Synthesis of 5,6-dihydro-4*H*-1,3-oxazines from neutral and cationic platinum(II) nitrile complexes. X-ray structure of *trans*-$[Pt(CF_3)\{\overline{N=C(Ph)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$

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Abstract

The 1,3-oxazine complexes *cis*- and *trans*-$[PtCl_2\{\overline{N=C(R)OCH_2CH_2CH_2}\}_2]$ (*cis*: R = CH_3 (**1a**), CH_2CH_3 (**2a**), $(CH_3)_3C$ (**3a**), C_6H_5 (**4a**); *trans*: R = CH_3 (**1b**), C_6H_5 (**4b**)) were obtained in 51–71% yield by reaction in THF at 0 °C of the corresponding nitrile complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ with 2 equiv. of $^-OCH_2CH_2CH_2Cl$, generated by deprotonation of 3-chloro-1-propanol with n-BuLi. The cationic nitrile complexes *trans*-$[Pt(CF_3)(NCR)(PPh_3)_2]BF_4$ (R = CH_3, C_6H_5) react with 1 equiv. of $^-OCH_2CH_2CH_2Cl$ to give a mixture of products, including the corresponding oxazine derivatives *trans*-$[Pt(CF_3)\{\overline{N=C(R)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$ (**5** and **6**), the chloro complex *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$ and free oxazine $\overline{N=C(R)OCH_2CH_2CH_2}$. For short reaction times (*c.* 5–15 min) the oxazine complexes **5** and **6** could be isolated in modest yield (37–49%) from the reaction mixtures and they could be separated from the corresponding chloro complex (yield 40%) by taking advantage of the higher solubility of the latter derivative in benzene. For longer reaction times (> 2 h), *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$ was the only isolated product. Complex **6** was crystallographically characterized and it was found to contain also crystals of *trans*-$[PtCl\{\overline{N=C(R)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$, which prevented a more detailed analysis of the bond lengths and angles within the metal coordination sphere. The 1,3-oxazine ring, which shows an overall planar arrangement, is characterized by high thermal values of the carbon atoms of the methylene groups indicative of disordering in this part of the molecule in agreement with fast dynamic ring processes suggested on the basis of ^1H NMR spectra. It crystallizes in the trigonal space group $P\bar{3}$, with $a = 22.590(4)$, $b = 15.970(3)$ Å, $\gamma = 120°$, $V = 7058(1)$ Å^3 and $Z = 6$. The structure was refined to $R = 0.059$ for 3903 unique observed ($I \geq 3\sigma(I)$) reflections. A mechanism is proposed for the conversion of nitrile ligands to oxazines in Pt(II) complexes.

Key words: Crystal structures; Platinum complexes; Oxazine complexes; Nitrile complexes

Introduction

5,6-Dihydro-4*H*-1,3-oxazines (1,3-oxazines hereafter) are useful intermediates for the construction of carbonyl derivatives and carboxylic acids [1, 2], convenient substrates for more complex heterocyclic systems [1] and compounds that have been reported to show biological activity [3]. 1,3-Oxazines are generally prepared from nitriles by the Ritter reaction [4], which consists of reacting a diol with a nitrile at low temperature under strongly acidic conditions, as reported in eqn. (1).

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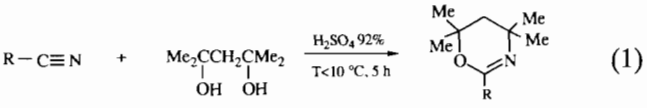
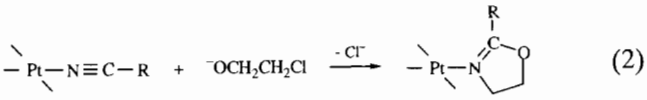


(1)

Other methods used for the preparation of this class of compounds involve the elimination of water from β-acylamino-aldehydes, ketones or esters [3, 5], or the reaction of chloroolefins with nitriles in an acidic medium [6].

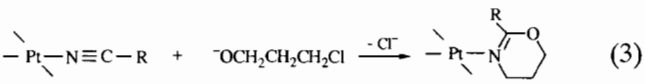
It was earlier demonstrated in this laboratory that the highly electrophilic nitrile complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = alkyl, aryl) [7a, b] and *trans*-$[Pt(R')(NCR)(PPh_3)_2]^+$ (R' = H, CH_3, CF_3; R = alkyl, aryl) [7c] readily cycloadd the alkoxide $^-OCH_2CH_2Cl$, generated either by deprotonation of the corresponding alcohol with a base or by Cl^- attack on the oxirane $\overline{OCH_2CH_2}$ ring, to give the corresponding oxazoline complexes as illustrated in the general reaction (2).



(2)

The first step in all of these reactions is believed to be the addition of the nucleophilic oxygen atom of the organic substrate to the electrophilic nitrile carbon, analogous to the several other nucleophiles which have been shown to add this carbon [8]. Reaction (2) is also of interest since it occurs for a wide series of RCN ligands showing no steric and/or electronic influence of the R group, it produces 2-oxazolines in high yield and proceeds under basic conditions, thus avoiding possible oxazoline ring cleavage which is reported to occur under acidic conditions [9].

In an attempt to form other types of heterocycles from nitrile complexes of Pt(II), we have since reacted these species with 3-chloro-1-propoxide (eqn. (3)).



(3)

These reactions have led to the synthesis of new 1,3-oxazine complexes and those results are described herein.

Experimental

General procedures

All reactions were carried out under an N_2 atmosphere. Tetrahydrofuran (THF) was distilled from sodium/benzophenone; all the other solvents were of reagent grade and used without further purification. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer, ^1H and ^{13}C NMR spectra were recorded on Bruker AM-400 and AC-200 spectrometers and ^{31}P NMR spectra were recorded on a Varian FT 80-A spectrometer. The fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB 2F instrument operating with a Xe-atom beam energy of 8 keV. The GC/MS analyses were performed on a QMD 1000 instrument using a PS 264 column, 30 m × 0.25 mm × 3 μm. *T*: 100 to 250 °C, 10°/min. The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected.

Starting complexes

The complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = CH_3 [10–12], C_6H_5 [10, 11], CH_2CH_3 [11], $C(CH_3)_3$ [11]) and the cationic complexes *trans*-$[Pt(CF_3)(NCR)(PPh_3)_2]BF_4$ (R = CH_3, C_6H_5) [7c] were prepared according to reported procedures.

Synthesis of oxazine complexes

Synthesis of cis-$[PtCl_2\{\overline{N=C(CH_3)OCH_2CH_2CH_2}\}_2]$ (1a)

A solution of $ClCH_2CH_2CH_2OH$ (1.0 ml, 11.6 mmol) in THF (70 ml) at 0 °C was treated with crystalline NaH (45.0 mg, 1.89 mmol) and then solid *cis*-$[PtCl_2(NCMe)_2]$ (300 mg, 0.86 mmol) was added. The pale green suspension was stirred at low temperature for 30 min and then slowly warmed to room temperature. During this time the suspension turned white and an IR spectrum of the solid formed showed a strong absorption at 1647 cm^{-1} due to the C=N stretch of the final product. After stirring for an additional 2 h, the reaction solution was taken to dryness under reduced pressure. The yellow oil formed was dissolved in CH_2Cl_2 (50 ml); this solution was treated with activated charcoal, filtered and concentrated to small volume (3 ml). On addition of Et_2O (20 ml), a white product precipitated, which was filtered off, washed with MeOH (2 × 5 ml), Et_2O (3 × 5 ml) and dried under vacuum. Yield 240 mg (60%); m.p. 232–233 °C (dec.). *Anal.* Calc. for $C_{10}H_{18}N_2Cl_2O_2Pt$: C, 25.87; H, 3.90; N, 6.03; Cl, 15.27. Found: C, 25.37; H, 3.86; N, 5.84; Cl, 15.25%. FAB mass spectrum, *m/z* (rel. int.%): $[M]^{\cdot+}$ 463 (0.05); $[M - \text{oxazine}]^{\cdot+}$ 365 (0.4).

