Transition-Metal-Promoted Cyclization Reactions of Nitrile Ligands in Complexes of Platinum(II): Synthesis of 2-Oxazoline Derivatives and X-ray Structure of cis-$Cl_2Pt[\overline{N=C(Ph)OCH_2CH_2}]_2$

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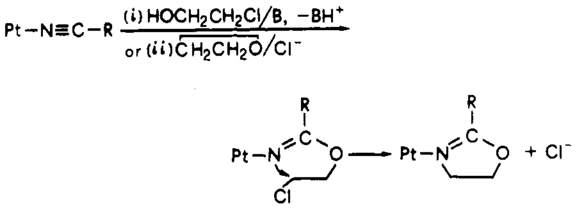
The reactions of *cis*- and *trans*-$Cl_2Pt(NCR)_2$ (R = Ph, Me) isomers with 2 equiv of $^-OCH_2CH_2Cl$, generated by deprotonation of $HOCH_2CH_2Cl$ with *n*-BuLi, afford in high yield the bis(2-oxazoline) derivatives *cis*- and *trans*-$Cl_2Pt[\overline{N{=}C(R)OCH_2CH_2}]_2$, respectively [cis R = Ph (**1**), Me (**2**); trans R = Ph (**3**), Me (**4**)]. No isomerization at the metal center occurs in the cyclization reactions of the nitrile ligands. Complexes **1**–**4** have been characterized by their elemental analyses, FAB mass spectra, and IR, ^1H NMR, $^{13}C\{^1H\}$, and ^1H-coupled ^{13}C NMR spectra. The structure of **1** was established also by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/c$, with $a = 16.242$ (3) Å, $b = 9.438$ (2) Å, $c = 12.679$ (2) Å, $\beta = 95.65$ (4)°, $V = 1934$ (1) Å^3, and $Z = 4$. The structure was refined to $R = 0.023$ ($R_w = 0.025$) for 3248 measured reflections with $I \geq 2.5\sigma(I)$. The average N–C(R) and (R)C–O bond distances of 1.277 (6) and 1.340 (6) Å suggest that there is extensive electron delocalization within the N–C(R)–O system. The two oxazoline ligands are almost planar, as is the coordination geometry around Pt(II). The reactions of oxirane in the presence of variable amounts of LiCl have been examined with the nitrile complex *cis*-$Cl_2Pt(NCPh)_2$ by using 2-chloroethanol as solvent. From these reactions it is found that, with a nitrile complex/Cl^- molar ratio in the range 1/2.1–1/0.4 and sufficiently long reaction times (46 h), complex **1** is isolated in high yield. At lower nitrile/Cl^- molar ratios a mixture of **1** and the bis(imido ester) complex *cis*-$Cl_2Pt[NH{=}C(OCH_2CH_2Cl)Ph]_2$ (**5**) is formed. The latter complex could be separated in a pure form by crystallization, and the spectroscopic data are reported. A possible mechanism of the oxirane/Cl^- reactions with the nitrile ligands is also discussed.

Introduction

Organonitrile complexes of transition metals are important reagents in many stoichiometric and catalytic processes.[1] The ability of nitriles to undergo nucleophilic attack at the nitrile carbon center has been shown to be facilitated by complexing with electron-withdrawing ions.[1] In particular, the electrophilicity of the nitrile carbon in Pt(II) complexes has been exploited in several investigations and includes (i) addition reactions of protic nucleophiles[1,2] such as alcohols, thiols, water, and amines, (ii) reactions with aprotic nucleophiles such as carbanions[3] and the azide ion,[1] (iii) mechanistic studies of amination[4] and metal-catalyzed hydration,[5] and (iv) catalytic hydration to amides.[1,5,6]

This paper describes the reactions of the nitrile complexes *cis*- and *trans*-$Cl_2Pt(NCR)_2$ (R = Ph, Me) with a new class of organic nucleophiles, i.e. (i) 2-chloroethanol/base and (ii) oxirane/Cl^-, to yield cyclic imido ester [2-(R)oxazoline] derivatives. With 2-chloroethoxide, which may be generated either by deprotonation of 2-chloroethanol with a base B or by ring opening of oxirane with the Cl^- ion, the reactions would occur as shown in eq 1. The nitrile–oxazoline conversion described in eq 1 is unprecedented in nitrile–(metal) reaction chemistry. However, similar reactions have been previously shown to occur with electrophilic CO[7] and RNC[8] ligands to yield cyclic carbene complexes. In the present study, the generality of the nitrile reactions is explored and the spec-



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(1) Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1.

(2) (a) Maresca, L.; Natile, G.; Intini, F. P.; Gasparini, F.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Am. Chem. Soc.* **1986**, *108*, 1180. (b) Fanizzi, F. P.; Intini, F. P.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1989**, 947.

(3) (a) Braunstein, P.; Matt, D.; Dusausoy, Y.; Protas, J. *J. Chem. Soc., Chem. Commun.* **1979**, 763. (b) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, *2*, 1410, (c) Uchiyama, T.; Takagi, K.; Matsumoto, K.; Ooi, S.; Nakamura, Y.; Klawaguchi, S. *Chem. Lett.* **1979**, 1197. (d) Idem. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1077.

