifts are referenced to $SiMe_4$ by taking the chemical shift of CD_2Cl_2 as δ +53.80; *J* in Hz.

Table 4 The FAB mass spectral data for some bis(oxazoline)platinum(II) compounds

		m/z [b]					
Compound	*M* [a]	$[M]^{\bullet +}$	$[M - Cl^{\bullet}]^+$	$[M - 2Cl^{\bullet}]^{\bullet +}$	$[M - oxz]^+$	$[M - Cl^{\bullet} - oxz]^{\bullet +}$	$[M - 2Cl^{\bullet} - oxz]^+$
1a	587	587 (14.3)	552 (3.6)	517 (100)	426 (43.0)	391 (42.8)	356 (50.0)
2a	587	587 (16.6)	552 (11.1)	517 (94.5)	426 (100)		356 (17.6)
3a [c]	695	695 (8.95)	660 (7.46)	625 (100)			410 (23.8)
4a	463	463 (10.5)	428 (7.0)	393 (100)			294 (10.5)
5a	491	491 (15.8)	456 (7.8)	421 (100)	378 (5.3)	343 (5.3)	308 (44.7)
6a	491	491 (18.8)	456 (12.5)	421 (100)	378 (12.0)	343 (6.25)	308 (25.0)
7a	519	519 (17.5)	484 (36.0)	449 (100)		357 (19.3)	322 (29.8)
7b [d]	519	519 (7.3)	484 (15.9)	449 (51.3)	392 (95.1)		

[a] Nominal molecular weight using the ^{194}Pt isotope. [b] oxz = Δ^2-1,3-oxazoline group. Relative abundances (%, in parentheses) are normalized to the most intense ion. [c] The ions at *m/z* 556 (6.0), which correspond to the loss of $^{\bullet}CF_3$ from ions at *m/z* 625, are also present. [d] The ions at *m/z* 469 (39.0) and 434 (100%), which correspond to the loss of $^{\bullet}CH_3$ from ions at *m/z* 484 and 449, respectively, are also present.



Scheme 2 (*i*) 2 $LiBu^n$, thf. **a** and **b** refer to *cis* and *trans* isomers, respectively. R = *o*-MeC_6H_4 **1a**, **1b**; *p*-MeC_6H_4 **2a**, **2b**; *p*-$CF_3C_6H_4$ **3a** + **3b**; Et **4a**, **4b**; Pr^n **5a**, **5b**; Pr^i **6a**, **6b**; Bu^t **7a**, **7b**

lines[8] and also for *trans*- and *cis*-bis(imido esters) of Pt^{II} derived from nucleophilic attack of MeOH on the co-ordinated benzonitrile ligands in *trans*- and *cis*-$[PtCl_2(NCPh)_2]$.[7b] The proton NMR spectra confirm the cyclic structure of the reaction products as evidenced by the value (*ca.* 10 Hz) of $^3J_{HH}$ for the NCH_2CH_2O system, which is higher than the corresponding value generally observed for a similar acyclic structure (*ca.* 5 Hz)[14] and also found for the acyclic imido esters reported below. Except for **1a** and **7a**, the NCH_2 and OCH_2 protons generally appear as triplets in the ranges δ 3.71–4.36 and 3.97–4.50, respectively.[8] As for **1a** and **7a**, which are of *cis* geometry and contain on the oxazoline ring the highly sterically demanding *o*-tolyl and *tert*-butyl groups, respectively, a more complex ^1H NMR pattern is observed. Thus, **1a** displays at 298 K the NCH_2 protons as a broad signal at δ 3.17, while the OCH_2 protons appear as a triplet at δ 4.24 (the assignment has been confirmed by decoupling experiments). By lowering the temperature to 201 K the NCH_2CH_2O protons show up as four distinct multiplets: those centred at δ 4.05 and 3.89 are tentatively assigned to the OCH_2 protons, while those centred at δ 4.52 and 2.16 are assigned to the NCH_2 protons. Molecular models indicate that the less-strained conformation leads to one of the NCH_2 protons being located in the shielding region of the phenyl ring of the second oxazoline ligand in *cis* position and this might reasonably explain the markedly upfield shift that is observed. On the other hand, the broadening of the NCH_2 resonance at room temperature may be due to the rapid (on the NMR time-scale) interconversion among different conformations of one oxazoline ring relative to the other. As for **7a**, four multiplets are observed at room temperature for the NCH_2CH_2O system, possibly due to the presence of only one conformation with four magnetically different protons owing to the two sterically hindered Bu^t groups. In **1**–**3**, the *o*-protons of the phenyl groups are shifted downfield (δ 8.96–8.31) due to a deshielding effect of the metal. A similar behaviour has been noted for related platinum(II) imido esters[7b] having a *cis* metal–phenyl conformation and in *cis*- and *trans*-$[PtCl_2\{\overline{NC(Ph)OCH_2CH_2}\}_2]$.[8] No *J*(Pt–$H_{ortho}$) is observed, presumably owing to the relatively free rotation about the aryl–oxazoline bond.[15]