Synthesis of trans-$[PtCl_2\{\overline{N=C(CH_3)OCH_2CH_2CH_2}\}_2]$ (1b)

To a solution of $ClCH_2CH_2CH_2OH$ (1 ml, 11.6 mmol) in THF (50 ml) at 0 °C was added a 1.6 M n-hexane solution of n-BuLi (1.61 ml, 2.58 mmol) and, after a few minutes, *trans*-$[PtCl_2(NCMe)_2]$ (408 mg, 1.17 mmol). The reaction mixture was then stirred at 0 °C for 10 min to give a clear solution. A solution IR spectrum

did not reveal any residual ν(C≡N) band of the starting nitrile complex, while a strong ν(C=N) absorption at 1652 cm^{-1} of the final product was present. The stirring was continued at room temperature for an additional 4 h. Then the reaction mixture was taken to dryness and the solid residue was treated with MeOH (2×5 ml) and Et_2O (3×5 ml), filtered off and dried under vacuum. Yield 285 mg (52.5%); m.p. 275–276 °C (dec.). *Anal.* Calc. for $C_{10}H_{18}N_2Cl_2O_2Pt$: C, 25.87; H, 3.90; N, 6.03; Cl, 15.27. Found: C, 25.85; H, 3.80; N, 5.96; Cl, 15.07%. FAB mass spectrum; *m/z* (rel. int.%): $[M]^{\cdot+}$ 463 (0.1); $[M-\text{oxazine}]^{\cdot+}$ 365 (0.6); $[M-\text{2-oxazine}]^{\cdot+}$ 265 (0.4).

Synthesis of cis-
$[PtCl_2\{\overline{N{=}C(CH_2CH_3)OCH_2CH_2CH_2}\}_2]$ (2a)

This was prepared as described for **1b** starting from $ClCH_2CH_2CH_2OH$ (0.5 ml, 5.82 mmol), 1.6 M n-hexane solution of n-BuLi (1 ml, 1.6 mmol) and *cis*-$[PtCl_2(NCCH_2CH_3)_2]$ (201 mg, 0.53 mmol). The immediate disappearance of ν(C≡N) of the nitrile and formation of the ν(C=N) absorption at 1634 cm^{-1} due to the oxazine are observed. Reaction time: 30 min at 0 °C; a whitish solid formed after 1 h at room temperature, but stirring was continued for an additional 10 h. Compound **2a** was isolated as reported for **1b**. Yield 360 mg (60.3%); m.p. 184–186 °C (dec.). *Anal.* Calc. for $C_{12}H_{22}N_2O_2Cl_2Pt$: C, 29.27; H, 4.50; N, 5.69; Cl, 14.40. Found: C, 30.01; H, 4.42; N, 5.59; Cl, 14.27%.

Synthesis of cis-
$[PtCl_2\{\overline{N{=}C(C(CH_3)_3OCH_2CH_2CH_2}\}_2]$ (3a)

This was prepared as **1b** starting from $ClCH_2CH_2CH_2OH$ (0.5 ml, 5.8 mmol), a 1.6 M n-hexane solution of n-BuLi (0.62 ml, 0.99 mmol) and *cis*-$[PtCl_2(NCC(CH_3)_3)_2]$ (194 mg, 0.45 mmol). The immediate formation of a strong ν(C=N) absorption at 1629 cm^{-1} and the disappearance of the C≡N stretching is observed. Reaction time: 15 min at 0 °C; after 1 h at room temperature a whitish solid was formed, but the reaction mixture was stirred for an additional 1 h. Compound **3a** was isolated as reported for **1b**. Yield 125 mg (50.7%); m.p. 147–149 °C (dec.). *Anal.* Calc. for $C_{16}H_{30}N_2O_2Cl_2Pt$: C, 35.04; H, 5.51; N, 5.11; Cl, 12.93. Found: C, 34.96; H, 5.48; N, 4.98; Cl, 13.05%. FAB mass spectrum *m/z* (rel. int.%): $[M]^{\cdot+}$ 547 (0.1); $[M-CH_3^{\cdot}]^{+}$ 532 (0.4); $[M-Cl^{\cdot}]^{+}$ 512 (0.1); $[M-Cl^{\cdot}-\text{oxazine}]^{+}$ 371 (0.9); $[M-2Cl^{\cdot}-\text{oxazine}]^{\cdot+}$ 336 (2.1); $[M-C_7H_{12}NO]^{\cdot+}$ 421 (2.0).

Synthesis of cis-
$[PtCl_2\{\overline{N{=}C(C_6H_5)OCH_2CH_2CH_2}\}_2]$ (4a)

This was prepared as described for **1b** starting from $ClCH_2CH_2CH_2OH$ (1.0 ml, 11.6 mmol), a 1.6 M n-hexane solution of n-BuLi (1.45 ml, 2.33 mmol) and solid *cis*-$[PtCl_2(NCC_6H_5)_2]$ (500 mg, 1.06 mmol). Reaction time and work up as for **1b**; a strong ν(C=N) absorption at 1630 cm^{-1} of the oxazine ligand and complete disappearance of ν(C≡N) was observed after 10 min. Yield 440 mg (71%); m.p. 169–170 °C. *Anal.* Calc. for $C_{20}H_{22}N_2O_2Cl_2Pt$: C, 40.82; H, 3.77; N, 4.76; Cl, 12.05. Found: C, 40.57; H, 3.77; N, 4.61; Cl, 12.22%. FAB mass spectrum, *m/z* (rel. int.%): $[M]^{\cdot+}$ 587 (0.2); $[M-Cl^{\cdot}]^{+}$ 552 (0.8); $[M-2Cl^{\cdot}]^{\cdot+}$ 517 (5.0); $[M-Cl^{\cdot}-\text{oxazine}]^{\cdot+}$ 391 (1.0); $[M-2Cl^{\cdot}-\text{oxazine}]^{\cdot+}$ 356 (3.5).

Synthesis of trans-
$[PtCl_2\{\overline{N{=}C(C_6H_5)OCH_2CH_2CH_2}\}_2]$ (4b)

This was prepared as **1b** starting from $ClCH_2CH_2CH_2OH$ (1 ml, 11.6 mmol), a 1.6 M n-hexane solution of n-BuLi (0.90 ml, 1.45 mmol) and *trans*-$[PtCl_2(NCC_6H_5)_2]$ (311 mg, 0.66 mmol). A strong ν(C=N) absorption at 1626 cm^{-1} and no ν(C≡N) stretching of the starting nitrile complex was immediately observed. Reaction time: 10 min at 0 °C; after 1 h at room temperature a pale yellow solid was formed, but stirring was continued for an additional 2 h. Compound **4b** was isolated as reported for **1b**. Yield 211 mg (54.5%); m.p. 189–190 °C. *Anal.* Calc. for $C_{20}H_{22}N_2O_2Cl_2Pt$: C, 40.82; H, 3.77; N, 4.76; Cl, 12.05. Found: C, 40.61; H, 3.79; N, 4.68; Cl, 11.96%. FAB mass spectrum, *m/z* (rel. int.%): $[M]^{\cdot+}$ 587 (0.6); $[M-Cl^{\cdot}]^{+}$ 552 (0.2); $[M-Cl^{\cdot}-\text{oxazine}]^{+}$ 391 (0.9); $[M-2Cl^{\cdot}]^{+}$ 517 (4.9); $[M-2Cl^{\cdot}-\text{oxazine}]^{\cdot+}$ 356 (1.1).

Synthesis of trans-
$[Pt(CF_3)\{\overline{N{=}C(CH_3)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$
(5)

To a solution of $ClCH_2CH_2CH_2OH$ (0.5 ml, 5.82 mmol) in THF (20 ml) at 0 °C was added a 1.6 M n-hexane solution of n-BuLi (0.4 ml, 0.64 mmol) and then *trans*-$[Pt(CF_3)(NCCH_3)(PPh_3)_2]BF_4$ (0.50 g, 0.55 mmol). The white suspension was stirred at 0 °C for 15 min and then the volume of the solution was reduced to 5 ml. Addition of Et_2O (30 ml) gave further precipitation of a white solid, which was filtered off and treated with warm benzene (3×10 ml). The solid residue was dissolved in CH_2Cl_2 (30 ml); addition of Et_2O (40 ml) gave the oxazine product as a white solid, which was filtered off, washed with Et_2O (2×5 ml) and dried under vacuum. Yield 0.19 g (37%); m.p. 226–227 °C (dec.). *Anal.* Calc. for $C_{42}H_{39}NOP_2BF_7Pt \cdot \frac{1}{2} CH_2Cl_2$: C, 50.22; H, 3.96; N, 1.38. Found: C, 50.56; H, 3.97; N, 1.39%. FAB mass spectrum *m/z* (rel. int.%): $[M^+]$ 887 (10); $[M-\text{oxazine}]^{+}$ 787 (100); $[M-\text{oxazine}-{}^{\cdot}CF_3]^{\cdot+}$ 718 (10).

The benzene filtrate was taken to dryness under reduced pressure and the white solid residue treated with Et_2O (20 ml), filtered off, washed with MeOH

(2×5 ml), Et_2O (2×5 ml) and dried under vacuum. This compound was identified by IR and NMR (^{19}F and ^{31}P) data as *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$ [7c]. Yield 0.189 g (40%).

