Synthesis of Δ^2-1,3-Oxazolines from Cationic Platinum(II) Nitrile Complexes. X-ray Structure of *trans*-$[\mathrm{Pt(CF_3)}\{\overline{\mathrm{N{=}C(Ph)OCH_2CH_2}}\}\mathrm{(PPh_3)_2]BF_4{\cdot}0.5H_2O{\cdot}0.25MeOH}$

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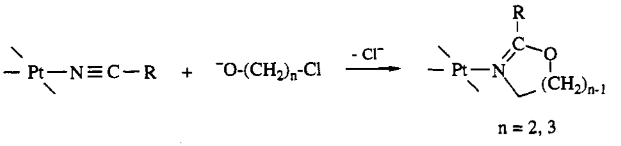
Cationic Pt(II) nitrile complexes of the type *trans*-$\mathrm{[Pt(R')(NCR)(PPh_3)_2]BF_4}$ (R′ = H (**1**), $\mathrm{CH_3}$ (**2**), R = $\mathrm{CH_3}$; R′ = $\mathrm{CF_3}$, R = $\mathrm{CH_3}$ (**3**), $\mathrm{CH_3CH_2}$ (**4**), $\mathrm{CH_3CH_2CH_2}$ (**5**), $\mathrm{(CH_3)_2CH}$ (**6**), $\mathrm{(CH_3)_3C}$ (**7**), $\mathrm{C_6H_5}$ (**8**), *p*-$\mathrm{CH_3C_6H_4}$ (**9**), *o*-$\mathrm{CH_3C_6H_4}$ (**10**), *p*-$\mathrm{OCH_3C_6H_4}$ (**11**)) have been prepared by reaction of the corresponding halo complexes *tans*-$\mathrm{[Pt(R')X(PPh_3)_2]}$ (X = Cl, Br) with $\mathrm{AgBF_4}$ in the presence of a 20–30-fold excess of RCN in $\mathrm{CH_2Cl_2}$. The complexes **1**–**11** readily react in THF at 0 °C or below with $\mathrm{HOCH_2CH_2Cl}$/*n*-BuLi (*n*-BuLi:complex molar ratio 1:1) to give a mixture of products, including the oxazoline complexes *trans*-$[\mathrm{Pt(R')}\{\overline{\mathrm{N{=}C(R)OCH_2CH_2}}\}\mathrm{(PPh_3)_2]BF_4}$ (**1a**–**11a**), the chloro complexes *trans*-$\mathrm{[Pt(Cl(R')(PPh_3)_2}$, and free oxazoline $\overline{\mathrm{N{=}C(R)OCH_2CH_2}}$. For short reaction times (ca. 10–15 min) the oxazoline complexes **1a**–**11a** could be isolated albeit in modest yield (26–49%) from the reaction mixtures and they could be separated from the corresponding chloro complexes (average yield ca. 35%) by taking advantage of the higher solubilty of the latter derivatives in benzene. For longer reaction times (>2 h), the *trans*-$\mathrm{[PtCl(R')(PPh_3)_2]}$ species were the only isolated products. Compounds **1a**–**11a** have been characterized by IR and multinuclear (^{1}H, ^{19}F, ^{31}P{^{1}H}, and ^{13}C{^{1}H}) NMR spectroscopies and also by an X-ray structural determination, which has been carried out for **3a**. It crystallizes in the orthorhombic space group $Pna2_1$, with $a = 19.130(4)$ Å, $b = 15.936(3)$ Å, $c = 16.312(3)$ Å, $V = 4973(2)$ Å^3, and $Z = 4$. The structure was refined to $R = 0.056$ ($R_w = 0.065$) for 2485 measured reflections with $I \geq 3\sigma(I)$. The 2-(phenyl)oxazoline ligand is almost planar and perpendicular to the mean coordination plane. A mechanism is proposed for the conversion of nitriles to 2-oxazolines in cationic Pt(II) complexes. The reactions of the isolated complexes *trans*-$[\mathrm{Pt(CF_3)}\{\overline{\mathrm{N{=}C(R)OCH_2CH_2}}\}\mathrm{(PPh_3)_2]BF_4}$ (**3a**–**11a**) with excess chloride ions gave *trans*-$\mathrm{[Pt(CF_3)Cl(PPh_3)_2]}$ and the corresponding free oxazolines, which were characterized by IR, ^{1}H NMR, and GC/MS techniques. Attempts to generate catalytically 2-(methyl)oxazoline have been performed using the *trans*-$\mathrm{[PtX(R)(PR_3)_2]/CH_3CN/}\overline{\mathrm{OCH_2CH_2}}$ system ($\mathrm{PR_3}$ = $\mathrm{PEt_3}$, $\mathrm{PMe_2Ph}$; R = H, $\mathrm{CH_3}$, $\mathrm{CF_3}$; X = Br, I). No oxazoline formation was observed between 50 and 75 °C and 36 and 160 h; however, addition of LiBr and $\overline{\mathrm{OCH_2CH_2}}$ to *trans*-$\mathrm{[PtBr(CH_3)(PEt_3)_2]}$ and *trans*-$\mathrm{[PtBr(CF_3)(PMe_2Ph)_2]}$ (salt:complex (1.5–3):1 molar ratio) led to the formation of 2-(methyl)oxazoline, albeit not catalytically.

Introduction

Recently, we have initiated a research project on some transition metal-promoted syntheses of organic heterocycles from nitriles. The results of those studies have indicated that RCN ligands in neutral Pt(II) complexes of the type *cis*- or *trans*-$\mathrm{[PtCl_2(NCR)_2]}$ (R = various alkyls and aryls) readily cycloadd the alkoxide ions $^-\mathrm{OCH_2CH_2Cl}$[1,2] and $^-\mathrm{OCH_2CH_2CH_2Cl}$[3] to yield Δ^2-1,3-oxazolines (2-oxazolines hereafter) and 5,6-dihydro-4*H*-1,3-oxazoles (1,3-oxazines hereafter), respectively, according to the following reaction:



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This type of reactivity is unprecedented in transition metal

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nitrile chemistry and is thought to proceed by nucleophilic attack of the haloalkoxide at the electrophilic nitrile carbon, as reported for other electrophilic RCN[4] as well as for CO[5] and RNC[6] ligands in certain transition metal nitrile, carbonyl, and isocyanide complexes, respectively. Interest in the organic heterocycles 2-oxazolines and 1,3-oxazines stems from their reported chemical relevance in several fields of application and also from their biological activity.[7]

In the present work we wish to report that reactions similar to those described above for neutral nitrile complexes occur also with cationic complexes of the type *trans*-$[Pt(R')(NCR)(PPh_3)_2]BF_4$ (R′ = H, CH_3, CF_3; R = alkyl, aryl), but with some significant differences, and those results are described herein for the synthesis of 2-oxazolines. Attempts of catalytic formation of 2-(methyl)oxazoline using Pt(II) species are also described.

Experimental Section

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 onto a Perkin-Elmer 983 spectrophotometer; ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer, while ^{31}P and ^{19}F NMR spectra were run on a Varian FT 80-A spectrometer (coupling constants are in hertz). 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 GLC/MS analyses were performed on a Carlo Erba QMD 1000 instrument using a capillary column SE 54, 25 m × 0.25 mm × 0.3 μm; 1 min at 50 °C, from 50 to 150 °C at 10 °C/min, from 150 to 200 °C at 20 °C/min, and from 200 to 250 °C at 10 °C/min; He flux 1 mL/min. The GLC analyses in the catalytic experiments were run on a Hewlett-Packard 5890A gas chromatograph, equipped with a 3390 automatic integrator, using a capillary column HP-FFAP (50 m × 0.2 mm × 0.3 μm); *T* 80 °C, He flux *ca.* 52 cm³/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 *trans*-$[PtBr(H)(PPh_3)_2]$,[8] *trans*-$[Pt(CH_3)Cl(PPh_3)_2]$,[9] *trans*-$[PtBr(CF_3)(PPh_3)_2]$,[10] *trans*-$[Pt(H)X(PEt_3)_2]$ (X = Cl, Br, I),[11] and *trans*-$[PtBr(CF_3)(PMe_2Ph)_2]$[12] were prepared according to reported procedures. The complex *trans*-$[Pt(CH_3)Cl(PEt_3)_2]$ was prepared from $[Pt(CH_3)Cl(COD)]$[9] (COD = 1,5-cyclooctadiene) (0.71 g, 2.02 mmol) in *n*-pentane (60 mL) and a 1 M THF solution of PEt_3 (4.23 mL, 4.23 mmol), which was added dropwise at room temperature over 15 min. The colorless solution was taken to dryness and the oily residue treated with MeOH (10 mL) and cooled at −25 °C for 3 days. White crystals of the complex were formed; yield 0.73 g (75%). IR (Nujol mull): ν(PtCl) 277 cm⁻¹. ^1H NMR ($CDCl_3$): δ 0.29 (t, CH_3, $^3J_{HP}$ 6.2, $^2J_{HPt}$ 84.2), 1.07 (dt, PCH_2CH_3, $^3J_{HH}$ 7.7, $^3J_{HP}$ 23.6), 1.83 (m, PCH_2, $^3J_{HPt}$ 22.9). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 15.9 (s, $^1J_{PPt}$ 2819). The complex *trans*-$[PtBr(CH_3)(PEt_3)_2]$ was obtained from *trans*-$[Pt(CH_3)Cl(PEt_3)_2]$ (0.21 g, 0.43 mmol) in acetone (50 mL) and LiBr (0.23 g, 2.65 mmol). The reaction mixture was stirred for 12 h at room temperature and then the solution taken to dryness. The solid residue was treated with a mixture of a 10/1 *n*-hexane/Et_2O and filtered off. It was taken to dryness and then treated with *n*-hexane (10 mL). After cooling at −25 °C, white needles were obtained. Yield: 0.17 g, 78%. ^1H NMR ($CDCl_3$): δ 0.39 (t, CH_3, $^3J_{HP}$ 6.0, $^2J_{HP}$ 84.1), 1.09 (dt, PCH_2CH_3, $^3J_{HH}$ 7.7, $^3J_{HP}$ 16.0), 1.91 (m, PCH_2, $^3J_{HPt}$ 22.8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.9 (s, $^1J_{PPt}$ 2797). The complex *trans*-$[Pt(CH_3)I(PEt_3)_2]$ was obtained from *trans*-$[Pt(CH_3)Cl(PEt_3)_2]$ (0.20 g, 0.42 mmol) in acetone (50 mL) and NaI (0.068 g, 0.45 mmol). After 1 h of stirring at room temperature, the solution was taken to dryness and worked up as above. Yield: 0.20 g, 84%. ^1H NMR ($CDCl_3$): δ 0.48 (t, CH_3, $^3J_{HP}$ 6.3, $^2J_{HPt}$ 81.9), 1.07 (dt, PCH_2CH_3, $^3J_{HH}$ 7.7, $^3J_{HP}$ 16.1), 2.00 (m, PCH_2, $^3J_{HP}$ 22.8). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 10.08 (s, $^1J_{PPt}$, 2753).