The ^{13}C-{^1H} NMR spectra of compounds **1**–**7** show the NCH_2 and the OCH_2 carbons in the range δ 54.80–58.80 and 66.89–69.55, respectively, as expected for Δ^2-oxazoline systems.[8,16] The C^2 oxazoline carbons appear in the range δ 166.86–179.17 with a generally downfield shift of the alkyl compared to the aryl-substituted carbons.

The FAB mass spectra (Table 4) of some of the derivatives show the presence of an abundant molecular ion with subsequent losses of the two chlorine radicals. It is worthwhile noting that the $[M]^{\bullet +}$ molecular ion, $[M - Cl^{\bullet}]^+$ and $[M - 2Cl^{\bullet}]^{\bullet +}$ show the loss of one Δ^2-oxazoline group. No oxazoline fragmentation, which is reported to occur with loss of CO and HCN for the metal-free ligands,[17] is observed. Thus, it appears that the N-metal co-ordination makes the ring stable toward ring opening, since the attack on the nitrogen atom to produce the *N*-substituted Δ^2-oxazolinium cation is reported to be the early stage of ring opening and polymerization of free oxazolines.[18]

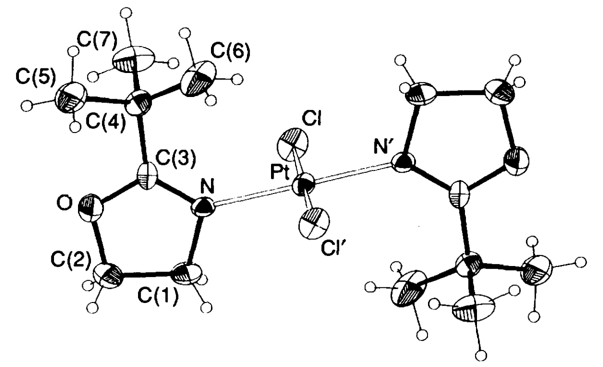


Fig. 1 An ORTEP view of *trans*-[PtCl$_2${N=C(Bu^t)OCH$_2$CH$_2$}$_2$] **7b** with the atomic numbering scheme. Ellipsoids are at the 50% probability level

Table 5 Crystal data, experimental conditions and refinement for *trans*-[PtCl$_2${NC(Bu^t)OCH$_2$CH$_2$}$_2$] **7b**

Formula	$C_{14}H_{26}Cl_2N_2O_2Pt$
M	520.37
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	11.233(2)
b/Å	8.741(2)
c/Å	9.394(2)
β/°	101.61(3)
U/Å^3	903.5(3)
Z	2
D_c/g cm^{-3}	1.91
F(000)	504
λ(Mo-Kα)/Å	0.710 69
μ(Mo-Kα)/cm^{-1}	81.5
Reflections measured	2514
Scan method	θ–2θ
Reflections [$I \geqslant 3\sigma(I)$]	1710
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.038
$R' = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.042
Weighting scheme, w	$[\sigma^2(F_o) + 0.005\,813(F_o^2)]^{-1}$
Goodness of fit, S	0.73
Transmission range	0.61–1
Parameters refined	107

Table 6 Atomic coordinates (× 10^4) for non-hydrogen atoms with estimated standard deviations in parentheses for *trans*-[PtCl$_2${NC(Bu^t)OCH$_2$CH$_2$}$_2$] **7b**

Atom	X/a	Y/b	Z/c
Pt	0	0	0
Cl	647(1)	2242(1)	−893(1)
N	922(3)	569(4)	1993(4)
O	1638(3)	1557(4)	4154(3)
C(1)	2197(9)	40(5)	2335(9)
C(2)	2660(4)	659(6)	3874(5)
C(3)	696(4)	1380(4)	3046(4)
C(4)	−448(4)	2225(5)	3179(4)
C(5)	−529(7)	2334(8)	4792(6)
C(6)	−1578(5)	1439(8)	2343(8)
C(7)	−343(6)	3853(6)	2558(7)