Synthesis of trans-
$[Pt(CF_3)\{\overline{N{=}C(C_6H_5)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$ (6)

To a solution of $ClCH_2CH_2CH_2OH$ (0.5 ml, 5.98 mmol) in THF (25 ml) at 0 °C were added a 1.6 M n-hexane solution of n-BuLi (0.5 ml, 0.84 mmol) and then solid *trans*-$[Pt(CF_3)(NCC_6H_5)(PPh_3)_2]BF_4$ (0.75 g, 0.76 mmol). After 5 min stirring at 0 °C a white solid started to precipitate. The volume of the solution was reduced to 2 ml and Et_2O (30 ml) was added. The white solid formed was filtered off and washed with warm benzene (3×5 ml). The solid residue was dissolved in CH_2Cl_2 (20 ml) and the solution treated with Et_2O (50 ml) to give the product as a white solid, which was filtered off, washed with Et_2O (2×5 ml) and dried under vacuum. Yield 0.38 g (49%); m.p. 198–199 °C (dec.). *Anal.* Calc. for $C_{47}H_{41}NOP_2BF_7Pt \cdot \frac{1}{2} CH_2Cl_2$: C, 52.86; H, 3.92; N, 1.29. Found: C, 53.30; H, 4.02; N, 1.22%. FAB mass spectrum *m/z* (rel. int.%): $[M^+]$ 948 (22); $[M-\text{oxazine}]^+$ 787 (100), $[M-\text{oxazine}-{}^{\bullet}CF_3]^{\cdot+}$ 718 (11). The benzene filtrate was worked up as for **5** to give *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield 0.25 g (40%).

Reaction of 3a with 1,2-bis(diphenylphosphino)ethane

The reaction of **3a** (54.8 mg, 0.1 mmol) with 1,2-bis(diphenylphosphino)ethane (80 mg, 0.2 mmol) was carried out in CD_2Cl_2 (0.7 ml) in an NMR tube at room temperature. The solution from light yellow immediately turned whitish. The ^{31}P NMR spectrum recorded after 30 min showed the formation of $[(Ph_2PCH_2CH_2PPh_2)_2Pt](Cl)_2$ (δ 46.77 s, $^1J_{PPt}$ 3269 Hz) as the only product [7a]. The reaction mixture was analyzed by GC/MS, ^1H NMR and IR spectroscopies. The ^1H NMR spectrum shows the presence after 1 h of only the free 1,3-oxazine $\overline{N{=}C(Bu^t)OCH_2CH_2CH_2}$: GC/MS: r.t. 2.40 min, *m/z* 141. IR (CH_2Cl_2): ν(C=N) 1659 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.09 t, (OCH_2, $^3J_{HH}$ 5.30 Hz; δ 3.33 t (NCH_2, $^3J_{HH}$ 5.59 Hz); δ 1.98 m, CH_2; δ 1.40 s, Bu^t.

Reactions of 5 and 6 with PPN^+Cl^-

Compounds **5** and **6** (49 and 51 mg, respectively; 0.049 mmol) were reacted with PPN^+Cl^- (34 mg, 0.059 mmol) in CH_2Cl_2 (1 ml) at room temperature. After 30 min the reaction mixtures were filtered off. The solid formed was identified by its IR and ^{31}P NMR spectra as *trans*-$[(CF_3)PtCl(PPh_3)_2]$ [7c], while the mother liquors were analyzed by IR and GC/MS. For 5,6-4*H*-1,3-(2-methyl)oxazine: IR (CH_2Cl_2): ν(C=N) 1670 cm^{-1}; GC/MS: r.t. 2.38 min; *m/z* 99. For 5,6-4*H*-1,3-(2-phenyl)oxazine: IR (CH_2Cl_2): ν(C=N) 1635 cm^{-1}; GC/MS: r.t. 2.35 min; *m/z* 161.

The same reactions were carried out in an NMR tube using CD_2Cl_2 as solvent (0.7 ml). The ^1H NMR spectra showed the complete disappearance of the signals due to the starting compounds and the presence of free 1,3-oxazines: for 2-(methyl)-1,3-oxazine: δ 3.69 t (OCH_2, $^3J_{HH}$ 6.2 Hz), 3.44 t (NCH_2, $^3J_{HH}$ 6.1 Hz), 2.04 m (CH_2), 0.05 s (CH_3); for 2-(phenyl)-1,3-oxazine: δ 4.35 t (OCH_2, $^3J_{HH}$ 5.3), 3.56 t (NCH_2, $^3J_{HH}$ 5.6), 1.96 m (CH_2), 7.91–7.10 m (Ph).

X-ray structural determination

Crystal data: $C_{45.8}H_{41}NOBP_2F_{6.4}Cl_{0.2}Pt$, $M_r = 1050.02$, trigonal $P\bar{3}$, $a = 22.590(4)$, $b = 15.970(3)$ Å, $\gamma = 120°$; $V = 7058(2)$ Å^3; $D_{calc} = 1.48$ g cm^{-3}; $Z = 6$; μ(Mo Kα) = 31.42, $T = 293$ K. The final R value of 0.059 for 3903 unique observed ($I \geqslant 3\sigma(I)$) reflections. A prismatic (white) crystal (from a solution of **6** in CH_2Cl_2/MeOH) of dimensions 0.32×0.22×0.24 mm was lodged in a Lindemann glass capillary and centered on a four-circle Philips PW 1100 diffractometer 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 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 $10 \leqslant \theta \leqslant 12°$ were considered. Integrated intensities for *hkl* reflections in the interval $h = 0 \pm 26$; $k = 0 \rightarrow 26$; $l = 0 \rightarrow 18$ were measured, and two standard reflections were measured every 180 min. There were no significant fluctuations of intensities other than those expected from Poisson statistics.

The intensity data were corrected for Lorentz–polarization effects and for absorption, by following the method of North *et al.* [13]; no correction was made for extinction.

The structure was first solved in the space group $P6_3/m$, compatible with the systematic absence of 00*il*, $l = 2n+1$. This requires the complex cation to lie on the crystallographic mirror plane at $z = 1/4$ with the Pt atom, the phenyl ring on the 1,3-oxazine and the $CF_3(Cl)$ group (see below) exactly in this plane and the 1,3-oxazine group disordered in two positions of equal probability about it. However, the 2-(phenyl)oxazinc ligand gave unrealistic bond distances and thermal parameters even when the phenyl group was considered to be statistically distributed on two positions of 50% probability. We also had difficulty in refining one of the phenyl groups of the PPh_3 moiety and the R factor could not be reduced below 8%. Observations were collected on two different crystals with two different

diffractometers and the same results obtained. Consequently, we considered that the absence of odd 00*il* reflections is accidental and the true space group is the trigonal $P\bar{3}$, in which no crystallographic symmetry is imposed on the cation, and this was used for structure solution and refinement.

The structure was then refined by full-matrix least-squares with anisotropic thermal parameters for the atoms of the coordination sphere and for the heterocyclic ligand, individual isotropic for the remaining non-hydrogen atoms. The BF_4 anions were located on the crystallographic threefold axis with three distinct positions. One of them was disordered owing to inversion of one fluorine on the threefold axis, and of the fluorines generated around the same axis. A disordered methanol molecule is also present in the structure. In the last stages of the refinement, a rather low thermal parameter of the carbon of the CF_3 moiety, accompanied by rather high thermal parameters of the bonded fluorine, was interpreted as a statistic distribution of chlorine (20%) and carbon (80%) (of the CF_3 unit) in close positions (the presence of a small percentage of chlorine was also evidenced by the IR spectrum of the compound, see 'Results and discussion'). Refinement with these occupancy factors resulted in more realistic thermal parameters for both fluorine and carbon atoms, and accounted for a rather long Pt–C(Cl) distance of 2.19(1) Å being in between 2.04(2) Å found in the analogous derivative with 2-(phenyl)oxazoline [7c] for a Pt–C bond distance and 2.32(4) Å for the reported Pt–Cl bond distances (average of about 200 distances for Pt(II) terminal chlorines) [14].

The function minimized was $\Sigma w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$. Final R values were $R = 0.059$. The largest peak in the final difference map (0.9 e Å^3) was located near the platinum atom positions.

Data processing and computation were carried out using the SHELX 76 program package [15] with the atomic scattering factors taken from ref. 16 and drawings by ORTEP [17]. The atomic coordinates are reported in Table 1.