Synthesis of Cationic Platinum(II) Nitrile Complexes. *trans*-$[Pt(H)(NCCH_3)(PPh_3)_2]BF_4$ (1). A solution of *trans*-$[PtBr(H)(PPh_3)_2]$ (1.46 g, 1.82 mmol) in CH_2Cl_2 (40 mL) was treated with a 0.508 M $AgBF_4$ solution in acetone (3.6 mL, 1.84 mmol) and then with an excess of CH_3CN (2.0 mL, 38.00 mmol). The reaction mixture was stirred at room temperature for 1 h and for an additional 15 min with activated charcoal. After filtration, the filtrate was evaporated under reduced pressure to *ca.* 2 mL and subsequently treated with Et_2O (30 mL). A white solid precipitated, which was filtered off, washed with Et_2O (2 × 5 mL), and dried under vacuum. Yield: 1.31 g, 85%. Mp: 189 °C dec. Anal. Calcd for $C_{38}H_{34}NP_2BF_4Pt$: C, 53.79; H, 4.04; N, 1.65. Found: C, 53.70; H, 3.92; N, 1.63. ^1H NMR (CD_2Cl_2): δ −16.53 (t, H, $^1J_{HPt}$ (1155, $^2J_{HP}$ 11.7), 1.52 (s, CH_3, $^4J_{HPt}$ 6.4), 7.62–7.48 (m, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 28.34 (s, $^1J_{PPt}$ 2908).

***trans*-$[Pt(CH_3)(NCCH_3)(PPh_3)_2]BF_4$ (2).** This compound was prepared as described for 1 starting from *trans*-$[Pt(CH_3)Cl(PPh_3)_2]$ (0.73 g, 0.95 mmol) in CH_2Cl_2 (40 mL), a 1.02 M $AgBF_4$ solution in acetone (1.0 mL, 1.02 mmol), and CH_3CN (5.0 mL, 95.36 mmol). Yield: 0.68 g, 83%. MP: 192 °C dec. Anal. Calcd for $C_{39}H_{36}NP_2BF_4Pt$: C, 54.31; H, 4.21; N, 1.62. Found: C, 54.22; H, 4.46; N, 1.60. ^1H NMR (CD_2Cl_2): δ 0.24 (t, CH_3, $^2J_{HPt}$ 78.1, $^3J_{HP}$ 7.1), 7.67–7.52 (m, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 26.52 (s, $^1J_{PPt}$ 3009).

***trans*-$[Pt(CF_3)(NCCH_3)(PPh_3)_2]BF_4$ (3).** A solution of *trans*-$[PtBr(CF_3)(PPh_3)_2]$ (0.51 g, 0.59 mmol) in CH_2Cl_2 (30 mL) was treated with a 0.19 M $AgBF_4$ solution in acetone (3.0 mL, 0.57 mmol). The mixture was stirred at room temperature for 30 min and then with activated charcoal for an additional 15 min. After filtration the filtrate was evaporated under vacuum to 5 mL and Et_2O (20 mL) was added to give the white solid *trans*-$[Pt(CF_3)(PPh_3)_2(solv)]BF_4$, which was filtered off, dissolved in CH_2Cl_2 (30 mL) and treated with an excess of CH_3CN (1.0 mL, 19.00 mmol). The solution was stirred at room temperature for *ca.* 1 h and then reduced to a small volume (3 mL). Addition of Et_2O (15 mL) gave **3** as a white precipitate, which was filtered off, washed with Et_2O (2 × 5 mL) and dried under vacuum. Yield: 0.49 g, 92. Mp: 224–225 °C dec. Anal. Calcd for $C_{39}H_{33}NP_2BF_7Pt\cdot{}^1/_2CH_2Cl_2$: C, 49.78; H, 3.55; N, 1.45. Found: C, 50.28; H, 3.58; N, 1.43. ^1H NMR (CD_2Cl_2): δ 1.17 (t, CH_3, $^5J_{HP}$

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0.9, $^4J_{HPt}$ 6.9). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 21.60 (q, $^1J_{PPt}$ 2870). ^{19}F NMR (CD_2Cl_2): δ −12.92 (t, $^2J_{FPt}$ 724, $^3J_{PF}$ 20.5).

***trans*-[Pt(CF_3)($NCCH_2CH_3$)(PPh_3)$_2$]BF_4 (4).** This compound was prepared as described for **3** starting from *trans*-[PtBr(CF_3)(PPh_3)$_2$] (1.50 g, 1.73 mmol) in CH_2Cl_2 (40 mL), a 1.1 M $AgBF_4$ solution in acetone (1.6 mL, 1.76 mmol), and an excess of CH_3CH_2CN (2.2 mL, 30.83 mmol). Yield: 1.15 g, 72%. Mp: 190–191 °C dec. Anal. Calcd for $C_{40}H_{35}NP_2BF_7Pt$: C, 51.60; H, 3.80; N, 1.50. Found: C, 51.58; H, 3.80; N, 1.49. ^1H NMR ($CDCl_3$): δ 0.27 (t, CH_3, $^3J_{HH}$ 7.5), 1.69 (q, CH_2, $^4J_{HPt}$ 1.21). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.89 (q, $^1J_{PPt}$ 2886). ^{19}F NMR ($CDCl_3$): δ −13.35 (t, $^2J_{FPt}$ 721, $^3J_{PF}$ 19.5).

***trans*-[Pt(CF_3)($NCCH_2CH_2CH_3$)(PPh_3)$_2$]BF_4 (5).** This compound was prepared as described for **3** starting from *trans*-[PtBr(CF_3)(PPh_3)$_2$] (1.41 g, 1.62 mmol) in CH_2Cl_2 (40 mL), a 0.508 M $AgBF_4$ solution in acetone (3.2 mL, 1.63 mmol), and an excess of $CH_3CH_2CH_2CN$ (2.6 mL, 29.87 mmol). Yield: 1.23 g, 80%. Mp: 196–197 °C dec. Anal. Calcd for $C_{41}H_{37}NP_2BF_7Pt{\cdot}{}^1/_2CH_2Cl_2$: C, 50.80; H, 3.86; N, 1.43. Found: C, 50.76; H, 3.79; N, 1.44. ^1H NMR ($CDCl_3$): δ 0.25 (t, CH_3, $^3J_{HH}$ 7.07), 0.64 (m, CH_2); 1.67 (t, CH_2, $^3J_{HH}$ 7.02, $^4J_{HPt}$ 2.1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.93 (q, $^1J_{PPt}$ 2886). ^{19}F NMR ($CDCl_3$): δ −13.47 (t, $^2J_{FPt}$ 725, $^3J_{PF}$ 19.7).

***trans*-[Pt(CF_3){$NCCH(CH_3)_2$}(PPh_3)$_2$]BF_4 (6).** This compound was prepared as described for **3** by starting from *trans*-[PtBr(CF_3)(PPh_3)$_2$] (1.51 g, 1.73 mmol) in CH_2Cl_2 (60 mL), a 0.508 M $AgBF_4$ solution in acetone (3.45 mL, 1.75 mmol), and an excess of $(CH_3)_2CHCN$ (2.7 mL, 29.69 mmol). Yield: 1.37 g, 84%. Mp 198–199 °C dec. Anal. Calcd for $C_{41}H_{37}NP_2BF_7Pt$: C, 52.13; H, 3.95; N, 1.48. Found: C, 51.76; H, 3.87; N, 1.44. ^1H NMR ($CDCl_3$): δ 0.31 (d, CH_3), 2.18 (st, CH, $^4J_{HPt}$ 2.06, $^3J_{HH}$ 7.03). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.23 (q, $^1J_{PPt}$ 2892). ^{19}F NMR ($CDCl_3$): δ −13.70 (t, $^2J_{FPt}$ 725, $^3J_{PF}$ 21.9).

***trans*-[Pt(CF_3){$NCC(CH_3)_3$}(PPh_3)$_2$]BF_4 (7).** This compound was prepared as described for **3** starting from *trans*-[PtBr(CF_3)(PPh_3)$_2$] (1.51 g, 1.74 mmol) in CH_2Cl_2 (60 mL), a 0.508 M $AgBF_4$ solution in acetone (3.45 mL, 1.75 mmol), and an excess of $(CH_3)_3CCN$ (3.3 mL, 29.85 mmol). Yield: 1.35 g, 81%. Mp: 219–220 °C dec. Anal. Calcd for $C_{42}H_{39}NP_2BF_7Pt$: C, 52.62; H, 4.10; N, 1.46. Found: C, 52.74; H, 4.27; N, 1.37. ^1H NMR ($CDCl_3$): δ 0.41 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.46 (q, $^1J_{PPt}$ 2794). ^{19}F NMR ($CDCl_3$): δ −13.94 (t $^2J_{FPt}$ 726, $^3J_{PF}$ 20.7).

***trans*-[Pt(CF_3)(NCC_6H_5)(PPh_3)$_2$]BF_4 (8).** This compound was prepared as described for **3** starting from *trans*-[PtBr(CF_3)(PPh_3)$_2$] (1.97 g, 2.27 mmol) in CH_2Cl_2 (80 mL), a 1.1 M $AgBF_4$ solution in acetone (2.1 mL, 2.31 mmol), and an excess of C_6H_5CN (2.0 mL, 19.39 mmol). Yield: 1.64 g, 74%. Mp: 210–211 °C dec. Anal. Calcd for $C_{44}H_{35}NP_2BF_7Pt{\cdot}{}^1/_2CH_2Cl_2$: C, 52.62; H, 3.53; N, 1.36. Found: C, 53.21; H, 3.67; N, 1.30. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.02 (q, $^1J_{PPt}$ 2870). ^{19}F NMR (CD_2Cl_2): δ −13.13 (t, $^2J_{FPt}$ 728, $^3J_{PF}$ 20.6).

***trans*-[Pt(CF_3)(NCC_6H_4)-*p*-CH_3)(PPh_3)$_2$]BF_4 (9).** This compound was prepared as described for **3** starting from *trans*-[PtBr(CF_3)(PPh_3)$_2$] (1.40 g, 1.61 mmol) in CH_2Cl_2 (40 mL), a 0.508 M $AgBF_4$ solution in acetone (3.2 mL, 1.63 mmol), and an excess of CH_3-*p*-C_6H_4CN (3.92 g, 33.00 mmol). Yield: 1.34 g, 84%. Mp: 180–181 °C dec. Anal. Calcd for $C_{45}H_{37}NP_2BF_7Pt{\cdot}{}^1/_2CH_2Cl_2$: C, 53.07; H, 3.86; N, 1.34. Found: C, 54.39; H, 3.25; N, 1.22. ^1H NMR ($CDCl_3$): δ 2.27 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 21.99 (q, $^1J_{PPt}$ 2878). ^{19}F NMR ($CDCl_3$): δ −13.50 (t, $^2J_{FPt}$ 726, $^3J_{PF}$ 20.7).