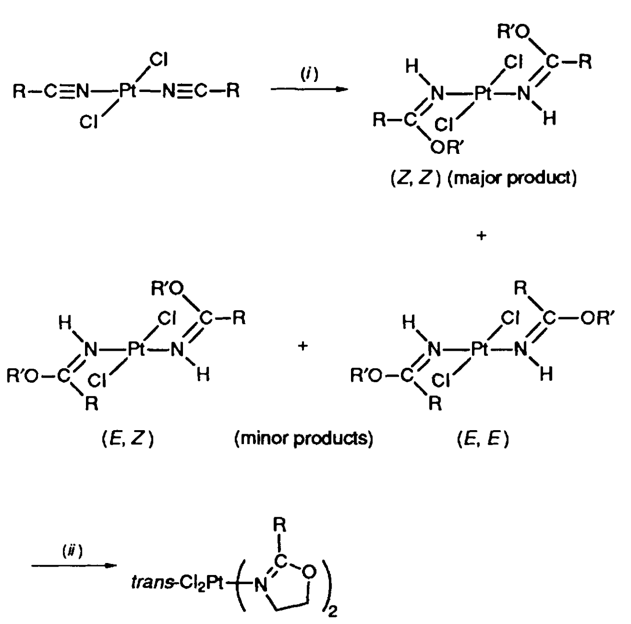
Table 7 Bond distances (Å) and angles (°) with e.s.d.s in parentheses for *trans*-[PtCl$_2${NC(Bu^t)OCH$_2$CH$_2$}$_2$] **7b**

Pt–Cl	2.307(1)	Pt–N	2.011(3)
N–C(1)	1.477(9)	N–C(3)	1.284(5)
O–C(2)	1.458(6)	O–C(3)	1.335(5)
C(1)–C(2)	1.533(9)	C(3)–C(4)	1.509(6)
C(4)–C(5)	1.539(7)	C(4)–C(6)	1.517(7)
C(4)–C(7)	1.552(7)		
Cl–Pt–N	89.3(1)	Pt–N–C(3)	135.2(3)
Pt–N–C(1)	114.9(4)	C(1)–N–C(3)	109.8(4)
C(2)–O–C(3)	109.0(3)	N–C(1)–C(2)	103.0(5)
O–C(2)–C(1)	103.3(5)	N–C(3)–O	114.6(4)
O–C(3)–C(4)	115.6(3)	N–C(3)–C(4)	129.7(4)
C(3)–C(4)–C(7)	106.7(4)	C(3)–C(4)–C(6)	111.9(4)
C(3)–C(4)–C(5)	109.4(4)	C(6)–C(4)–C(7)	109.9(4)
C(5)–C(4)–C(7)	109.7(4)	C(5)–C(4)–C(6)	109.2(4)

Structure of trans-[PtCl$_2${NC(Bu^t)OCH$_2$CH$_2$}$_2$] **7b**.—An ORTEP view of the molecule is shown in Fig. 1 with the atom-numbering scheme. The molecular structure is characterized by the presence of a crystallographic inversion centre where the Pt lies, then the asymmetric unit in the crystal is half a molecule and the overall molecular geometry is *trans*-planar. Bond distances and angles are reported in Table 7. The Pt–N bond distance [2.011(3) Å] and Pt–Cl [2.307(1) Å] are in good agreement with the values reported for analogous compounds. In particular they are comparable to the values for the complex *cis*-[PtCl$_2${NC(Ph)OCH$_2$CH$_2$}$_2$][8] with the Pt–N$_{av}$ 2.013(3) and Pt–Cl 2.298(1) Å.

The values 89.3(1)° for Cl–Pt–N and 90.7(1)° for Cl–Pt–N' could be related to the weaker intramolecular interactions of the chlorides than in *trans*-dichloro(cyclohexylamine)-platinum(II)[19] which has bond distances similar to that of the present compound but different co-ordination plane angles, 94.6 and 85.4°, respectively, due to intramolecular chloride interactions (of the order of 3.3–3.7 Å) with the cyclohexyl ring. The bond distances and the slightly twisted conformation of the oxazoline ring N–C(1)–C(2)–O–C(3) [deviations from the best mean plane: N 0.002(4), C(1) 0.040(8), C(2) −0.031(5), O 0.016(3), C(3) −0.015(4)] are comparable to that of the phenyl-substituted oxazoline in the previously cited compound.[8] This suggests that the hindrance of the substituent in position 2 does not influence the geometry of the oxazoline moiety. The dihedral angle between the co-ordination plane and the oxazoline ring is 87.7(1)°. The quasi-orthogonal arrangement of the ligand is in order to avoid close intramolecular contacts with the bulky Bu^t group. The crystal packing is determined solely by van der Waals forces and none of the intramolecular contact distances is shorter than the sum of the van der Waals radii.