TABLE 1. Atomic coordinates and equivalent isotropic thermal parameters (Å^2) for *trans*-$[Pt(CF_3)\{\overline{N=C(Ph)OCH_2CH_2CH_2}\}(PPh_3)_2]^+$ (**6**)

Atom	x	y	z	$U_{iso/eq}$*[a]
Pt	0.31169(4)	0.37499(4)	0.25003(4)	0.049(1)*
N	0.4005(7)	0.3693(8)	0.2501(8)	0.056(3)*
O	0.5157(7)	0.4078(9)	0.249(1)	0.113(4)*
C(1)	0.462(1)	0.418(1)	0.251(1)	0.071(4)*
C(2)	0.444(2)	0.289(2)	0.250(2)	0.175(4)*
C(3)	0.506(2)	0.341(2)	0.246(2)	0.171(4)*
C(4)	0.385(1)	0.298(1)	0.248(1)	0.077(4)*
C(5)	0.4847(9)	0.493(1)	0.250(1)	0.073(4)*
C(6)	0.443(1)	0.520(1)	0.250(2)	0.104(4)*
C(7)	0.468(2)	0.591(1)	0.249(2)	0.127(4)*
C(8)	0.535(2)	0.631(1)	0.251(2)	0.145(4)*
C(9)	0.581(2)	0.605(2)	0.247(2)	0.202(5)*
C(10)	0.554(2)	0.536(2)	0.250(3)	0.207(4)*
P(1)	0.3056(3)	0.3662(3)	0.1036(3)	0.058(2)*
P(2)	0.3054(3)	0.3662(3)	0.3965(3)	0.057(2)
C(11)	0.3122(9)	0.4401(9)	0.046(1)	0.062(4)
C(12)	0.316(1)	0.436(1)	−0.045(1)	0.094(4)
C(13)	0.322(1)	0.496(1)	−0.085(2)	0.108(4)
C(14)	0.329(1)	0.552(1)	−0.043(2)	0.111(4)
C(15)	0.323(1)	0.552(1)	0.041(1)	0.091(4)
C(16)	0.3157(9)	0.494(1)	0.088(1)	0.070(4)
C(17)	0.2234(9)	0.2886(9)	0.077(1)	0.065(4)
C(18)	0.188(1)	0.290(1)	0.005(2)	0.110(4)
C(20)	0.124(1)	0.225(1)	−0.007(2)	0.125(5)
C(19)	0.103(1)	0.176(1)	0.048(2)	0.105(4)
C(21)	0.136(1)	0.172(1)	0.117(2)	0.115(4)
C(22)	0.202(1)	0.235(1)	0.132(1)	0.091(4)
C(23)	0.3721(8)	0.3555(9)	0.052(1)	0.057(3)
C(24)	0.438(1)	0.4117(9)	0.051(1)	0.068(4)
C(25)	0.490(1)	0.404(1)	0.012(1)	0.088(4)
C(26)	0.476(1)	0.342(1)	−0.023(1)	0.096(4)
C(27)	0.412(1)	0.285(1)	−0.021(1)	0.105(4)
C(28)	0.356(1)	0.292(1)	0.018(1)	0.084(4)
C(29)	0.3127(9)	0.440(1)	0.453(1)	0.069(4)
C(30)	0.3153(9)	0.495(1)	0.413(1)	0.069(4)
C(31)	0.323(1)	0.552(1)	0.458(2)	0.095(4)
C(32)	0.329(1)	0.553(1)	0.542(2)	0.104(4)
C(33)	0.322(1)	0.496(1)	0.585(1)	0.103(4)
C(34)	0.316(1)	0.436(1)	0.544(1)	0.089(4)
C(35)	0.2236(9)	0.2876(9)	0.423(1)	0.066(4)
C(36)	0.203(1)	0.234(1)	0.366(1)	0.097(4)
C(37)	0.137(1)	0.172(1)	0.381(2)	0.114(4)
C(38)	0.101(1)	0.173(1)	0.449(2)	0.119(5)
C(39)	0.122(2)	0.224(2)	0.505(2)	0.136(5)
C(40)	0.186(1)	0.289(1)	0.494(1)	0.106(4)
C(41)	0.3733(8)	0.3567(9)	0.447(1)	0.057(3)
C(42)	0.4373(9)	0.4114(9)	0.449(1)	0.064(4)
C(43)	0.490(1)	0.405(1)	0.487(1)	0.087(4)
C(44)	0.478(1)	0.346(1)	0.522(1)	0.095(4)
C(45)	0.413(1)	0.288(1)	0.522(1)	0.105(4)
C(46)	0.357(1)	0.291(1)	0.483(1)	0.081(4)
C(Cl)[b]	0.2149(5)	0.3758(5)	0.2495(6)	0.053(2)
F(1)	0.201(1)	0.391(1)	0.188(1)	0.139(4)
F(2)	0.203(1)	0.393(1)	0.310(1)	0.156(4)
F(3)	0.166(1)	0.306(1)	0.249(1)	0.170(5)

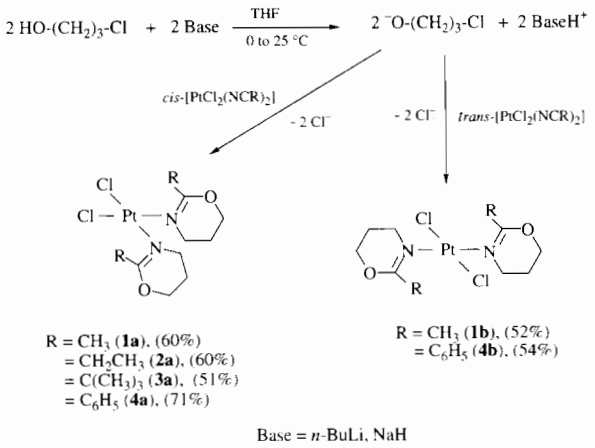
[a] U equivalent is defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] See 'Experimental'.

Results and discussion

Reactions of neutral Pt(II) nitrile complexes

The neutral bis(nitrile) complexes *cis*- and *trans*-$[PtCl_2(NCR)_2]$ readily react in THF under mild conditions with $HO(CH_2)_3Cl$ in the presence of a strong base to afford the corresponding bis(1,3-oxazine) derivatives in *c.* 50–70% yield according to Scheme 1.

These reactions do not occur without added base, which in most cases was n-BuLi, but also crystalline NaH was found effective (see preparation of **1**). Compounds **1–4** are pale yellow solids, air stable in the solid state, soluble in DMSO and in CH_2Cl_2, and insoluble in saturated hydrocarbons. However, it is observed that the oxazine derivatives are not indefinitely stable in chlorinated solvents and some decomposition to unidentified black solid material is observed after several days at room temperature.



Scheme 1.

The spectral data for **1–4** are collected in Table 2 and they indicate that no isomerization at the metal center occurs in the reactions reported in Scheme 1 and provide evidence for the cyclic structure of the reaction products. The IR spectra of the 1,3-oxazine compounds display the characteristic C=N stretching, which appears as a strong absorption in the range 1609–1655 cm^{-1}, at lower wavenumbers with respect to the corresponding free oxazines (see 'Experimental'). Compounds **1–4** display medium absorptions in the Pt–Cl region (296–346 cm^{-1}), but in the case of **1b** and **4a** their number is not that expected for *cis* (two Pt–Cl bands) and *trans* (one Pt–Cl band) dichloro complexes of Pt(II) [18]. This feature was also observed for *trans*- and *cis*-$[PtCl_2(NCPh)_2]$ [19] and *trans*- and *cis*-bis(2-oxazoline)dichloroplatinum(II) complexes [7a, b]. In the IR spectra of **1–4** are also present characteristic bands due to the hydro-oxazine ring in the regions 1274–1280 and 1063–1157 cm^{-1} [20] and C–H wagging absorptions of monosubstituted aromatic systems at 772 cm^{-1} for **4a** and 770 cm^{-1} for **4b** due to the presence of the C_6H_5–C=N conjugated system as reported for free 5,6-dihydro-4*H*-1,3-(2-phenyl)oxazine [20a].