***trans*-[Pt(CF_3)(NCC_6H_4-*o*-CH_3)(PPh_3)$_2$]BF_4 (10).** This compound was prepared as described for **3** starting from *trans*-[PtBr(CF_3)(PPh_3)$_2$] (1.32 g, 1.51 mmol) in CH_2Cl_2 (40 mL), a 0.508 M $AgBF_4$ solution in acetone (3.0 mL, 1.52 mmol), and an excess of CH_3-*o*-C_6H_4CN (3.5 mL, 29.45 mmol). Yield: 1.18 g, 79%. Mp: 229–230 °C dec. Anal. Calcd for $C_{45}H_{37}NP_2BF_7Pt$: C, 54.45; H, 3.75; N, 1.41. Found: C, 54.48; H, 3.55; N, 1.42. ^1H NMR (CD_2Cl_2): δ 1.537 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.05 (q, $^1J_{PPt}$ 2876). ^{19}F NMR ($CDCl_3$): δ −13.52 (t, $^2J_{FPt}$ 727, $^3J_{PF}$ 20.4).

***trans*-[Pt(CF_3)(NCC_6H_4-*p*-OCH_3)(PPh_3)$_2$]BF_4 (11).** This compound was prepared as described for **3** starting from *trans*-[PtBr(CF_3)(PPh_3)$_2$] (1.11 g, 1.27 mmol) in CH_2Cl_2 (40 mL), a 0.508 M $AgBF_4$ solution in acetone (2.6 mL, 1.32 mmol), and an excess of CH_3O-*p*-C_6H_4CN (3.42 g, 25.68 mmol). Yield: 0.97 g, 76%. Mp: 176 °C dec. Anal. Calcd for $C_{45}H_{37}NOP_2BF_7Pt{\cdot}{}^1/_2CH_2Cl_2$: C, 52.27; H, 3.62; N, 1.34. Found: C, 52.70; H, 3.66; N, 1.24. ^1H NMR ($CDCl_3$): δ 3.74 (s, OCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.08 (q, $^1J_{PPt}$ 2882). ^{19}F NMR ($CDCl_3$): δ −13.38 (t, $^2J_{FPt}$ 722, $^3J_{PF}$ 20.3).

Synthesis of Cationic Δ^2-1,3-Oxazoline Complexes of Platinum(II). *trans*-[PtH{$\overline{N{=}C(CH_3)OCH_2CH_2}$}($PPh_3$)$_2$]$BF_4$ (1a). A solution of $ClCH_2CH_2OH$ (0.50 mL, 7.46 mmol) in THF (15 mL), at −8 °C, was treated with a 1.6 M *n*-BuLi solution in *n*-hexane (0.6 mL, 0.96 mmol) and then solid **1** (0.71 g, 0.83 mmol). After 1 min a clear solution formed. An IR spectrum of the solution showed ν(C=N) at 1662 cm^{-1} and did not reveal any ν(C≡N) absorption of the starting nitrile complex. The bath was removed and the reaction mixture allowed to reach room temperature (10 min). The solution was then concentrated under reduced pressure to *ca.* 10 mL and Et_2O (40 mL) added. The white solid formed was filtered off and the solution was taken to dryness, taken up with Et_2O (1 mL) and analyzed by IR and GLC/MS techniques. The IR and GLC/MS spectra showed the presence of 2-(methyl)oxazoline (see text). The white solid was washed with benzene (50 mL) and then dissolved in CH_2Cl_2 (30 mL). Upon addition of a 1/4 mixture of *n*-pentane/Et_2O (50 mL) a white precipitate of **1a** was formed, which was filtered off, washed with Et_2O (2 × 5 mL), and dried under vacuum. Yield: 0.32 g, 45%. Mp: 173 °C dec. Anal. Calcd for $C_{44}H_{38}NOP_2BF_4Pt$: C, 53.82; H, 4.29; N, 1.58. Found: C, 53.76; H, 4.26; N, 1.51. The benzene washing was concentrated under reduced pressure and Et_2O added. The white solid formed was filtered off and washed with MeOH (2 × 3 mL), Et_2O (2 × 5 mL), dried under vacuum, and identified by IR and NMR (^1H and ^{31}P) data as *trans*-$(PPh_3)_2Pt(H)Cl$ [see ref 18]; yield 0.25 g, 36%.

***trans*-[Pt(CH_3){$\overline{N{=}C(CH_3)OCH_2CH_2}$}($PPh_3$)$_2$]$BF_4$ (2a).** To a solution of $ClCH_2CH_2OH$ (0.5 mL, 7.45 mmol) in THF (15 mL), at 0 °C, was added a 1.6 M *n*-hexane solution of *n*-BuLi (0.4 mL, 0.64 mmol) and then **2** (0.48 g, 0.56 mmol). The suspension was stirred at 0 °C for 5 min, and then the volume of the solution was reduced to 10 mL. Addition of Et_2O (40 mL) gave further precipitation of a white solid, which was filtered off. The solution was taken to dryness and treated with Et_2O (1 mL) and the ethereal solution analyzed by IR and GLC/MS spectroscopies. The IR and GLC/MS spectra showed the presence of 2-(methyl)oxazoline. The solid was washed with warm benzene (2 × 10 mL) and dissolved in CH_2Cl_2 (30 mL). Upon addition of a 1/6 mixture of petroleum ether/Et_2O (35 mL) a white precipitate of **2a** was formed, which was filtered off, washed with Et_2O (2 × 5 mL), recrystallized from CH_2Cl_2/Et_2O, and dried under vacuum. Yield: 0.25 g, 47%. Mp: 220 °C dec. Anal. Calcd for $C_{41}H_{40}NOP_2BF_4Pt$: C, 54.31; H, 4.44; N, 1.55. Found: C, 53.68; H, 4.45; N, 1.54. The combined benzene washings were concentrated under reduced pressure, and Et_2O (15 mL) was added. The white solid formed was filtered off and washed with MeOH (2 × 3 mL) and Et_2O (2 × 5 mL), dried under vacuum, and identified as *trans*-[Pt(CH_3)Cl(PPh_3)$_2$].[9] Yield: 0.13 g, 26%.

***trans*-[Pt(CF_3){$\overline{N{=}C(CH_3)OCH_2CH_2}$}($PPh_3$)$_2$]$BF_4$ (3a).** To a solution of $ClCH_2CH_2OH$ (0.4 mL, 5.96 mmol) in THF (10 mL) at 0 °C was added a 1.6 M *n*-hexane solution of *n*-BuLi (0.4 mL, 0.61 mmol) and then **3** (0.56 g, 0.61 mmol). The suspension was stirred at 0 °C for 20 min and then the volume of the solution was reduced to 5 mL. Addition of petroleum ether (20 mL) gave further precipitation of a white solid, which was filtered off. The solution was taken to dryness and the oily residue treated with Et_2O (2 mL). The ethereal solution was analyzed by IR and GLC/MS techniques, which showed the presence of 2-(methyl)oxazoline. The white solid was washed with warm benzene (6 × 10 mL) and then dissolved in CH_2Cl_2 (20 mL). Upon addition of a 1/3 mixture of petroleum ether/Et_2O (40 mL) a white precipitate of **3a** was formed which was filtered off, washed with Et_2O (2 × 10 mL), and dried under vacuum. Yield: 0.24 g, 41%. Mp: 243–244 °C dec. Anal. Calcd for $C_{41}H_{31}NOP_2BF_7Pt$: C, 51.26; H, 3.88; N, 1.46. Found: C, 49.50; H, 3.75; N, 1.48. The combined benzene washings were taken to dryness under reduced pressure, and the white solid residue was taken up with Et_2O (40 mL), filtered off, washed with MeOH (3 × 5 mL) and Et_2O (2 × 10 mL), and dried under vacuum. This compound was identified as *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$.[10] Yield: 0.21 g, 42%.

***trans*-$[Pt(CF_3)\{N{=}C(CH_2CH_3)OCH_2CH_2\}(PPh_3)_2]BF_4$ (4a).** This compound was prepared as described for **3a** starting from $ClCH_2CH_2OH$ (0.5 mL, 7.45 mmol) in THF (20 mL) at 0 °C, a 1.6 M *n*-hexane solution of *n*-BuLi (0.6 mL, 0.96 mmol), and **4** (0.75 g, 0.81 mmol). Yield: 0.31 g, 39%. Mp: 205 °C dec. Anal. Calcd $C_{42}H_{39}NOP_2BF_7Pt$: C, 51.76; H, 4.03; N, 1.44. Found: C, 51.16; H, 4.04; N, 1.40. The ethereal solution was analyzed by IR and GLC/MS, showing the presence of 2-(ethyl)oxazoline (see text). Workup as for **3a** gave *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield: 0.27 g, 40%.

***trans*-$[Pt(CF_3)\{N{=}C(CH_2CH_2CH_3)OCH_2CH_2\}(PPh_3)_2]BF_4$ (5a).** To a solution of $ClCH_2CH_2OH$ (0.5 mL, 7.45 mmol) in THF (20 mL) at 0 °C was added a 1.6 M *n*-hexane solution of *n*-BuLi (0.6 mL, 0.96 mmol) and then **5** (0.79 g, 0.83 mmol). After 5 min an IR spectrum of the solid precipitate showed the presence of the $\nu(C{=}N)$ absorption at 1643 cm^{-1} and the absence of the $\nu(C{\equiv}N)$ band of the starting nitrile at 2296 cm^{-1}. The suspension was stirred at 0 °C for an additional 15 min and then the volume of the solution was reduced to 10 mL. Addition of *n*-pentane (20 mL) gave further precipitation of a white solid, which was filtered off and washed with *n*-pentane (2 × 5 mL). The solution was taken to dryness and the oily product treated with Et_2O (2 mL). IR and GLC/MS analyses showed the presence of 2-(*n*-propyl)oxazoline (see text). The solid was washed with warm benzene (4 × 5 mL) and then dissolved in CH_2Cl_2 (20 mL). Upon addition of a 1/3 mixture of *n*-pentane/Et_2O (40 mL) a white precipitate of **5a** was formed, which was filtered off, washed with Et_2O (2 × 5 mL), and dried under vacuum. Yield: 0.24 g, 30%. Mp: 219 °C dec. Anal. Calcd for $C_{43}H_{41}NOP_2BF_7Pt{\cdot}{}^1/_2CH_2Cl_2$: C, 50.96; H, 4.08; N, 1.35. Found: C, 50.94; H, 4.18; N, 1.28. The combined benzene washings were worked up as for **3a** to give *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield: 0.29 g, 42%.

***trans*-$[Pt(CF_3)\{N{=}C(CH(CH_3)_2)OCH_2CH_2\}(PPh_3)_2]BF_4$ (6a).** This compound was prepared as described for **5a** by starting from $ClCH_2CH_2OH$ (0.5 mL, 7.45 mmol) in THF (15 mL) at 0 °C, a 1.6 M *n*-hexane solution of *n*-BuLi (0.7 mL, 1.12 mmol), and **6** (0.90 g, 0.95 mmol). After 10 min an IR spectrum of the solid precipitate showed the presence of the $\nu(C{=}N)$ absorption at 1626 cm^- and the absence of the $\nu(C{\equiv}N)$ band of the starting nitrile at 2288 cm^{-1}. Yield: 0.25 g, 28%. Mp: 208 °C dec. Anal. Calcd for $C_{43}H_{41}NOP_2BF_7Pt{\cdot}{}^1/_2CH_2Cl_2$: C, 50.96; H, 4.08; N, 1.35. Found: C, 51.58; H, 4.19; N, 1.30. IR and GLC/MS analyses revealed the presence of 2-(isopropyl)oxazoline (see text). Workup as for **3a** gave also *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield: 0.46 g, 59%.