Reactions with HOCH$_2$CH$_2$Cl–NEt$_3$.—In order to investigate the influence of the nature of the base in promoting the reactions of 2-chloroethanol with nitrile ligands, we have examined the reactions of different co-ordinated RCN ligands in *cis*- and *trans*-[PtCl$_2$(NCR)$_2$] complexes with the 2-chloroethanol–triethylamine system. The reaction of *trans*-[PtCl$_2$(NCPh)$_2$] with 2-chloroethanol (1 cm^3, 14.8 mmol) and NEt$_3$ (0.5 cm^3, 3.58 mmol) has also been monitored by ^{1}H NMR spectroscopy in CD$_2$Cl$_2$ at room temperature. It proceeds with the formation of the bis(imido ester) complex *trans*-[PtCl$_2${NH=C(Ph)OCH$_2$CH$_2$Cl}$_2$] which is present as a mixture of (*E*,*E*), (*E*,*Z*) and (*Z*,*Z*) isomers, corresponding to *cis* (*E*) or *trans* (*Z*) 2-chloroethanol addition to the C≡N triple bond (Scheme 3). It is observed that the (*Z*,*Z*) imido ester isomer is mainly formed (*ca.* 80%) at the beginning of the reaction (*ca.* 30 min) together with smaller amounts of the other isomers and the final oxazoline product. The signal assignment for the three different isomers has been made as previously reported;[7b,8] in particular, the OCH$_2$ protons in the (*Z*) conformation are shifted downfield due to their position close to Pt. During the course of the reaction the (*Z*,*Z*) isomer is observed to convert into the other (*E*,*E*) and (*E*,*Z*) isomers through a process likely to be catalysed by $^-$OCH$_2$CH$_2$Cl (formed by reaction of the halogenoalcohol with NEt$_3$) and involving the formation of the amidoketal species Pt–NHC-



Scheme 3 R = Ph, R′ = CH_2CH_2Cl. (*i*) R′OH, NEt_3; (*ii*) $-[NHEt_3]Cl$

$(OCH_2CH_2Cl)_2Ph$, which re-eliminates the halogenoalkoxide ion regenerating the imido ester species. A similar mechanism has been previously suggested for the interconversions of (*E*) and (*Z*) imido ester conformers of *cis*- and *trans*-$[PtCl_2\{NHC(OMe)Ph\}_2]$, which is catalysed by ^-OMe.[7b]

A behaviour similar to that of the benzonitrile ligand in *trans*-$[PtCl_2(NCPh)_2]$ is observed also in the reactions of other nitrile ligands such as acetonitrile, *p*-toluonitrile and trimethylacetonitrile in *cis*- or *trans*-$[PtCl_2(NCR)_2]$ complexes, since they proceed through the formation of a mixture of the imido esters *cis*-$[PtCl_2\{NH{=}C(R)OCH_2CH_2Cl\}_2]$ with a composition of the (*E,E*), (*Z,Z*) and (*E,Z*) conformers which appears to be determined by the nature of the R substituent and/or their different solubilities. For instance, for the bis(acetonitrile) complex reactions only, the (*E,E*) isomer is isolated initially due to its very low solubility in the reaction medium, thus making the subsequent ring-closure reaction more difficult.

Discussion

Nitrile co-ordination to the electron-withdrawing platinum(II) metal centre leads to an increase in the electrophilicity of the nitrile carbon as indicated by an increase in $\Delta\nu = \nu(C{\equiv}N)_{co\text{-}ord} - \nu(C{\equiv}N)_{free}$, which is about 50 cm^{-1} for complexes of the type *cis*- and *trans*-$[PtCl_2(NCR)_2]$.[9] Positive $\Delta\nu$ values (81–109 cm^{-1}) have been found previously for the isoelectronic isocyanide complexes *cis*-$[PtCl_2(CNR)_2]$ (R = alkyl or aryl)[20] and they have been related to the susceptibility of the isocyanide carbon to nucleophilic attack to produce carbene complexes. However, it has also been noticed that a positive value of $\Delta\nu$ (> 60 cm^{-1}) appears to be a necessary but not sufficient condition for facilitating reactions of isocyanide ligands with nucleophiles such as alcohols and amines.[21] Steric and electronic factors appear to influence these reactions and when R is a sterically bulky group such as cyclohexyl or *tert*-butyl only one isocyanide is converted into a carbene.[20,22] For the nitrile reactions of the complexes *cis*- or *trans*-$[PtCl_2(NCR)_2]$ reported in this work it is observed that both nitrile ligands are converted in good yield into the corresponding oxazolines whatever the complex geometry and the steric and/or electronic properties of the R substituent. Furthermore, the conversion of both nitriles is very fast and no experimental (IR and ^1H NMR) evidence is obtained for a nitrile–oxazoline intermediate. Conversely, for the similar bis(isocyanide) reactions with amines or alcohols, the reaction proceeds stepwise with rapid formation of the carbene–isonitrile intermediate, which can be isolated.[20] However, imido ester–nitrile derivatives were previously obtained by reaction of *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ with ^-OMe in the presence of a catalytic amount of base.[7b]