(4) (a) Calligaro, L.; Michelin, R. A.; Uguagliati, P.; *Inorg. Chim. Acta* **1983**, *76*, L83. (b) Uguagliati, P.; Belluco, U.; Michelin, R. A.; Guerriero, P. *Inorg. Chim. Acta* **1984**, *81*, 61. (c) Amodio, C. A.; Nolan, K. B. *Inorg. Chim. Acta* **1986**, *113*, 27. (d) Amodio, C. A.; Eastwood, D. J. *Inorg. Chim. Acta* **1986**, *122*, L3.

(5) Trogler, W. C.; Jensen, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 723.

(6) (a) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 1027. (b) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

(7) (a) Motschi, H.; Angelici, R. J. *Organometallics* **1982**, *1*, 343. (b) Singh, M. M.; Angelici, R. J. *Inorg. Chem.* **1984**, *23*, 2691. (c) Idem. *Ibid.* **1984**, *23*, 2699.

(8) (a) Michelin, R. A.; Zanotto, L.; Braga, D.; Sabatino, P.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 85. (b) Bertani, R.; Mozzon, M.; Michelin, R. A. *Inorg. Chem.* **1988**, *27*, 2809.

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troscopic and structural properties of the oxazoline products are reported.

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 on a Perkin-Elmer 983 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer. ^1H NMR spectra at 80 MHz and ^{31}P NMR spectra at 32 MHz 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. The elemental analyses were performed by the Department of Analytical Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected.

Starting Complexes. The complexes *cis*- and *trans*-$Cl_2Pt(NCPh)_2$[2,3c,d] and *cis*-[9a] and *trans*-$Cl_2Pt(NCMe)_2$[9b] were prepared according to published procedures.

Synthesis of *cis*-$Cl_2Pt[\overline{N{=}C(Ph)OCH_2CH_2}]_2$ (1). Method A. A solution of $ClCH_2CH_2OH$ (0.50 mL, 7.46 mmol) in THF (100 mL) at 0 °C was treated with a 1.5 M *n*-hexane solution of *n*-BuLi (1.14 mL, 1.70 mmol). Then, solid *cis*-$Cl_2Pt(NCPh)_2$ (350 mg, 0.74 mmol) was added. After 15 min at 0 °C, a pale yellow solution was formed and an IR spectrum of the solution showed $\nu(C{=}N)$ at 1635 cm^{-1} and did not reveal any $\nu(C{\equiv}N)$ stretching of the starting complex. The reaction mixture was then stirred for an additional 15 min at 0 °C and then at room temperature for 1 h. The solution was taken to dryness under reduced pressure, and the pale yellow solid was washed with MeOH (3 × 5 mL) and Et_2O (3 × 5 mL) and dried under vacuum. Yield: 338 mg (81%). Mp: 209–210 °C. Anal. Calcd for $C_{18}H_{18}N_2Cl_2O_2Pt$: C, 38.58; H, 3.23; N, 5.00; Cl, 12.65. Found: C, 38.02; H, 3.15; N, 4.89; Cl, 12.55. FAB mass spectrum, *m/e*: 560 ($[M]^+$), 561 ($[MH]^+$).

Method B. Compound 1 was obtained also by starting from oxirane and LiCl in 2-chloroethanol as solvent as reported below. In a typical experiment, to a mixture of oxirane (10 mL) and LiCl (29 mg, 0.70 mmol) in 2-chloroethanol (30 mL) was added *cis*-$Cl_2Pt(NCPh)_2$ (300 mg, 0.63 mmol). After 3 h at 0 °C, the ice bath was removed, and stirring was continued for 43 h. During this time a clear solution was obtained. The solution was taken to dryness under vacuum. The solid residue was washed with MeOH (2 × 5 mL) and Et_2O (2 × 5 mL) and dried under vacuum. Yield: 290 (81%).

***cis*-$Cl_2Pt[\overline{N{=}C(Me)OCH_2CH_2}]_2$ (2).** To a solution of $ClCH_2CH_2OH$ (0.5 mL, 7.46 mmol) in THF (70 mL) at 0 °C was added in one portion a 1.5 M *n*-hexane solution of *n*-BuLi (1.32 mL, 1.98 mmol) and then *cis*-$Cl_2Pt(NCMe)_2$ (300 mg, 0.86 mmol). The reaction mixture was stirred at low temperature for 30 min and then slowly warmed to room temperature. Solid samples taken periodically from the reaction mixture were analyzed by IR spectroscopy. After 2 h, no $\nu(C{\equiv}N)$ band of the starting nitrile complex was present. Then the pale yellow solid was filtered out, washed with MeOH (3 × 5 mL) and Et_2O (3 × 5 mL), and dried under vacuum. Yield: 270 mg (72%). Mp: 228–229 °C. Anal. Calcd for $C_8H_{14}N_2Cl_2O_2Pt$: C, 22.03; H, 3.23; N, 6.42; Cl, 16.25. Found: C, 21.84; H, 3.16; N, 6.14; Cl, 15.98. FAB mass spectrum, *m/e*: 436 ($[M]^+$), 437 ($[MH]^+$).