***trans*-$[Pt(CF_3)\{N{=}C(C(CH_3)_3)OCH_2CH_2\}(PPh_3)_2]BF_4$ (7a).** This compound was prepared as described for **5a** starting from $ClCH_2CH_2OH$ (0.3 mL, 4.47 mmol) in THF (15 mL) at 0 °C, a 1.6 M *n*-hexane solution of *n*-BuLi (0.3 mL, 0.48 mmol), and **7** (0.39 g, 0.40 mmol). Yield: 0.15 g, 37%. Mp: 215–216 °C dec. Anal. Calcd for $C_{44}H_{43}NOP_2BF_7Pt$: C, 52.71; H, 4.32; N, 1.39. Found: C, 52.07; H, 4.50; N, 1.29. IR and GLC/MS analyses revealed the presence of 2-(*tert*-butyl)oxazoline (see text). Workup as for **3a** gave *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield: 0.10 g, 30%.

***trans*-$[Pt(CF_3)\{N{=}C(C_6H_5)OCH_2CH_2\}(PPh_3)_2]BF_4$ (8a).** This compound was prepared as described for **5a** starting from $ClCH_2CH_2OH$ (0.5 mL, 7.45 mmol) in THF (15 mL) at 0 °C, a 1.6 M *n*-hexane solution of *n*-BuLi (0.5 mL, 0.8 mmol), and *trans*-$[Pt(CF_3)(NCC_6H_5)(PPh_3)_2]BF_4$ (0.74 g, 0.75 mmol). Yield: 0.37 g, 49%. Mp: 179–180 °C dec. Anal. Calcd for $C_{46}H_{39}NOP_2BF_7Pt$: C, 54.02; H, 3.84; N, 1.37. Found: C, 53.77; H, 3.95; N, 1.31. IR and GLC/MS analyses showed the presence of C_6H_5CN and of 2-(phenyl)oxazoline (see text). Workup as for **3a** gave *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield: 0.21 g, 34%.

Table 1. IR and $^{13}C\{^1H\}$ NMR Data for Cationic Nitrile Complexes 1–11

	IR, cm^{-1}				$^{13}C\{^1H\}$ NMR^b	
	$\nu(C{\equiv}N)_{coord}$		$\nu(C{\equiv}N)_{free}$			
compd	Nujol	CH_2Cl_2	CH_2Cl_2	$\Delta\nu^a$	δ(NC)	$^2J_{CPt}$
1	2321	2322	2257	65	122.49 (s)	81.4
2	2315	2320	2257	63	120.65 (s)	*c*
3	2330	2325	2257	68	125.66 (s)	92.4
4	2311	2302	2248	54	123.28 (s)	*c*
5	2305	2296	2251	45	124.93 (s)	*c*
6	2300	2288	2245	43	124.43 (s)	93.3
7	2293	2280	2237	43	121.37 (s)	93.3
8	2274	2274	2233	41	123.87 (s)	94.1
9	2276	2270	2228	42	123.90 (s)	95.0
10	2270	2267	2230	37	123.96 (s)	*c*
11	2274	2265	2224	41	124.50 (s)	95.0

[a] $\Delta\nu = \nu(C{\equiv}N)_{coord} - \nu(C{\equiv}N)_{free}$; in CH_2Cl_2. [b] In CD_2Cl_2; the signals are referred to Me_4Si by taking the chemical shift of CD_2Cl_2-d_2 as +53.80 ppm; δ in ppm, J in Hz. Abbreviations: s = singlet. [c] Signal of too low intensity to be observed.

***trans*-$[Pt(CF_3)\{N{=}C(C_6H_4\text{-}p\text{-}CH_3)OCH_2CH_2\}(PPh_3)_2]BF_4$ (9a).** This compound was prepared as described for **5a** by starting from $ClCH_2CH_2OH$ (0.5 mL, 7.45 mmol) in THF (15 mL) at 0 °C, a 1.6 M *n*-hexane solution of *n*-BuLi (0.6 mL, 0.96 mmol), and **9** (0.87 g, 0.88 mmol). Yield: 0.36 g, 39%. Mp: 194 °C dec. Anal. Calcd for $C_{47}H_{41}NOP_2BF_7Pt{\cdot}{}^1/_2CH_2Cl_2$: C, 53.13; H, 3.90; N, 1.29. Found: C, 52.87; H, 4.08; N, 1.25. IR and GLC/MS analyses showed the presence of *p*-CH_3-C_6H_4CN and 2-(*p*-tolyl)oxazoline (see text). Workup as for **3a** gave *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield: 0.36 g, 48%.

***trans*-$[Pt(CF_3)\{N{=}C(C_6H_4\text{-}o\text{-}CH_3)OCH_2CH_2\}(PPh_3)_2]BF_4$ (10a).** This compound was prepared as described for **5a** by starting from $ClCH_2CH_2OH$ (0.5 mL, 7.45 mmol) in THF (15 mL) at 0 °C, a 1.6 M *n*-hexane solution of *n*-BuLi (0.7 mL, 1.12 mmol), and **10** (1.00 g, 1.00 mmol). Yield: 0.43 g, 42%. Mp: 145–146 °C dec. Anal. Calcd for $C_{47}H_{41}NOP_2BF_7Pt{\cdot}{}^1/_2CH_2Cl_2$: C, 53.13; H, 3.90; N, 1.29. Found: C, 53.82; H, 4.07; N, 1.27. IR and GLC/MS showed the presence of *o*-$CH_3C_6H_4CN$ and 2-(*o*-tolyl)oxazoline. Workup as for **3a** gave *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield: 0.33 g, 41%.

***trans*-$[Pt(CF_3)\{N{=}C(C_6H_4\text{-}p\text{-}OCH_3)OCH_2CH_2\}(PPh_3)_2]BF_4$ (11a).** This compound was prepared as described for **3a** by starting from $ClCH_2CH_2CH_2OH$ (0.5 mL, 7.45 mmol) in THF (15 mL) at 0 °C, a 1.6 M *n*-hexane solution of *n*-BuLi (0.5 mL, 0.8 mmol), and **11** (0.68 g, 0.67 mmol). Yield: 0.31 g, 43%. Mp: 230 °C dec. Anal. Calcd for $C_{47}H_{41}NO_2P_2BF_7Pt$: C, 53.62; H, 3.93; N, 1.34. Found: C, 52.43; H, 3.98; N, 1.22. IR and GLC/MS analyses showed the presence of *p*-$CH_3OC_6H_4CN$ and 2-(*p*-$CH_3OC_6H_4$)oxazoline. Workup as for **3a** gave *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$. Yield: 0.14 g, 26%.

Reactions of 3a–11a with PPN^+Cl^-. Each one of the compounds **3a–11a** (typically 0.050 mmol) was reacted with a slight excess (10%) of PPN^+Cl^- (0.054 mmol) in CH_2Cl_2 (1 mL) at room temperature. After 30 min the reaction mixture was filtered off. The white solid formed was identified as *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$, while the mother liquor was analyzed by IR (Table 7) and GLC/MS (Table 8,, see below). The same reactions were run in an NMR tube using CD_2Cl_2 as solvent (0.7 mL). The ^1H NMR spectra showed after *ca.* 30 min the presence of free 2-(*R*)oxazoline (Table 7) and the disappearance of the signals corresponding to the complexes **3a–11a**. The white solid precipitated was filtered off and identified as *trans*-$[Pt(CF_3)Cl(PPh_3)_2]$.[10]

X-ray Measurements and Structure Determination for 3a. A colorless prismatic crystal (from a solution of **3a** in CH_2Cl_2/MeOH) of dimensions 0.23 × 0.28 × 0.14 mm was lodged in a Lindemann glass capillary and centered on a four-circle Philips PW 1100 diffractometer with graphite-monochromated (Mo Kα)

Table 2. IR and $^{13}C\{^1H\}$ NMR Data for Complexes 1a–11a

	IR, cm^{-1} [a]	$^{13}C\{^1H\}$ NMR[b]			
compd	ν(C=N)	δ(OCH$_2$)	δ(NCH$_2$)	δ(C=N)	δ(others)
1a	1656 (s) ν(PtH) 2208 (m)	69.07 (s, $^3J_{CPt}$ 24.5)	54.09 (s, $^2J_{CPt}$ 12.4)	170.55 (s, $^2J_{CPt}$ 29.6)	15.25 (s, CH$_3$, $^3J_{CPt}$ 13.5)
2a	1664 (s)	68.89 (s, $^3J_{CPt}$ 23.7)	54.12 (s, $^2J_{CPt}$ 11.4)	170.33 (s, $^2J_{CPt}$ 25.7)	15.44 (s, CH$_3$, $^3J_{CPt}$ 14.3) −13.59 (t, $^2J_{CP}$ 6.1, $^2J_{CPt}$ 594)
3a	1653 (s)	69.37 (s, $^3J_{CPt}$ 25.6)	53.52 (s)	171.64 (s)[c]	16.32 (s, CH$_3$, $^3J_{CPt}$ 14.6)
4a	1643 (s)	69.29 (s, $^3J_{CPt}$ 23.1)	53.19 (s)	174.50 (s, $^2J_{CPt}$ 31.4)	24.18 (s, CH$_2$, $^3J_{CPt}$ 15.7) 8.22 (s, CH$_3$)
5a	1644 (s)	69.49 (s, $^3J_{CPt}$ 22.6)	53.20 (s)	173.80 (s, $^2J_{CPt}$ 32.5)	32.73 (s, CH$_2$, $^3J_{CPt}$ 13.2) 17.84 (s, CH$_2$) 14.04 (s, CH$_3$)
6a	1627 (s)	69.43 (s, $^3J_{CPt}$ 23.3)	52.83 (s)	177.30 (s, $^2J_{CPt}$ 32.3)	30.32 (s, CH, $^3J_{CPt}$ 12.6) 19.24 (s, CH$_3$)
7a	1611 (s)	68.31 (s)[c]	57.86 (s)	171.91 (s)[c]	34.52 (s, C) 28.34 (s, CH$_3$)
8a	1624 (s)	67.92 (s)[c]	54.99 (s)	168.45 (s)[c]	135.04–127.80 (m, Ph)
9a	1617 (s)	67.73 (s, $^3J_{CPt}$ 25.5)	54.82 (s)	168.5 (s, $^2J_{CPt}$ 19.5)	21.97 (s, CH$_3$) 146.58–121.10 (m, Ph)
10a	1609 (s)	69.31 (s, $^3J_{CPt}$ 28.5)	56.16 (s)	170.09 (s, $^2J_{CPt}$ 16.2)	22.84 (CH$_3$) 142.14–122.65 (m, Ph)
11a	1618 (s)	67.59 (s, $^3J_{CPt}$ 25.9)	54.70 (s)	168.00 (s, $^2J_{CPt}$ 23.1)	56.30 (s, OCH$_3$) 134.91–114.64 (m, Ph) 164.98[d]

[a] Nujol mulls. Abbreviation: s = strong. [b] In CD$_2$Cl$_2$; the signals are referred to Me$_4$Si by taking the chemical shift of CD$_2$Cl$_2$-d_2 as +53.80 ppm; δ in ppm; J in Hz. Abbreviations: s = singlet, t = triplet, m = multiplet. [c] ^{195}Pt satellites are too low intense to be observed. [d] *C*–OCH$_3$ resonance.