As suggested in previous work,[8] the nitrile–oxazoline conversion is likely to occur by nucleophilic attack of $^-OCH_2CH_2Cl$ on the nitrile carbon to give the imino intermediate **I** (see Introduction), which eventually cyclizes intramolecularly by chloride displacement. Intermediate **I** could not be isolated or detected spectroscopically even when R is an efficient electron-withdrawing substituent such as *p*-$CF_3C_6H_4$, which would make the imino nitrogen less nucleophilic for the intramolecular cyclization; conversely, this latter proceeds to give the oxazoline derivative **3** in high yield. It is also observed that there is no difference in the reactivity of an alkyl compared to an aryl nitrile ligand, since the corresponding oxazolines are obtained in comparable yields and comparable reaction times. This feature may be interpreted by a balance of electronic effects, which are likely to affect these reactions: the first step (nucleophilic attack of the $^-OCH_2CH_2Cl$ ion on the RCN carbon) is favoured when R is an electron-withdrawing aryl group, which will make the nitrile carbon electrophilic and thus more susceptible to nucleophilic attack by the halogenoalkoxide; the second step (ring-closure process) is favoured when R is an electron-releasing alkyl group, which will make the N atom of **I** more nucleophilic for chloride displacement.

The $HOCH_2CH_2Cl$–NEt_3 system is not as effective as $HOCH_2CH_2Cl$–$LiBu^n$ in the conversion of nitriles into 2-oxazolines, since these reactions proceed with longer reaction times and give lower yields of the oxazoline products. All these reactions proceed initially with the formation of the bis(imido ester) complexes $[PtCl_2\{NH{=}C(R)OCH_2CH_2Cl\}_2]$ which are present as a mixture of (*E*) and (*Z*) conformers. The formation of (*E*) and (*Z*) isomers derived from alcohol addition to co-ordinated nitriles has been previously observed in some cases such as in *trans*-$[Ni(C_6Cl_5)(PMe_2Ph)_2\{HN{=}C(OR')R\}]$ (R = Me, Ph or CH_2Ph; R′ = Me or Et),[23] in *cis* and *trans*-$[PtCl_2\{NH{=}C(OMe)Ph\}(NCPh)]$[7b] and *cis*- and *trans*-$[PtCl_2\{NH{=}C(OMe)Ph\}_2]$.[7b] It is interesting that the reaction of $[W\{HB(N_2C_3HMe_2\text{-}3,5)_3\}(CO)(RC{\equiv}CR')(N{\equiv}CMe)]BF_4$ with $LiBEt_3H$ leads to the azavinylidene complex $[W\{HB(N_2C_3HMe_2\text{-}3,5)_3\}(CO)(RC{\equiv}CR')\{N{=}C(H)Me\}]$ which by acidification with HBF_4 yields as the only product $[W\{HB(N_2C_3HMe_2\text{-}3,5)_3\}(CO)(RC{\equiv}CR')\{NH{=}C(H)Me\}]BF_4$, containing the imine ligand with the hydrogens *trans* to one another.[24]

The (*E*) and (*Z*) conformers of $[PtCl_2\{NH{=}C(R)OCH_2CH_2Cl\}_2]$ complexes are observed to interconvert under the experimental conditions and the interconversion is accompanied by an increase in the relative amount of the oxazoline product, as evidenced by the analysis of the reaction products at different times (see Experimental section). It is likely that the ring closure is facilitated from the (*E*) conformer, which in the presence of a base would give intermediate **I**, where the N atom and the CH_2Cl moiety are in a favourable position to interact intramolecularly to yield the oxazoline.

It is finally worthwhile noting that in the reactions of $HOCH_2CH_2Cl$–$LiBu^n$ or $HOCH_2CH_2Cl$–NEt_3 with the $[PtCl_2(NCR)_2]$ complexes there is complete retention of configuration around the Pt atom, as previously observed in nucleophilic attack with alcohols on co-ordinated nitriles in *cis*- and *trans*-$[PtCl_2(NCR)_2]$,[7b,8] and also that platinum(II)-promoted nitrile to oxazoline conversion occurs under mild conditions with no evidence of ring-degradation processes as reported for some organic syntheses.[1]

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