The ^1H NMR spectra of **1–4** are reported in Table 2. On the basis of assignments of protons in free 1,3-oxazines [20] and related systems [7a], the methylene protons adjacent to the oxygen are assigned at lower field resonances (δ 4.36–3.69) with respect to the $-NCH_2-$ protons (δ 4.13–3.38). As a general feature, the room temperature ^1H NMR spectra of the *trans* isomers show the expected patterns of the oxazine ring protons, i.e. triplets for $-NCH_2-$ and $-OCH_2-$ moieties and a multiplet for the central $-CH_2-$ methylene group. However, the corresponding spectra of the *cis* isomers are more complex, suggesting the presence of different conformers likely to result from the mutual sterical hindrance of the R groups of the two oxazine rings, which prevents free rotation around the Pt–N bond. This behavior was not observed for analogous bis(oxazoline) derivatives [7a, b]. As a typical example, the room temperature ^1H NMR spectrum of the *trans*-2-(methyl)oxazine derivative **1b** shows a triplet at 3.58 ppm for the $-NCH_2-$ protons, a triplet at 4.20 ppm for the $-OCH_2-$ protons and a multiplet centered at 1.95 ppm for the $-CH_2-$ protons; the CH_3 protons appear as a singlet at 2.66 ppm. Conversely, the room temperature ^1H NMR spectrum of the *cis* isomer **1a**, shows very broad signals of the oxazine ring protons (Fig. 1(a)). Upon lowering the temperature (229 K), the spectrum shows two distinct resonances at 2.71 and 2.60 ppm integrating in a *c.* 2:1 ratio, and corresponding to two different methyl groups, thus indicating the presence of two conformers (Fig. 1(b)). For each isomer, the $-NCH_2-$ protons appear magnetically inequivalent since each of them gives rise to a doublet of triplets owing to coupling with the geminal proton and with the $-CH_2-$ protons (for the more abundant isomer: δ 3.25 (dt), $^2J_{HH}$ 16.3, $^3J_{HH}$ 6.4 Hz and δ 3.77 (dt), $^2J_{HH}$ 16.7, $^3J_{HH}$ 6.3 Hz; for the less abundant isomer: δ 3.37 (dt), $^2J_{HH}$ 16.5, $^3J_{HH}$ 6.5 Hz and δ 3.86 (dt), $^2J_{HH}$ 16.5, $^3J_{HH}$ 6.4 Hz). At the same low temperature the $-OCH_2-$ protons give rise to two partially overlapping complex multiplets integrating in a *c.* 2:1 ratio centered at 4.20 and 4.26 ppm; also the $-CH_2-$ protons appear as a complex multiplet centered at 1.97 ppm. By using the Eyring equation [21a] an approximate value of the energy barrier for the isomer interconversion at the coalescence temperature ($T_c = 280$ K, corresponding to the coalescence of the two methyl signals), can be obtained, i.e. $\Delta G^{\neq} = 19.14\ T_c\ (9.97 + \log T_c/\Delta\nu)$ (J mol^{-1}) = 59 775 J mol^{-1} = 14.2 kcal mol^{-1}. This value, which is very close to that reported for the rotational barrier around the amide bond [21b], is approximately twice that calculated for ring inversion processes in cyclohexene-type systems (6–7 kcal mol^{-1}) [21c].

It is likely that a further contribution to the signal broadening in the ^1H NMR spectra of **1–4** might be due also to a ring inversion process from one chair form to the alternate chair form which is known to occur in six-membered rings [21c, d], although detailed studies about conformational processes in 5,6-dihydro-4*H*-1,3-oxazines have not been reported.

The ^{13}C NMR spectra of **1a** and **1b** confirm the spectroscopic results found in their ^1H NMR spectra. Thus, the room temperature ^{13}C NMR spectrum of **1b** shows the presence in solution of only one species as evidenced by the observation that the $-OCH_2-$, $-NCH_2-$ and CH_3 carbons appear as singlets at δ 65.93, 48.35 and 24.02, respectively. On the other hand, the ^{13}C NMR spectrum of **1a** at room temperature (299 K) displays broad resonances for the ring protons indicating the presence of dynamic ring processes in

TABLE 2. Spectroscopic data for complexes **1–4**

Compound	IR[a]		^{1}H NMR[b]				^{13}C{^{1}H} NMR[b]				
	ν(C=N)	Pt–Cl(region)	δ(OCH$_2$)	δ(NCH$_2$)	δ(CH$_2$)	δ(other)	δ(OCH$_2$)	δ(NCH$_2$)	δ(CH$_2$)	δ(C=N)	δ(other)
1a	1644s	326br 334br	4.25br	3.85br 3.38br	2.01s, br	2.71s, br[c]	66.17	49.54	22.044	167.69	24.53[d]
1b	1655s	312m 327m	4.20t $^3J_{HH}$ 5.53	3.58t $^3J_{HH}$ 3.71	1.95m	2.66[c] $^4J_{PtH}$ 2.2	65.93	48.35	22.00	166.40	24.02[d]
2a	1634s	332s, br	4.27br	3.83br 3.40br	2.00br	CH$_3$: 1.23t $^3J_{HH}$ 7.51 CH$_2$: 2.01q					
3a	1609s	336s 346s	4.27t $^3J_{HH}$ 5.82	4.13t[g] $^3J_{HH}$ 6.49 4.05t[f] $^3J_{HH}$ 5.64 3.84[f] $^3J_{HH}$ 5.33 3.76[g] $^3J_{HH}$ 6.28	1.98m	CH$_3$: 1.68[e] 1.43[f]	66.74	51.63	22.61	175.07 174.55	CH$_3$: 29.265s[e] 27.95s[f] [c] 30.61
4a	1629s	296m 323s 345m		4.27[g] 3.91[g] 3.69[g]	1.46m 1.77m[e]	8.47–8.45[h] 7.62–7.60[h]	63.15[e] 66.82[f]	47.12[e] 48.79[f]	22.152 [j]	164.35[e] 165.18[f]	127.93–134.52[i]
4b	1630s	308m 335m	4.36t $^3J_{HH}$ 5.34	3.64t $^3J_{HH}$ 6.09	2.006m	8.55–8.48[h] 7.58–7.43[h]	66.71	49.78	22.53	164.82	126.87–134.92[i]

[a]Nujol mull, cm^{-1}; abbreviations: s = strong, m = medium, br = broad. [b]The ^{1}H and ^{13}C NMR spectra were recorded in CD_2Cl_2 at room temperature. Proton chemical shifts are reported from Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm; carbon chemical shifts are referenced to Me_4Si by taking the chemical shift of dichloromethane-d_2 as +53.80 ppm; δ is given in ppm; J is given in Hz; abbreviations: s = singlet, t = triplet, q = quartet, m-multiplet, br = broad. [c]CH$_3$ protons. [d]CH$_3$ carbon. [e]More abundant isomer (see text). [f]Less abundant isomer (see text). [g]Signals partially overlapping (see text). [h]Phenyl protons. [i]Phenyl carbons. [j]Unique signal for both isomers.

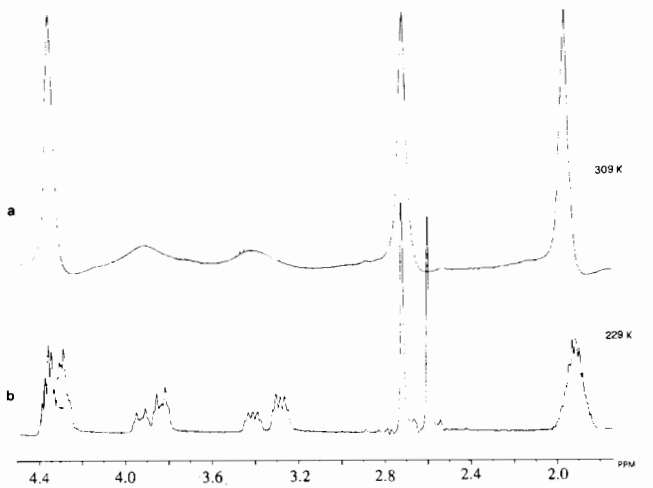


Fig. 1. ^{1}H NMR spectra of the *cis* isomer **1a** at room temperature (a) and at 229 K (b).

agreement with the ^{1}H NMR findings; upon warming to 309 K the signals sharpen to average singlet resonances. A behavior closely recalling that observed for **1a** is shown by the ethyl derivative **2a**, whose ^{1}H NMR spectrum at room temperature shows only broad signals for the ring protons.

Features similar to those reported above for the 2-(methyl)oxazine complexes are observed also for the corresponding phenyl derivatives **4a** and **4b**. It is noted, however, that the ^{1}H NMR spectrum of **4a** indicates the presence of the two conformers even at room temperature and again this behavior may be ascribed to the more hindered phenyl substituent compared to the methyl one. Thus, the room temperature ^{1}H NMR spectrum of **4a** shows three complex multiplets at 4.27, 3.91 and 3.69 ppm due to $-OCH_2-$ and $-NCH_2-$ protons accompanied by two multiplets integrating in a *c.* 3:1 ratio centered at 1.46 and 1.77 ppm, respectively, due to the $-CH_2-$ protons of the two isomers. Decoupling experiments indicate that $-OCH_2-$ and $-NCH_2-$ protons give rise to partially overlapping signals, thus preventing a detailed spectroscopic assignment; upon lowering the temperature to 231 K, the ^{1}H NMR spectrum of **4a** remains unchanged. Conversely, the ^{1}H NMR spectrum of **4b** shows the expected triplets at 4.36 and 3.64 ppm for the $-OCH_2-$ and $-NCH_2-$ protons, respectively.