Table 3. ^1H NMR, $^{31}P\{^1H\}$ NMR, and ^{19}F NMR Data for Complexes 1a–11a

	^1H NMR[a]			$^{31}P\{^1H\}$ NMR[b]			^{19}F NMR[c]	
compd	δ(OCH$_2$)	δ(NCH$_2$)	δ(others)	δ	$^1J_{PPt}$	$^3J_{PF}$	δ	$^2J_{FPt}$
1a	3.65 (t, $^3J_{HH}$ 9.8)	2.90 (t)	1.46 (s, CH$_3$) −15.55 (t, H, $^2J_{HP}$ 12.2, $^1J_{HPt}$ 1008)	28.65 (s)	2945			
2a	3.46 (t, $^3J_{HH}$ 9.8)	2.73 (t)	1.64 (s, CH$_3$) 0.15 (t, CH$_3$, $^3J_{HP}$ 7.0, $^2J_{HPt}$ 70.4)	 27.37 (s)	 3040			
3a	3.37 (t, $^3J_{HH}$ 9.7)	2.69 (t)	1.69 (s, CH$_3$)	19.72 (q)	2898	18.6	−12.19 (t)	625
4a	3.34 (t, $^3J_{HH}$ 10.0)	2.52 (t)	2.77 (s, CH$_2$, $^3J_{HH}$ 7.5) 0.77 (t, CH$_3$)	19.40 (q)	2904	18.3	−12.06 (t)	623
5a	3.30 (t, $^3J_{HH}$ 10.1)	2.33 (t)	2.23 (t, NCH$_2$, $^3J_{HH}$ 8.3) 1.18 (m, CH$_2$) 0.77 (t, CH$_3$, $^3J_{HH}$ 7.5)	19.09 (q)	2905	18.6	−12.02 (t)	624
6a	3.32 (t, $^3J_{HH}$ 10.0)	2.03 (t)	2.95 (st, CH) 0.90 (d, CH$_3$, $^3J_{HH}$ 6.9)	18.02 (q)	2920	18.7	−11.27 (t)	623
7a	3.52 (t, $^3J_{HH}$ 10.1)	2.98 (t)	1.17 (s, CH$_3$)	18.7 (q)	2958	19.9	−10.41 (t)	615
8a	3.41 (t, $^3J_{HH}$ 10.0)	3.19 (t)	7.45–7.69 (m, Ph) 8.59–8.57 (m, Ph)	19.80 (q)	2907	18.5	−11.03 (t)	634
9a	3.36 (t, $^3J_{HH}$ 9.3)	3.15 (t)	2.47 (s, CH$_3$) 8.67–8.44 (m, Ph) 7.60–7.25 (m, Ph)	19.50 (q)	2909	18.8	−10.97 (t)	631
10a	3.61 (t, $^3J_{HH}$ 10.0)	3.15 (t)	7.20–7.60 (m, Ph) 9.85–9.84 (m, Ph) 2.06 (s, CH$_3$)	19.30 (q)	2928	18.6	−10.00 (t)	632
11a	3.34 (t, $^3J_{HH}$ 8.8)	3.14 (t)	8.57–8.52 (m, Ph) 6.97–6.96 (m, Ph) 3.93 (s, OCH$_3$)	19.6 (q)	2907	17.7	−10.98 (t)	630

[a] In CD$_2$Cl$_2$; the signals are referred to Me$_4$Si; δ in ppm; J in Hz. Abbreviations: s = singlet, d = doublet, t = triplet, st = sextet, m = multiplet. [b] In CD$_2$Cl$_2$; the signals are referred to external H$_3$PO$_4$ 85%; δ in ppm; J in Hz. Abbreviations: s = singlet, q = quartet. [c] In CD$_2$Cl$_2$; the signals are referred to external CFCl$_3$; δ in ppm; J in Hz. Abbreviation: t = triplet.

radiation $\lambda = 0.710\,69$ Å). 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 $6 \leq \theta \leq 9°$. For the determination of precise lattice parameters, 25 strong reflections with $9 \leq \theta \leq 13°$ were considered. Integrated intensities for *hkl* reflections ($h = 0 \rightarrow 22$; $k = 0 \rightarrow 16$, $l = 0 \rightarrow 19$) were measured in the interval θ = 2–25°, using $\theta/2\theta$ scans. Three standard reflections, 251, −4, 0, 2, and 232, were collected 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 as described by North et al.[13] No correction was made for extinction.

The molecule lies on a crystallographic mirror plane containing the platinum metal ion, half of the coordinated CF$_3$ ligand, and the oxazoline ligand. Obviously, the C(2) and C(3) carbon atoms of the pentaatomic ring are statistically (50%) distributed about the mirror plane due to their sp^3 hybridation. The latter was confirmed by the anomalously high values of their carbon thermal parameters when constrained to lie on the mirror plane. The structure was refined by full-matrix least squares with anisotropic thermal parameters for the atoms of the coordination sphere including also the fluorine of the CF$_3$ moiety. All the remaining nonhydrogen atoms were refined isotropically. Hydrogen atoms were introduced at calculated positions (d_{C-H} = 0.98 Å and U = 0.07 Å^2). In the last stages of refinement residual electron densities of about 2–3 e/Å^3 were interpreted as four water and two methanol molecules per cell. The function minimized was $\sum w\Delta^2$ where $\Delta = (|F_o| - |F_c|)$ and $w = [\sigma^2(F_0) + 0.003061(F_0{}^2)]^{-1}$. Final R values were R = 0.056, R_w = 0.065 and S = 1.64. Data

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[13] North, A. C. T.; Philiphs, D. C.; Mathews, F. S. *Acta Crystallogr.* 1968, *87*, 902.

Table 4. Crystal Data, Experimental Conditions, and Refinement for *trans*-[Pt(CF$_3$){N═C(Ph)OCH$_2$CH$_2$}(PPh$_3$)$_2$]BF$_4$·0.5H$_2$O·0.25MeOH

formula	$C_{46.25}H_{40}F_7P_2BO_{1.75}NPt$
mol wt	1038.68
cryst syst	orthorhombic
a, Å	19.130(4)
b, Å	15.936(3)
c, Å	16.312(3)
V, Å^3	4973(2)
space group	$Pna2_1$
Z	4
D_{calcd}, g cm^{-3}	1.39
F(000)	2063
λ(Mo K*α*), Å	0.710 69
μ(Mo K*α*), cm^{-1}	28.06
transmn coeff (rel)	79/100
no. of reflns measd	4852
scan method	$\theta/2\theta$
reflections [$I \geq 3\sigma(I)$]	2485
$R = \sum[F_o\| - \|F_c\|]/\sum\|F_o\|$	0.056
$R_w = [\sum(F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.065
weighting scheme *w*	$[\sigma^2(F_o) + 0.003061(F_o^2)]^{-1}$
goodness of fit, *S*	1.63

Table 5. Atomic Coordinates and Thermal Parameters U_{eq} (Å^2) for *trans*-[Pt(CF$_3$){N═C(Ph)OCH$_2$CH$_2$}(PPh$_3$)$_2$]BF$_4$·0.5H$_2$O·0.25MeOH

Atom	*x*	*y*	*z*	$U_{is/eq}$[a]	PP[b]
Pt	0.22659(3)	0.2500	0.24349(3)	52.4(3)*	0.5
P	0.2288(1)	0.3971(2)	0.2392(2)	54.8(9)*	
N	0.1367(6)	0.2500	0.1736(7)	59(2)*	0.5
C(10)	0.3038(9)	0.2500	0.3263(9)	57(2)*	0.5
F(1)	0.3720(6)	0.2500	0.2914(9)	112(3)*	0.5
F(2)	0.3046(5)	0.3143(5)	0.3776(5)	101(2)*	
O(1)	0.0520(7)	0.2500	0.0760(8)	88(3)*	0.5
C(1)	0.1215(9)	0.2500	0.0972(10)	66(3)	0.5
C(2)[c]	0.0109(11)	0.2691(14)	0.1585(12)	93(4)	0.5
C(3)[c]	0.068(10)	0.2389(18)	0.2228(11)	78(4)	0.5
C(4)	0.1707(9)	0.2500	0.0235(9)	60(3)	0.5
C(5)	0.1444(12)	0.2500	−0.0563(12)	91(4)	0.5
C(6)	0.1848(11)	0.2500	−0.1208(13)	92(4)	0.5
C(7)	0.257(10)	0.2500	−0.1134(12)	82(4)	0.5
C(8)	0.2787(11)	0.2500	−0.0368(12)	89(4)	0.5
C(9)	0.2409(9)	0.2500	0.0318(11)	65(3)	0.5
C(11)	0.3167(7)	0.4418(8)	0.2405(6)	64(3)	
C(12)	0.3675(6)	0.4056(8)	0.1889(7)	66(3)	
C(13)	0.4317(8)	0.4384(9)	0.1861(8)	86(3)	
C(14)	0.4500(9)	0.5079(11)	0.2306(8)	94(3)	
C(15)	0.4022(8)	0.5439(10)	0.2826(10)	97(3)	
C(16)	0.3351(7)	0.5104(8)	0.2858(8)	79(3)	
C(17)	0.1790(6)	0.4466(8)	0.3208(6)	63(3)	
C(18)	0.1627(6)	0.5307(8)	0.3185(7)	68(3)	
C(19)	0.1220(6)	0.5667(9)	0.3803(7)	79(3)	
C(20)	0.0978(7)	0.5140(9)	0.4452(8)	77(3)	
C(21)	0.1160(6)	0.4352(8)	0.4470(7)	71(3)	
C(22)	0.1552(6)	0.4002(8)	0.3853(7)	66(3)	
C(23)	0.1875(6)	0.4398(7)	0.1476(7)	62(3)	
C(24)	0.1179(7)	0.4493(8)	0.1416(8)	79(3)	
C(25)	0.0860(9)	0.4764(10)	0.0721(10)	112(4)	
C(26)	0.1276(9)	0.5058(10)	0.0087(11)	115(4)	
C(27)	0.1982(8)	0.4961(10)	0.0104(9)	92(3)	
C(28)	0.2308(7)	0.4640(9)	0.0785(8)	75(3)	
F(3)	0.545(1)	0.250	0.074(1)	198(12)	0.5
F(4)	0.471(1)	0.317(1)	−0.005(2)	208(14)	
F(5)	0.432(1)	0.250	0.073(1)	226(15)	0.5
B	0.487(1)	0.250	0.0312	128(11)	0.5
O(2)	0.203(1)	0.161(1)	0.638(1)	108(10)	0.5
C(29)	0.422(1)	0.2500	0.655(1)	131(12)	0.25
O(3)	0.455(1)	0.2500	0.725(2)	111(14)	0.25

[a] *U* equivalent is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Starred values indicate that the atoms are refined anisotropically. [b] Population parameters (PP) are reported when they are not equal to 1. [c] One of the two positions is reported.

Table 6. Selected Bond Distances (Å) and Angles (deg) for *trans*-[Pt(CF$_3$){N═C(Ph)OCH$_2$CH$_2$}(PPh$_3$)$_2$]BF$_4$·0.5H$_2$O·0.25MeOH

Pt–P	2.346(4)	Pt–N	2.06(1)
Pt–C(10)	2.00(2)	P–C(11)	1.83(1)
P–C(17)	1.82(1)	P–C(23)	1.82(1)
C(1)–C(4)	1.53(2)	C(1)–N	1.28(2)
C(1)–O(1)	1.37(2)	C(2)–C(3)	1.58(3)
C(2)–O(1)	1.59(2)	C(3)–N	1.56(2)
C(4)–C(5)	1.40(2)	C(4)–C(9)	1.35(2)
C(5)–C(6)	1.31(3)	C(6)–C(7)	1.39(3)
C(7)–C(8)	1.31(3)	C(8)–C(9)	1.33(3)
C(10)–F(1)	1.35(3)	C(10)–F(2)	1.39(3)
N–Pt–C(10)	171.1(6)	P(1)–Pt–C(10)	90.39(7)
P–Pt–N	89.9(1)	Pt–P–C(23)	113.0(4)
Pt–P–C(17)	113.7(4)	Pt–P–C(11)	114.0(4)
C(17)–P–C(23)	102.2(5)	C(11)–P–C(17)	107.8(5)
N–C(1)–O(1)	118(1)	C(4)–C(1)–O(1)	113(1)
C(4)–C(1)–N	129(1)	C(3)–C(2)–O(1)	99(1)
C(2)–C(3)–N	102(1)	C(1)–C(4)–C(9)	122(1)
C(1)–C(4)–C(5)	121(1)	C(5)–C(4)–C(9)	117(1)
C(4)–C(5)–C(6)	122(1)	C(5)–C(6)–C(7)	121(2)
C(6)–C(7)–C(8)	113(1)	C(7)–C(8)–C(9)	129(2)
C(4)–C(9)–C(8)	117(1)	C(1)–N–C(3)	107.9(9)
Pt–N–C(3)	115.0(7)	Pt–N–C(1)	137(1)
C(1)–O(1)–C(2)	105.4(8)	Pt–C(10)–F(2)	115.8(4)
Pt–C(10)–F(1)	114(1)	F(1)–C(10)–F(2)	104.0(4)

processing and computations were carried out using the SHELX 76 program package[14] with the atomic scattering factors taken from ref 15; drawings were produced using ORTEP II.[16] The crystal and refinement data for **3a** are summarized in Table 4. The atomic coordinates are reported in Table 5.

Catalytic Experiments. The reactions of *trans*-[Pt(R)X(PR$_3$)$_2$] (PR$_3$ = PEt$_3$, R = H, CH$_3$; X = Br, I; PR$_3$ = PMe$_2$Ph, R = CF$_3$, X = Br) complexes and CH$_3$CN (1 mL) in the presence of oxirane, OCH$_2$CH$_2$, were performed according to the following procedure. The Pt(II) complex (0.04 mmol) was charged in a gastight Schlenk vessel that was evacuated and filled with N$_2$. Upon cooling to 0 °C, reagent grade CH$_3$CN (1 mL) and OCH$_2$CH$_2$ (0.4 mL) were added, and the resulting solution was heated with stirring, for 160 h at 50 °C or 36 h at 75 °C (Table 9, see below) with an external thermostated oil bath. Then the solution was cooled down to 0 °C and analyzed with GLC to check for the presence of organic products. Identification of 2-(methyl)oxazoline was made with GLC or GLC/MS by comparison with the commercially available sample. Quantitative data were obtained from calibration curves using 2-(methyl)oxazoline in different amounts. It must be noted that, in the absence of any Pt(II) complex added, no oxazoline was detected in the reactions of CH$_3$CN (1.0 mL, 19.00 mmol) with OCH$_2$CH$_2$ (0.4 mL, 8.17 mmol) at 75 °C for 30 h in the presence of LiBr (0.0065 g, 0.075 mmol) or NaI (0.0109 g, 0.066 mmol).

Results and Discussion

Synthesis of Cationic Platinum(II) Nitrile Complexes. The cationic nitrile complexes of the type *trans*-[Pt(R′)(NCR)(PPh$_3$)$_2$]BF$_4$ have been prepared by displacement reactions of the corresponding halo derivatives *trans*-[Pt(R′)X(PPh$_3$)$_2$] with an excess of RCN in the presence of a stoichiometric amount of AgBF$_4$, as illustrated in eq 2. Compounds 1–11 have been isolated in *ca.* 80% yield, and they are all white solids, stable in air and in solution, and soluble in chlorinated solvents, particularly CH$_2$Cl$_2$. They have been characterized by IR and multinuclear (^{1}H, ^{31}P{^{1}H}, ^{19}F, and ^{13}C{^{1}H}) NMR spectroscopy.

The ^{1}H, ^{31}P, and ^{19}F NMR data are reported in the Experimental Section, while selected IR and ^{13}C NMR

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(14) Sheldrick, G. M. SHELX 76. University of Cambridge, 1976.

(15) *International Tables for X-Ray Crystallography*, 2nd ed.; Kynoch Press: Birmingham, U.K., 1974; Vol. 4, p 101.

(16) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Table 7. IR and ^{1}H NMR Data for Free Oxazolines $\overline{N{=}C(R)OCH_2CH_2}$

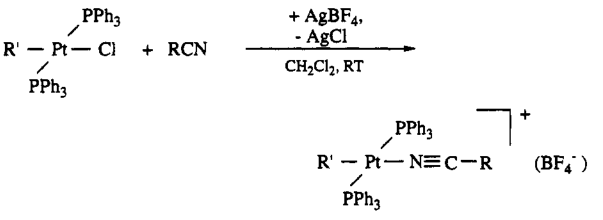
R	IR[a] cm^{-1} ν(C=N)	^{1}H NMR[b]		
		$\delta(NCH_2)$	$\delta(OCH_2)$	δ(others)
CH_3[c]	1670	3.749 (m, $^5J_{HH}$ 1.4)	4.185 (t, $^3J_{HH}$ 9.5) 4.180 (t, $^3J_{HH}$ 9.4)	CH_3: 1.910
CH_2CH_3	1661	3.749 (tt, $^5J_{HH}$ 1.3) 3.743 (tt, $^5J_{HH}$ 1.4)	4.179 (t, $^3J_{HH}$ 9.4) 4.175 (t, $^3J_{HH}$ 9.5)	CH_2: 2.220 (tt) CH_3: 1.134 (t, $^3J_{HH}$ 7.6)
$CH_2CH_2CH_3$	1662	3.748 (tt, $^5J_{HH}$ 1.2) 3.744 (tt, $^5J_{HH}$ 1.2)	4.167 (t, $^3J_{HH}$ 9.8) 4.164 (t, $^3J_{HH}$ 9.2)	CH_2: 2.200 (tt, $^3J_{HH}$ 7.7) CH_2: 1.615 (m) CH_3: 0.938 (t, $^3J_{HH}$ 7.3)
$CH(CH_3)_2$	1659	3.736 (td, $^5J_{HH}$ 1.0) 4.168 (t, $^5J_{HH}$ 9.7)	4.173 (t, $^3J_{HH}$ 9.8)	CH: 2.520 (st) CH_3: 1.150 (d, $^3J_{HH}$ 6.9)
$C(CH_3)_3$	1626	3.740 (t) 3.737 (t)	4.180 (t, $^3J_{HH}$ 9.3) 4.182 (t, $^3J_{HH}$ 9.2)	CH_3: 1.180
C_6H_5	1644	4.009 (t)	4.429 (t, $^3J_{HH}$ 9.5) 4.430 (t, $^3J_{HH}$ 9.3)	Ph: 7.960–7.160 (m)
C_6H_4-*p*-CH_3	1643	3.979 (t)	4.378 (t, $^3J_{HH}$ 9.3) 4.374 (t, $^3J_{HH}$ 9.5)	CH_3: 2.37 Ph: 7.19–7.82 (m)
C_6H_4-*o*-CH_3	1639	4.035 (t) 4.026 (t)	4.350 (t, $^3J_{HH}$ 9.1) 4.340 (t, $^3J_{HH}$ 9.4)	CH_3: 2.558 Ph: 7.78–7.18 (m)
C_6H_4-*p*-OCH_3	1644	3.981 (t)	4.387 (t, $^3J_{HH}$ 9.7)	OCH_3: 3.835 Ph: 6.89–7.89 (m)

[a] In CH_2Cl_2. [b] In CD_2Cl_2; the signals are referred to Me_4Si; δ in ppm; J in Hz. Abbreviations: d = doublet, t = triplet, tt = triplet of triplets, td = triplet of doublets, st = sextet, m = multiplet. [c] $^{13}C\{^1H\}$ NMR spectrum: δ 163.25 (s, N=*C*), 65.62 (s, O*C*H$_2$), 52.99 (s, N*C*CH$_2$), 11.71 (s, *C*H$_3$).

Table 8. GLC/MS Data for Free Oxazolines $\overline{N{=}C(R)OCH_2CH_2}$

R	retention time/min	*M*[a]	*m/z*[b]		
			$M^{\bullet+}$	$M^{\bullet+} - CH_2O$	others
CH_3	1.51	85	85 (73)	55 (100)	
CH_2CH_3	2.23	99	99 (81)	69 (100)	54 (44): $M^{\bullet+} - CH_2O - CH_3^{\bullet}$
$CH_2CH_2CH_3$	3.15	113	113 (2)	83 (5)	98 (18): $M^{\bullet+} - CH_3^{\bullet}$ 112 (5): $M^{\bullet+} - H^{\bullet}$
$CH(CH_3)_2$	2.53	113	113 (5)	83 (25)	98 (100): $M^{\bullet+} - CH_3^{\bullet}$ $M^{\bullet+} - H^{\bullet}$ (10)
$C(CH_3)_3$	2.78	127	127 (8)	97 (5)	126 (15): $M^{\bullet+} - H^{\bullet}$ 112 (100): $M^{\bullet+} - CH_3^{\bullet}$ 82 (15): $M^{\bullet+} - CH_2O - CH_3^{\bullet}$ 69 (40): $M^{\bullet+} - C(CH_3)_3^{\bullet}$
C_6H_5	10.33	147	147 (60)	117 (100)	77 (40): $C_6H_5^+$
C_6H_4-*p*-CH_3	11.63	161	161 (60)	131 (100)	91 (20): $C_7H_7^{\bullet+}$ 116 (10): $M^{\bullet+} - CH_2O - CH_3^{\bullet}$
C_6H_4-*o*-CH_3	12.05	161	161 (85)	131 (100)	91 (30): $C_7H_7^+$ 77 (30): $C_6H_5^+$
C_6H_4-*p*-OCH_3	14.50	177	177 (80)	147 (100)	132 (60): $M^{\bullet+} - CH_2O - CH_3^{\bullet}$ 77 (50): $C_6H_5^+$

[a] Nominal molecular weight. [b] Relative intensities (%, in parentheses) are referred to the most intense ion.