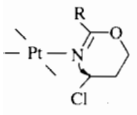
In both the ^{1}H NMR spectra of **4a** and **4b** the *ortho* protons of the phenyl group, which are *cis* to platinum, are shifted downfield (δ 8.47–8.45 for **4a**, δ 8.55–8.48 for **4b**) due to a deshielding effect of the metal, but no coupling with ^{195}Pt is observed, presumably owing to the relatively free rotation about the phenyl–oxazine bond as previously reported for Pt(II) systems of the type *trans*-$[PtCl_2(PPh_3)(L)]$ (L=N(R)=CH(Ph)) [22]. A similar effect has been observed in related Pt(II)–imido esters having *cis*-metal–phenyl conformations [19b] and N-coordinated 2-(aryl)oxazoline derivatives [7a, b].

The room temperature ^{13}C NMR spectra of **4a** and **4b** confirm for **4a** the presence in solution of two species in a *c.* 3:1 ratio (Table 2) and for **4b** of only one species likely resulting from average dynamic ring processes.

As the size of the R substituent of the oxazine increases, the rotation around the Pt–N bond becomes progressively more restricted. This steric effect is clearly observed in the case of **3a** having R=Bu^t, for which the room temperature ^{1}H NMR spectrum resembles that of **1a** at low temperature. The proton NMR indicates that **3a** is present as a 1.5:1 mixture of two isomers, since the Bu^t group shows up as two sharp singlets at δ 1.68 and 1.43, respectively. The $-OCH_2-$ protons give rise to a single complex multiplet at δ 4.27, while the $-NCH_2-$ protons display four broad triplets (at δ 4.13 and 3.76 for the less abundant isomer and δ 4.05 and 3.84 for the more abundant isomer). The resonance pattern of the $-NCH_2-$ protons may be explained assuming that each proton of the amino group couples with the $-CH_2-$ moiety, while coupling with the germinal proton is lost owing to the ring inversion process still present at room temperature. Noteworthy in the ^{13}C NMR spectrum of **3a** is the presence of two signals due to the Bu^t carbons at δ 29.26 and 27.95, thus confirming the presence of two conformers.

The FAB mass spectrometric behavior of compounds **1–4** may also be related to the hindered rotation about the Pt–N bond proposed on the basis of the ^{1}H and ^{13}C NMR results described above. Thus, **1a** and **1b** display very poor molecular ions and also formation of fragments of the type $[MCl_2-\text{oxazine}]^{\cdot+}$ and $[MCl_2-\text{2-oxazine}]^{\cdot+}$, generated by the successive loss of an oxazine ligand, but still having the chlorine ligands coordinated to the metal. Conversely, in the FAB mass spectra of **4a** and **4b** the molecular ions are well evidenced and the loss of the heterocyclic ligands occurs together with the loss of chlorines. This behavior may be explained by the occurrence to some extent of Pt–N–C–Ph delocalization, which increases the Pt–N bond strength thus making its rupture more difficult. Elsewhere, we reported that for other systems of Pt(II) the FAB fragmentation pattern may be related to the reactivity and stability observed in solution [23].

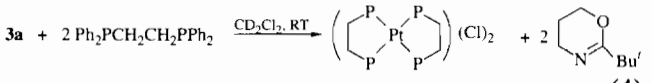
As reported in earlier work on the synthesis of the five-membered heterocycles 2-oxazolines from Pt(II) nitriles and $HOCH_2CH_2Cl$/base or $\overline{OCH_2CH_2}/Cl^-$ systems, we suggest that the reactions shown in Scheme 1 proceed similarly, i.e. via the intermediacy of a species like **I**, which is formed by nucleophilic attack at the electrophilic nitrile carbon by $^-OCH_2CH_2CH_2Cl$.



I

Complex **I** could not be isolated or even spectroscopically detected in solution, rearranging rapidly to the final oxazine product by intramolecular imino nitrogen displacement of chloride. It might be noted that the cyclization reaction of intermediate **I** to oxazine in neutral nitrile Pt(II) complexes is not influenced by the steric hindrance of the R group. Thus, the t-BuCN complex (Scheme 1) reacts as fast as the Me analogues to give the final t-Bu-oxazine product **3a** with a comparable yield (*c.* 50%) to those of the Me products **1a** and **1b** (*c.* 52–60%). Furthermore, both nitriles in $[PtCl_2(NCR)_2]$ are cyclized to the final heterocycles. Thus the overall behavior of nitrile complexes of Pt(II) differs significantly from that of the corresponding isocyanide analogs $PtCl_2(CNR)_2$ for which steric and electronic effects of the R group have been shown to affect their reactions with alcohols and amines [24].

The oxazine ligands in complexes **1–4** are displaced rapidly at room temperature by diphosphines as found for the following reaction of **3a** (eqn. (4)), thus paralleling the behavior of similar oxazoline compounds [7a]:

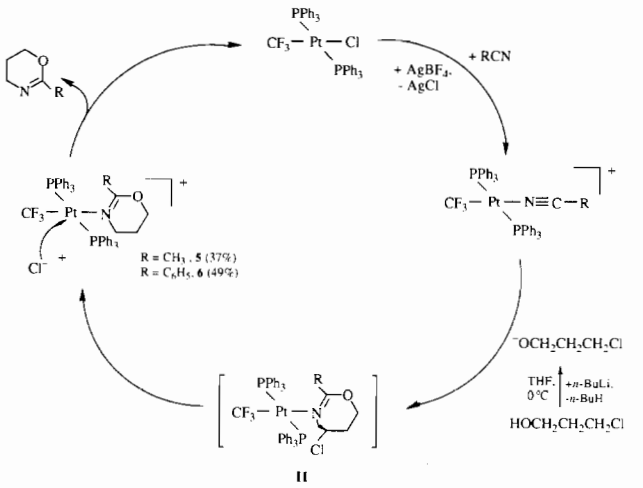


(4)

Reactions of cationic Pt(II) nitrile complexes

We have found that reactions similar to those reported above for neutral nitrile complexes occur also with the cationic complexes described herein, but with some significant differences as illustrated in Scheme 2.

The reactions proceed with the initial formation of the cationic nitrile complexes *trans*-$[(PPh_3)_2(CF_3)Pt(NCR)]BF_4$ (R = Me, Ph) from the corresponding chloro derivatives by treatment with $AgBF_4$ in the presence of excess RCN. Subsequent reaction with $^-O(CH_2)_3Cl$ gives presumably the intermediate imino derivative **II**, which upon intramolecular cyclization affords the 1,3-oxazine derivatives **5** and **6**. These complexes could be isolated from the reaction mixture in relatively low yield owing to their further reaction with the liberated Cl^- ion, which displaces the coordinated oxazine, regenerating the initial halo complex *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. This latter was recovered in 40% yield for reaction times of 5–15 min (see 'Experimental'), but it was the only isolated complex for longer reactions times (> 2 h). Thus, the overall process involving cationic Pt(II) complexes may be considered a stoichiometric



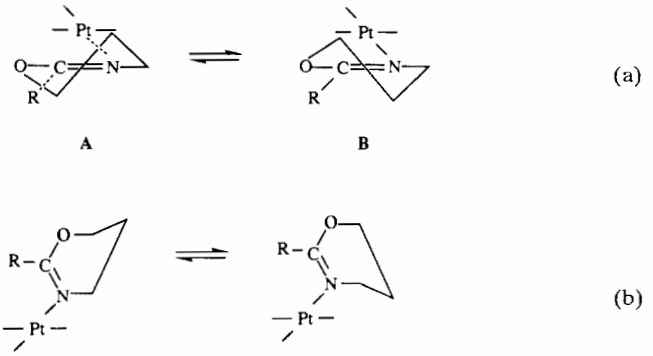
II

Scheme 2.

cycle for the synthesis of 1,3-oxazines from nitriles, paralleling an analogous cycle reported for the synthesis of 2-oxazolines [7c].