(2)

1-11

data are listed in Table 1. Taken all together the spectroscopic information indicates that compounds **1**–**11** are all of trans geometry. Noteworthy the IR spectra in CH_2Cl_2 solution show the ν(C≡N) band in the range 2325–2257 cm^{-1}, at higher wavenumbers than those observed for the corresponding free nitriles (Table 1). The positive values of $\Delta\nu = \nu(C{\equiv}N)_{coord} - \nu(C{\equiv}N)_{free}$, which fall in the range 68–37 cm^{-1}, indicate the susceptibility of the nitrile carbon to undergo nucleophilic attack.[2,4] In contrast to the behavior of isoelectronic isocyanide, R—N≡C, ligands in transition metal complexes, whose C≡N stretching and hence reactivity toward nucleophiles are sensitive to the electronic properties of the trans ligand,[6a,17] the corresponding nitriles are not, as is observed from the values of ν(C≡N) and $\Delta\nu$ (63–68 cm^{-1}) of the coordinated CH_3CN for **1**–**3**, which are not influenced by the nature of the trans ligand R′ (the σ-donating ability for Pt(II) complexes of trans geometry is in the order H > CH_3 > CF_3).[18] As the size of the R group of the RCN ligand decreases and/or its electron-withdrawing property increases as one goes from an alkyl to an aryl nitrile ligand (compounds **4**–**11**), the $\Delta\nu$ values become lower with respect to **3**, falling in the range 37–54 cm^{-1}. However, the IR ν(C≡N) shifts are not accompanied by parallel variations of the $^2J_{CPt}$ values of the nitrile carbon, which could also reflect the changes in electronic and steric properties either of the trans ligand R′ or of the nitrile group R. The observed values of $^2J_{CPt}$ are all about 90 Hz, which agree with those previously reported for other Pt(II) cationic complexes,[19] but they are significantly lower than those reported for neutral nitrile complexes $[PtCl_2(NCR)_2]$ of cis (218–234 Hz) or trans (237–298 Hz) geometry.[20]

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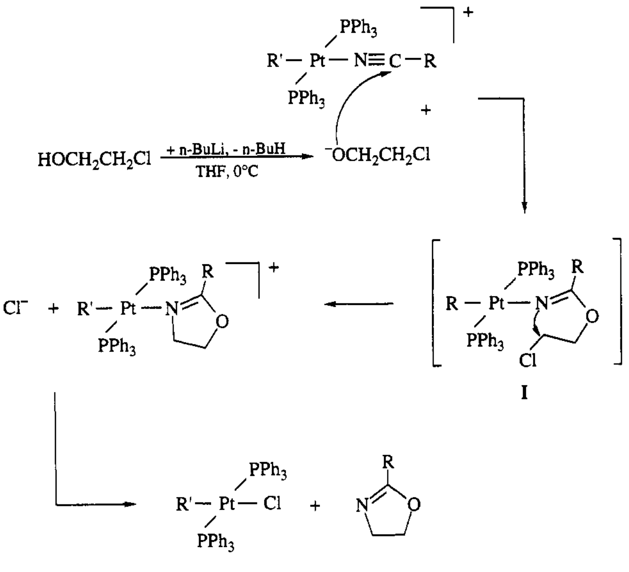
[18] Michelin, R. A.; Ros, R. *J. Chem. Soc., Dalton Trans.* **1989**, 1149.

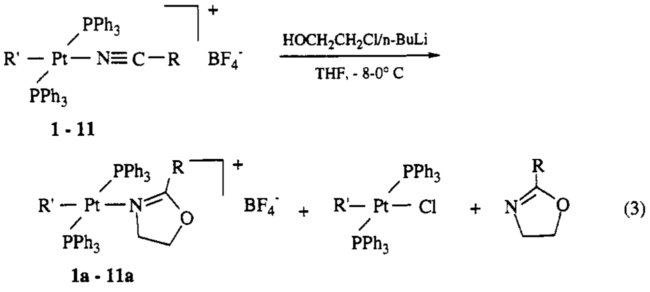
[19] Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Strothers, J. B.; Ward, J. E. H. *J. Am. Chem. Soc.* **1973**, *95*, 8574.

[20] Fraccarollo, D.; Bertani, R.; Mozzon, M.; Belluco, U.; Michelin, R. A. *Inorg. Chim. Acta* **1992**, *201*, 1751.

Scheme 1



Synthesis of Cationic Δ^2-1,3-Oxazoline Complexes of Platinum(II). Compounds 1–11 readily react in THF at 0 °C or below with $HOCH_2CH_2Cl$/*n*-BuLi (*n*-BuLi: complex molar ratio 1:1) to give under the experimental conditions used (see Experimental Section) a mixture of products containing the desired cationic oxazoline complex of the type 1a–11a, the neutral halo complex *trans*-[PtCl(R')$(PPh_3)_2$], and free oxazoline, as described in the following equation:



(3)

For reaction times of *ca.* 10–15 min the oxazoline complexes could be isolated, albeit in modest yield (26–49%), from the reaction mixtures and they could be separated from the corresponding halo complexes (average yield *ca.* 35%) by taking advantage of the higher solubility of the latter derivatives in benzene. For longer reaction times (>2h), the *trans*-[PtCl(R')$(PPh_3)_2$] species were the only isolated complexes.

The results of the chemical reactivity of the cationic nitrile complexes described in eq 3 led us to suggest Scheme 1, which accounts for the observed reaction products. Nucleophilic attack of $^-OCH_2CH_2Cl$, generated from the reaction of the corresponding alcohol with *n*-BuLi, at the nitrile carbon atom affords intermediate **I** which, upon intramolecular cyclization affords the coordinated oxazoline and liberates the Cl^- ion. The oxazoline is then replaced by Cl^-, perhaps by an associative pathway as is common in reactions of square planar Pt(II) complexes, with the formation of the neutral halide complex *trans*-[PtCl(R')$(PPh_3)_2$]. This latter process has been also independently confirmed by reacting the isolated oxazoline compounds with chloride ions (see further on).

The intermediacy of **I** is supported by other studies in which RCN ligands are converted to oxazolines by $HOCH_2CH_2Cl$/base[1,2] or $Cl^-/\overline{OCH_2CH_2}$[1] and also those in which CO[5] and RNC[6a,c] ligands cycloadd $^-OCH_2CH_2Cl$ to produce five-membered carbenes.

The presence of free 2-oxazoline in the reaction medium has been confirmed by IR and GC/MS analyses of the mother liquors, and the data have been compared with those obtained from the reactions of **3a–11a** with Cl^- ions (see below). In the reaction mixtures of **8a–11a** also the presence of free RCN was observed.

Compounds **1a–11a** are all white, air-stable solids, and soluble in chlorinated solvents. They have been characterized by IR (Table 2) and multinuclear ^1H, ^{31}P, ^{19}F, and ^{13}C NMR spectroscopies (Tables 2 and 3) as well as by an X-ray structural determination which has been carried out for **8a**.

The IR spectra show the C=N stretching as a strong absorption in the range 1609–1664 cm^{-1} (Nujol mull), similar to those reported earlier for 2-oxazolines[1] of Pt(II). The trans geometry of **1a–11a** is readily confirmed by ^{31}P NMR (Table 3) and also by ^{19}F NMR data (Table 3) for the trifluoromethyl derivatives **3a–11a**.

The ^1H NMR spectra of **1a–11a** show a common pattern for the ring methylene protons; i.e. the protons adjacent to the oxygen are assigned to a lower field (range 3.30–3.65 ppm) than those adjacent to the nitrogen (range 2.03–3.19 ppm) in analogy to similar systems.[5,6a] The $-OCH_2-$ and $-NCH_2-$ protons show up as triplets by coupling each other ($^3J_{HH}$ 8.8–10.1 Hz). In the aryl derivatives **8a–11a**, the ortho protons of the phenyl groups of the R substituent, which are in a cis position to Pt, are shifted to a lower field (*ca.* 1 ppm) compared to the other phenyl protons owing to a deshielding effect of the metal, as reported for other Pt(II) systems.[4b,c] However, no $^{195}Pt-^1H_{ortho}$ coupling is observed, likely owing to free rotation around the phenyl–oxazoline bond.[21]

The $^{13}C\{^1H\}$ NMR data are in agreement with those reported in the literature for coordinated[1] and free[22] 2-oxazoline systems. The $^{13}C\{^1H\}$ NMR spectra show a singlet for the $-OCH_2-$ carbon resonance in the range δ 67.5–69.5 often flanked by ^{195}Pt satellites ($^3J_{CPt}$ 22.6–25.9 Hz). The $-NCH_2-$ carbons appear as singlets at a higher field in the range δ 52.8–57.8. For these latter carbons coupling to ^{195}Pt was not detected in most cases (*i.e.* **3a–11a**) since the resonances were masked by the signals due to the deuterated solvent (CD_2Cl_2). However, for **1a** and **2a** coupling to ^{195}Pt was observed ($^2J_{CPt}$ *ca.* 11 Hz). The lower values of $^2J_{CPt}$ compared to those of $^3J_{CPt}$ are observed in other Pt(II) oxazolines[2] and also for several other ligands coordinated to Pt(II).[23] The $-N{=}C(R)-$ carbons appear as singlets in the range δ 168.5–177.3, and almost all of the resonances are flanked by ^{195}Pt satellites ($^2J_{CPt}$ *ca.* 30 Hz for (alkyl)oxazolines and *ca.* 20 Hz for (aryl)oxazolines).

Description of the Structure of *trans*-[Pt(CF_3){$\overline{N{=}C(Ph)OCH_2CH_2}$}$(PPh_3)_2$]$BF_4$ (3a). The crystal contains *trans*-[Pt(CF_3){$\overline{N{=}C(Ph)OCH_2CH_2}$}$(PPh_3)_2$]$^+$-$BF_4^-$ molecules, and the cation complex is illustrated in Figure 1 with the atom numbering scheme (labeled atoms are related to primed atoms by the mirror plane). Selected

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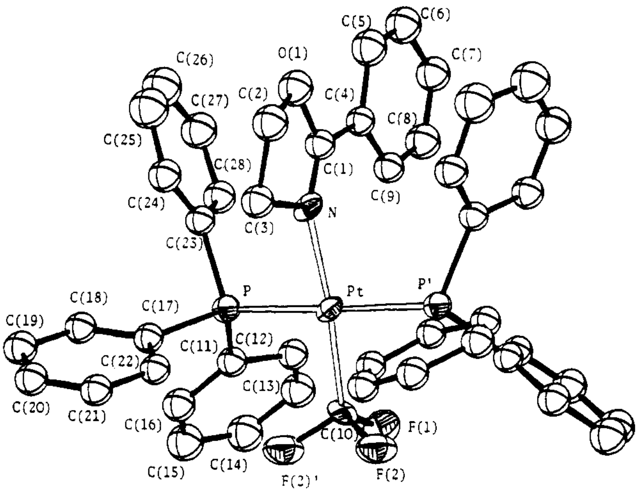
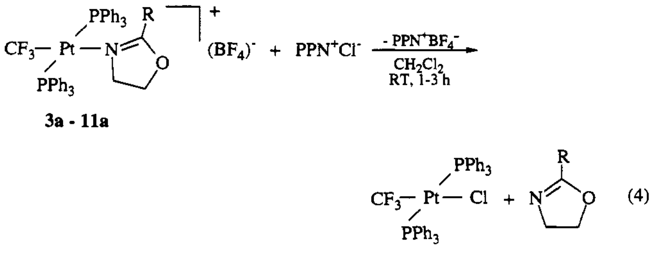


Figure 1. ORTEP view of the cation of *trans*-$[Pt(CF_3)\{\overline{N{=}C(Ph)OCH_2CH_2}\}(PPh_3)_2]BF_4$ (**3a**) with the atomic numbering scheme.

bond distances and angles are reported in Table 6. The coordination geometry around Pt(II) is far from square planar. The best mean plane of the coordinated atoms shows deviations of −0.15(1) and −0.31(2) Å for nitrogen and carbon atoms, respectively, while the platinum center is out of this plane by −0.0740(7) Å. The P–Pt–P′ angle is 176.0(1) and N–Pt–C(10) is 171.1(6)° with significant deviation from linearity. The Pt–N distance of 2.06(1) Å is significantly larger than the value of 2.012(3) Å (average) found in the *cis*-dichlorobis[2-(phenyl)oxazoline]platinum(II) complex,[1] where the heterocyclic ligand is trans to chlorine. The Pt–P bond distance of 2.346(4) Å is significantly longer than that found in *trans*-$[Pt(CF_3)H(PPh_3)_2]$[24] (2.274(2) Å), owing to a higher steric pressure of the oxazoline ligand compared to the hydride.