In contrast to the reactions of neutral nitrile complexes, the cyclization reactions in cationic nitrile compounds appear to be influenced by steric factors related to the R group of the nitrile ligand and also to the presence of two bulky PPh_3 ligands. Thus, for instance, for R = Et a complex mixture of products is formed, while for R = Bu^t no reaction occurs, the starting nitrile complex being recovered unchanged from the reaction mixture.

Spectroscopic data of **5** and **6** are collected in Table 3 and they confirm the presence of the N-coordinated oxazine, which is also established for **6** by an X-ray diffraction determination (see below). The IR spectra of **5** and **6** show a strong ν(C=N) absorption at 1651 and 1609 cm^{-1}, respectively. The absence of a band at *c.* 540 cm^{-1} [25] indicates a *trans* arrangement of the PPh_3–Pt–PPh_3 moiety, which is confirmed also by ^{31}P NMR (a quartet for the PPh_3 resonance, flanked by ^{195}Pt satellites, due to the coupling with the trifluoromethyl group) and by ^{19}F NMR (a triplet for the CF_3 resonance, flanked by ^{195}Pt satellites, due to coupling with the two equivalent phosphorus atoms). The ^1H NMR spectra show two triplets for the $-OCH_2-$ and $-NCH_2-$ protons (see Table 3) due to coupling with the central $-CH_2-$ moiety. The value of $^3J_{HH}$ (*c.* 5 Hz) is lower than those observed for analogous neutral [5a] and cationic [7c] N-coordinated-2-oxazoline derivatives (*c.* 10 Hz). The observed first order ^1H NMR spectra suggest that fast ring dynamic processes occur (Scheme 3), which may correspond to the inversion between the two half-chair conformations **A** and **B** (equilibrium (a)) as reported in six-membered rings [21c, d] and also to a local ring inversion involving only the central $-CH_2-$ moiety (equilibrium (b)).



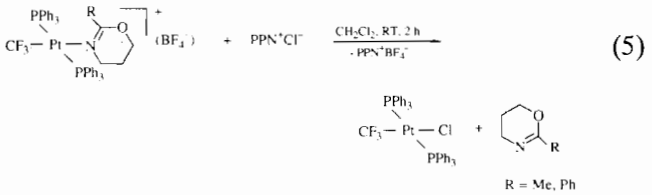
(a)

(b)

Scheme 3.

Similar to what is observed in neutral derivatives, the FAB mass spectrum of the phenyl–oxazine complex (**6**) shows a more intense molecular ion than that of the methyl–oxazine derivative (**5**) (this comparison is made relating the intensity of the molecular ion to that of the ion at *m/z* 787, which represents the base peak in both spectra and corresponds to the loss of the oxazine ring). Again this might be attributed to a higher stability of the Pt–N bond in **6** than in **5** as previously observed for the corresponding neutral derivatives.

Complexes **5** and **6** react with Cl^- ions (10% excess) in CH_2Cl_2 at room temperature to give quantitative formation of *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$ and the corresponding 1,3-oxazines (eqn. (5)). This type of reactivity parallels that observed for similar displacement reactions of 2-oxazolines from cationic Pt(II) complexes [7c].



(5)

R = Me, Ph

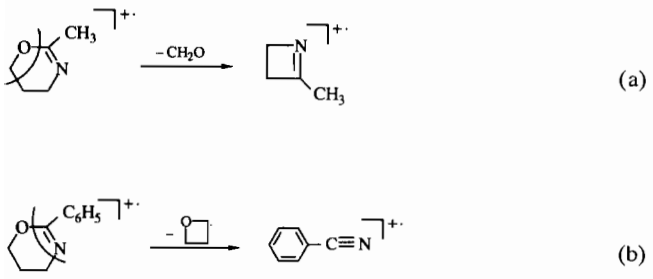
The free heterocycles were analyzed by IR and ^1H NMR spectroscopies and by GC/MS. In particular, their mass spectra show the molecular ions at *m/z* 99 and 161 for the methyl- and phenyl-1,3-oxazine, respectively. In the case of the former, the most relevant fragmentation pathway occurs with loss of CH_2O (path (a) of Scheme 4), in a similar manner to that reported for related five-membered heterocycles 2-oxazolines [26], while for the latter it occurs with the loss of oxetane, $\dot{O}CH_2CH_2\dot{C}H_2$, and formation of nitrile (path (b)).

Path (b) may be considered a retrosynthetic process leading to the synthesis of oxazine from nitrile and oxetane. However, attempts to carry out the reactions of Pt(II)–nitrile complexes *cis*-$[PtCl_2(NCR)_2]$ (R = Ph, t-Bu) with oxetane, also in the presence of Cl^- ions, gave no results, although oxetane has been reported

TABLE 3. Spectroscopic data for complexes **5** and **6**

Compound	IR[a]	^1H NMR[b]				$^{13}C\{^1H\}$ NMR[c]				$^{31}P\{^1H\}$ NMR[d]		^{19}F NMR[e]	
	ν(C=N)	δ(CH_2)	δ(NCH_2)	δ(OCH_2)	δ(other)	δ(OCH_2)	δ(NCH_2)	δ(C=N)	δ(other)	δ	$^3J_{PF}$	δ	$^3J_{FP}$
5	1651s	0.60m	2.63t $^3J_{HH}$ 5.3	3.11t $^3J_{HH}$ 5.1	CH_3: 2.10s	66.02s	40.74s	170.64s	CH_2: 31.21s CH_3: 17.86s	20.31q $^1J_{PPt}$ 2956	17.6	−11.73t $^2J_{FPt}$ 612	17.6
6	1609s	0.67m	3.13t $^3J_{HH}$ 5.5	3.30t $^3J_{HH}$ 5.5	Ph: 8.67s, 8.63s, 7.65–7.45m	65.68s	48.43s	163.98s	CH_2: 19.56s Ph: 134.45–128.03m	19.06q $^1J_{PPt}$ 2997	19.8	−10.69t $^2J_{FPt}$ 621	19.8

[a]CH_2Cl_2, cm^{-1}; abbreviations: s = strong. [b]^1H NMR spectra were recorded in CD_2Cl_2 at room temperature; proton chemical shifts are relative to Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm; *J* is given in Hz; abbreviations: t = triplet, m = multiplet. [c]^{13}C NMR spectra were recorded in CD_2Cl_2 at room temperature; carbon chemical shifts are referenced to Me_4Si by taking the chemical shift of dichloromethane-d_2 as +53.30 ppm; δ is given in ppm; *J* is given in Hz; abbreviations: s = singlet, m = multiplet. [d]^{31}P NMR spectra were recorded in CD_2Cl_2 at room temperature; the signals are referenced to external H_3PO_4 85%; δ is given in ppm; *J* is given in Hz; abbreviations: q = quartet. [e]^{19}F NMR spectra were recorded in CD_2Cl_2 at room temperature; the signals are referenced to external $CFCl_3$; δ is given in ppm; *J* is given in Hz; abbreviations: t = triplet.



Scheme 4.

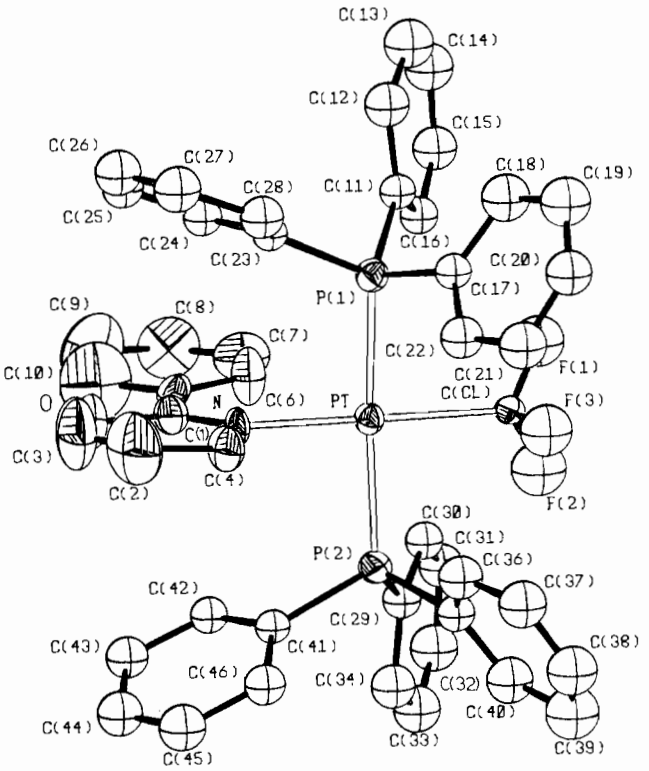


Fig. 2. ORTEP view of the cation of *trans*-$[Pt(CF_3)\{\overline{N{=}C(Ph)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$ (**6**) with the atomic numbering scheme.

to undergo ring opening in the presence of halide ions [27].