The 2-(phenyl)oxazoline ligand is almost planar and perpendicular to the mean coordination plane (for the sake of crystallographic symmetry), also taking into account the small deviations from planarity (−0.30(3) and 0.18(4) Å for C(2) and C(3) sp³ hybridized carbon atoms, respectively). However it is observed that the ligand has a conformation significantly different from that found in the aforementioned *cis*-dichlorobis[2-(phenyl)oxazoline]platinum(II) complex,[1] where each phenyl is tilted with respect to the corresponding oxazoline ring by 149.8(2) and 58.8(2)°, respectively. In the present case the phenyl group is coplanar with the ring system. Finally, the dihedral angle between the planes of the heterocyclic ligand and the closest phenyl of PPh_3 is 22.6(3)°. This rather parallel arrangement of the two phenyls of the two mirrored PPh_3 moieties accounts for the planarity of the ligand, which thus minimizes the intramolecular contacts.

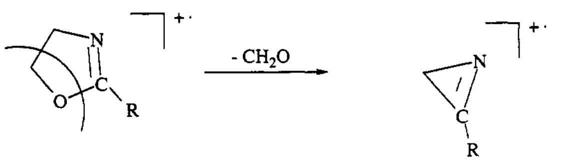
Reactions of 3a–11a with PPN⁺Cl⁻. Compounds **3a–11a** react with 1 equiv of PPN^+Cl^- at room temperature within 30 min to give quantitatively the free oxazolines and the corresponding halide complexes (eq 4). The reaction mixtures have been analyzed by IR and ¹H NMR spectroscopies (Table 7) and GC/MS analysis (Table 8). The IR spectra of the oxazoline products show ν(C=N) in the range 1626–1670 cm⁻¹, in agreement with literature data.[22,25] These values are, however, at higher wavenumbers (*ca.* 20 cm⁻¹) compared to those of the coordinated ligands. The ¹H NMR spectra show that the $-NCH_2-$ and $-OCH_2-$ protons are no longer simple triplets as in **3a–11a**, but each of the $-NCH_2-$ or $-OCH_2-$ protons gives rise to a different resonance pattern. Thus, for the (methyl)oxazoline, $\overline{N{=}C(CH_3)OCH_2CH_2}$, each of the two $-OCH_2-$ protons occurs as a triplet resulting from coupling with the $-NCH_2-$ protons, without geminal coupling. The $-NCH_2-$ protons also couple with the $-CH_3$ group. These results suggest that the four ring protons are not magnetically equivalent, being located on opposite sides with respect to the −N=C—O− plane. Furthermore, the $^3J_{HH}$ values between each OCH proton and the NCH_2 protons are slightly different: this feature may be explained by considering that each −O—C—H moiety forms with the $-NCH_2-$ system slightly different dihedral angles, and it is known that the geminal coupling constants depend on the dihedral angle between bonds of the atoms involved.[26]



3a - 11a

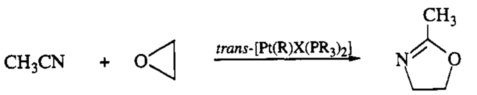
(4)

The GLC/MS analyses of the reaction mixtures show that the free oxazolines have retention times increasing with increasing molecular weight and also that (aryl)oxazolines have longer retention times compared to those of (alkyl)oxazolines. All the oxazolines examined display the molecular peak $M^{\bullet+}$ and also typical fragmentation,[27] which involves loss of formaldehyde with intense peaks corresponding to $[M^{\bullet+} - 30]$ (eq 5).



(5)

Catalytic Experiments. Taken together, eq 3 and Scheme 1 represent a stoichiometric cycle for the synthesis of 2-oxazolines from cationic Pt(II) nitrile complexes and suggest also that these heterocycles might be formed catalytically using Pt(II) species. To test this possibility, we have investigated the *trans*-$[Pt(R)X(PPh_3)_2]/CH_3CN/\overline{OCH_2CH_2}$ system in order to realize the following reaction:



(6)

in which the metal has a bifunctional role, *i.e.* a nitrile activator and also a source of X⁻ ions, as described in Scheme 2. In the first step (a), the nitrile displaces the X⁻ ion to give the cationic complex Pt—N≡C—R⁺. This step is not known for Pt(II), but the reverse reaction has been reported.[28] On the other hand, displacement of Br⁻ has been suggested to occur for $[MnBr(CO)_5]$ in the

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Scheme 2

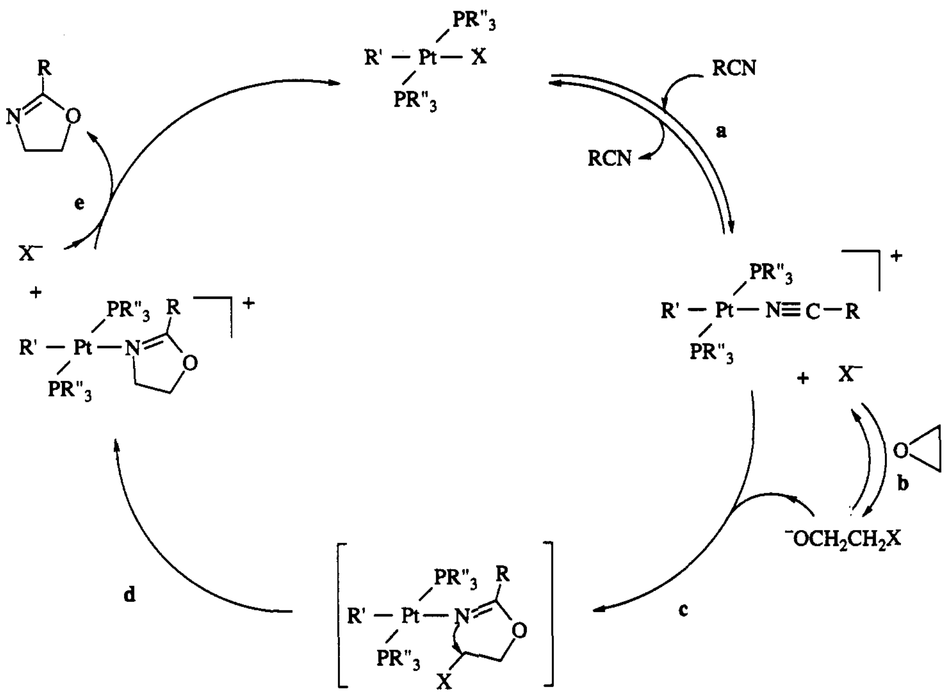

Table 9. Catalytic Experiments[a]

entry	complex	reactn conditions	results
1	*trans*-[Pt(H)X(PEt_3)$_2$] (X = I, Br)	160 h at 50 °C	no oxazoline detected
2	*trans*-[Pt(CH_3)X(PEt_3)$_2$] (X = I, Br)	160 h at 50 °C	no oxazoline detected
3	*trans*-[PtBr(CF_3)(PMe_2Ph)$_2$]	36 h at 75 °C	no oxazoline detected
4[b]	*trans*-[Pt(H)X(PEt_3)$_2$] (X = I, Br)	30 h at 75 °C	no oxazoline detected
5[c]	*trans*-[PtBr(CH_3)(PEt_3)$_2$]	120 h at 75 °C	oxazoline detected
6[b]	*trans*-[PtBr(CF_3)(PMe_2Ph)$_2$]	36 h at 75 °C	oxazoline detected

[a] Complex: CH_3CN:$\overline{OCH_2CH_2}$ molar ratio 1:500:200. [b] NaI or LiBr added in a complex:X^- molar ratio of 1:2. [c] LiBr added in a complex:Br^- molar ratio 1:(1.5–3).

presence of CH_3CN in the formation of a five-membered cyclic carbene derivative.[29] A similar equilibrium seems possible for the Pt^{II}—X complex, taking into account that CH_3CN, albeit a poor nucleophile, is on the other hand a good coordinating solvent. Furthermore, the Pt—X bond will be labilized if the trans ligand R and the cis phosphines PR_3 are good σ-electron donors, thus favoring the shift to the right of equilibrium (a). Therefore, we have investigated complexes of the type *trans*-[Pt(R)X(PEt_3)$_2$] (R = H, CH_3; X = Cl, Br, I) and *trans*-[PtBr(CF_3)(PMe_2Ph)$_2$]. In step (b), the liberated X^- ion attacks the oxirane ring to give $^-OCH_2CH_2X$. Ring opening of oxirane by halide ions is a known reaction,[30] and it has been used specifically in the synthesis of oxazolines from nitriles[1] and also to convert metal coordinated CO[5] and RNC[6c] ligands to five-membered cyclic carbenes. Subsequent attack of $^-OCH_2CH_2X$ on the nitrile carbon of Pt—N≡C—R^+ will give the oxazoline (steps c and d) and regenerate the Pt—X complex (step e), which will continue the catalytic cycle. Steps (c–e) are identical to those discussed previously for the stoichiometric cycle (eqs 2 and 3 and Scheme 1). Some of the results of the "catalytic" runs are collected in Table 9. No oxazoline formation is observed under the experimental conditions used (entries 1–3), indicating that equilibrium (a) is unfavorable toward X^- dissociation by CH_3CN and, consequently, also equilibrium (b) is shifted to the left. Addition of X^- ions to the reaction systems containing the hydrido complexes (entry 4) does not lead to the formation of oxazoline; however oxazoline is detected when similar runs are performed with the CH_3– and CF_3– derivatives (entries 5 and 6). However, the conversion of RCN to oxazoline is not catalytic, the oxazoline being formed in an almost stoichiometric amount with respect to the complex. These poor results, which still deserve further investigation, can be explained either by an unfavorable equilibrium (a) and/or it could result from step (a) being very slow. Futhermore, the low observed conversion is likely to be affected by a possible competitive nucleophilic attack of $^-OCH_2CH_2X$ on the metal center with subsequent reductive elimination processes, which are known to occur for Pt(II)/alkoxo systems,[31] as suggested by the yellowing of the reaction mixtures.

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Supplementary Material Available: Listings of hydrogen atom coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

OM930671O

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