Description of the structure of trans- $[Pt(CF_3)\{\overline{N{=}C(Ph)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$ *(6)*

The molecular structure of the compound is constituted by complex cation units *trans*-$[Pt(CF_3)_{0.8}Cl_{0.2}\{\overline{N{=}C(Ph)OCH_2CH_2CH_2}\}(PPh_3)_2]^+$ and BF_4^- anions, derived from a mixture of *trans*-$[Pt(CF_3)\{\overline{N{=}C(Ph)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$ and *trans*-$[PtCl\{\overline{N{=}C(Ph)OCH_2CH_2CH_2}\}(PPh_3)_2]BF_4$. An ORTEP drawing of **6** is shown in Fig. 2. Selected bond distances and angles are reported in Table 4.

The presence of the chloro–oxazine complex was revealed by IR (ν(PtCl) 302 cm^{-1}, nujol mull), ^1H NMR (CD_2Cl_2: δ 3.50 (t, OCH_2, $^3J_{HH}$ 5.69 Hz; the $-NCH_2-$ resonance was masked by the corresponding signals of **6**: δ 1.64 (m, $-CH_2-$, $^3J_{HH}$ 5.76 Hz) and $^{31}P\{^1H\}$ NMR (CD_2Cl_2: δ 16.30 (PPh_3, $^1J_{PPt}$ 2640 Hz) and it may be explained by the fact that the preparation of the starting complex *trans*-$[Pt(CF_3)(X)(PPh_3)_2]$ (X = Cl, Br) [7c] is always accompanied by the formation of some *trans*-$[PtX_2(PPh_3)_2]$ (X = Cl, Br), which cannot be completely removed. It is likely that the dihalo complex would react with $AgBF_4$ in the presence of PhCN to give the cationic nitrile complex *trans*-$[Pt(Cl)(NCPh)(PPh_3)_2]BF_4$, which then cycloadds $^-OCH_2CH_2CH_2Cl$ to give the final oxazine chloro complex.

The structure is characterized by a high degree of disorder involving the heterocyclic ligand, BF_4 anions, methanol solvent molecules and alternative positions of CF_3 (80%) and Cl (20%) moieties in the Pt coordination sphere. Except for BF_4 anions, residing on a crystallographic threefold axis, no other crystallographic constraints are imposed to the molecules. The complex exhibits a rather distorted square geometry of the ligands about the central platinum ion, with the PPh_3 units in *trans* position. The main deviation from planarity in the Pt coordination sphere is observed in the value of the angle P1–Pt–P2 of 171.4(2)°, while the N–Pt–C(Cl angle) is about linear (177.3(5)°). A best

TABLE 4. Relevant bond lengths (Å) and angles (°) for *trans*-$[Pt(CF_3)\{\overline{N{=}C(Ph)OCH_2CH_2CH_2}\}(PPh_3)_2]^+$ (**6**)

Pt–N	2.07(2)	Pt–P(1)	2.345(5)
Pt–P(2)	2.345(5)	Pt–C(Cl)	2.19(1)
N–C(1)	1.28(2)	N–C(4)	1.47(3)
O–C(1)	1.33(3)	O(1)–C(3)	1.42(5)
C(1)–C(5)	1.51(3)	C(2)–C(3)	1.31(4)
C(2)–C(4)	1.43(5)	C(6)–C(7)	1.42(4)
C(6)–C(5)	1.35(4)	C(7)–C(8)	1.33(4)
C(8)–C(9)	1.43(7)	C(9)–C(10)	1.36(5)
C(10)–C(5)	1.37(4)	P(1)–C(11)	1.85(2)
P(1)–C(17)	1.86(2)	P(1)–C(23)	1.83(2)
P(2)–C(29)	1.83(2)	P(2)–C(35)	1.86(2)
P(2)–C(41)	1.84(2)		
P(2)–Pt–C(Cl)	89.2(3)	P(1)–Pt–C(Cl)	88.9(3)
P(1)–Pt–P(2)	171.4(2)	N–Pt–C(Cl)	177.3(5)
N–Pt–P(2)	90.8(4)	N–Pt–P(1)	90.8(4)
Pt–N–C(4)	111(1)	Pt–N–C(1)	129(1)
C(1)–N–C(4)	120(1)	C(1)–O–C(3)	121(2)
N–C(1)–O(1)	123(2)	O(1)–C(1)–C(5)	112(2)
N–C(1)–C(5)	125(2)	C(3)–C(2)–C(4)	123(3)
O(1)–C(3)–C(2)	118(3)	N–C(4)–C(2)	115(2)
C(7)–C(6)–C(5)	122(2)	C(6)–C(7)–C(8)	117(2)
C(7)–C(8)–C(9)	122(2)	C(8)–C(9)–C(10)	118(3)
C(9)–C(10)–C(5)	122(3)	C(6)–C(5)–C(10)	119(2)
C(1)–C(5)–C(10)	115(2)	C(1)–C(5)–C(6)	126(2)
Pt–P(1)–C(23)	116.0(6)	Pt–P(1)–C(17)	107.4(6)
Pt–P(1)–C(11)	116.6(6)	Pt–P(2)–C(41)	115.6(6)
Pt–P(2)–C(35)	107.2(6)	Pt–P(2)–C(29)	116.2(6)

mean plane calculated with the Pt bonded atoms shows deviations of 0.44(2) Å for C(1) and −0.33(2) Å for N in the opposite direction while Pt is 0.167(1) Å out of the plane in the C(1) direction.

The heterocyclic ring is characterized by high thermal values of the C(2), C(3) and C(4) atoms indicative of disordering also in this part of the molecule in agreement with fast dynamic ring processes suggested on the basis of ^{1}H NMR spectra (see above), thus preventing a detailed discussion of the bond distances and conformation of the six-membered heterocyclic ring. However, a rather overall planar arrangement is present as in the case of the closely related 2-(phenyl)oxazoline derivative *trans*-[Pt(CF_3){N=C(Ph)OCH_2CH_2}(PPh_3)$_2$]-BF_4 [7c]; the oxazine ring, as in the oxazoline compound, is comprised between two triphenyl ligands 'quasi' mirrored one to each other and is perpendicular to the platinum coordination plane. The dihedral angles between the heterocyclic ligand and the two neighboring phenyl rings, each from one PPh_3 unit, are 28.3(5)° (C23–C28) and 29.3(6)° (C41–C46) comparable to the value of 23° reported for the 2-(phenyl)oxazoline derivative. While the Pt–P and Pt–N bond distances (2.345(4) and 2.07(2) Å, respectively) are practically superimposable on the corresponding distances found in the 2-(phenyl)oxazoline derivative (2.348(4) and 2.08(2) Å [7c]), the Pt–C(CF_3) distance of 2.19(1) Å in **6** is longer than that (2.04(2)) in the oxazoline analog.

Conclusions

The results described above extend the known chemistry of transition metal nitrile complexes and give in particular some significant new insight in the reactivity properties of Pt(II) nitrile complexes. In fact, the cycloaddition reactions with $^-OCH_2CH_2CH_2Cl$ represent, as far as we known, the first examples of such [4+2] cycloadditions with nitrile complexes and the resultant six-membered heterocycles 1,3-oxazines appear to be new types of coordination ring systems. These transformations are clearly related to those already mentioned of Pt(II) nitriles with $HOCH_2CH_2Cl$/base or $\overline{OCH_2CH_2}/Cl^-$ to yield the five-membered heterocycles 2-oxazolines [7] and also to the analogous reactions of CO [28] and RNC [24] ligands in carbonyl and isocyanide complexes, respectively, to form five-membered cyclic carbene complexes. However, it is interesting to note that the reactions of $HOCH_2CH_2CH_2Br$/base with carbonyl complexes do not afford the corresponding six-membered carbenes [28], thus indicating that the ring closure is unfavorable with CO compared to RCN ligands.

The high reactivity of Pt(II) nitrile complexes toward 3-chloro-1-propanol in this study as well as the other organic substrates described earlier [7] is clearly a consequence of the high electrophilicity of the nitrile carbon, which is likely to react with other nucleophiles yet to be examined to give novel heterocyclic derivatives. It is finally noted that reaction (4) and Scheme 2 provide a stoichiometric transition metal mediated synthesis of 1,3-oxazines from nitriles, suggesting the possibility of obtaining these and other heterocycles catalytically.

Supplementary material

Listing of anisotropic thermal parameters (2 pages) and a list of observed and calculated structure factors (22 pages) are available from F.B. on request.

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