***trans*-$Cl_2Pt[\overline{N{=}C(Ph)OCH_2CH_2}]_2$ (3).** To a solution of $ClCH_2CH_2OH$ (0.50 mL, 7.46 mmol) in THF (40 mL) at 0 °C was added a 1.5 M *n*-hexane solution of *n*-BuLi (1.13 mL, 1.70 mmol). After a few minutes, *trans*-$PtCl_2(NCPh)_2$ (350 mg, 0.74 mmol) was added and the reaction mixture was stirred at 0 °C for 15 min to give a clear solution. A solution IR spectrum did not reveal a $\nu(C{\equiv}N)$ band due to the starting nitrile complex. The stirring was then continued at room temperature for 2 h. During this time a pale yellow precipitate formed, which was filtered, washed with MeOH (2 × 5 mL) and Et_2O (3 × 5 mL), and dried under vacuum. Yield: 299 mg (73%). Mp: 229–230 °C. Anal. Calcd for $C_{18}H_{18}N_2Cl_2O_2Pt$: C, 38.58; H, 3.23; N, 5.00; Cl, 12.65. Found: C, 38.22; H, 3.05; N, 4.60; Cl, 12.13. FAB mass spectrum, *m/e*: 560 ($[M]^+$), 561 ($[MH]^+$).

***trans*-$Cl_2Pt[\overline{N{=}C(Me)OCH_2CH_2}]_2$ (4).** To a solution of $ClCH_2CH_2OH$ (1 mL, 14.92 mmol) in THF (30 mL) at 0 °C was added a 1.6 M *n*-hexane solution of *n*-BuLi (1.61 mL, 2.58 mmol) and subsequently *trans*-$Cl_2Pt(NCMe)_2$ (408 mg, 1.17 mmol). The reaction mixture was stirred at this temperature for 30 min to give slowly a clear solution. A solution IR spectrum did not reveal any residual $\nu(C{\equiv}N)$ band but showed the presence of a $\nu(C{=}N)$ absorption at 1656 cm^{-1}. The ice bath was removed, and stirring was continued at room temperature. After 90 min, a white solid precipitated, but stirring was continued for an additional 2 h. Then the reaction mixture was taken to dryness. The residue was washed with MeOH (2 × 10 mL) and Et_2O (2 × 10 mL) and dried under vacuum. Yield: 360 mg (71%). Mp: 242–243 °C. Anal. Calcd for $C_8H_{14}N_2Cl_2O_2Pt$: C, 22.03; H, 3.23; N, 6.42; Cl, 16.25. Found: C, 21.98; H, 3.12; N, 6.15; Cl, 16.02.

***cis*-$Cl_2Pt[NH{=}C(OCH_2CH_2Cl)Ph]_2$ (5).** In a typical experiment this complex was prepared from *cis*-$Cl_2Pt(NCPh)_2$ (347 mg, 0.735 mmol), oxirane (10 mL), and a 0.25 M LiCl solution in 2-chloroethanol (0.24 mL, 0.060 mmol) in 2-chloroethanol (30 mL). The reaction mixture was stirred at 0 °C for 3 h and then at room temperature for 43 h. Then it was taken to dryness to give an oily residue, which was dissolved in CH_2Cl_2 (5 mL). Addition of *n*-pentane (59 mL) afforded a yellow precipitate, which was filtered, washed with H_2O (3 × 5 mL), and redissolved in CH_2Cl_2 (10 mL). The solution was treated with anhydrous Na_2SO_4, filtered, taken to dryness, and washed with a mixture of Et_2O/*n*-hexane (30 mL, 1:1 v/v). The white solid was filtered off and dried under vacuum. Yield: 250 mg (54%). Mp: 146–148 °C. Anal. Calcd for $C_{18}H_{20}N_2Cl_4O_2Pt$: C, 34.14; H, 3.18; N, 4.42; Cl, 22.39. Found: C, 33.90; H, 3.07; N, 4.38; Cl, 22.20.

Reaction of 5 with *n*-BuLi. To a solution of 5 (107 mg, 0.169 mmol) in THF (20 mL) at 0 °C was added a 1.6 M *n*-hexane solution of *n*-BuLi (0.22 mL, 0.356 mmol). The reaction mixture was stirred for 15 min at 0 °C and then 45 min at room temperature. Then it was concentrated to ca. 10 mL, and Et_2O (20 mL) was added to give a white precipitate, which was filtered and washed with MeOH (2 × 5 mL) and Et_2O (3 × 5 mL). Yield: 66 mg, 70%. The complex was identified by IR and ^1H NMR data as complex 1.

Reactions with Diphosphines. Reaction of 1 with Bis(diphenylphosphino)ethane (diphos). Compound 1 (200 mg, 0.35 mmol) was treated with diphos (170 mg, 0.42 mmol) in CH_2Cl_2 (30 mL) at room temperature. The solution turned immediately yellow, and an IR spectrum of the solution revealed the presence of the band at 1644 cm^{-1} due to $\nu(C{=}N)$ of the free oxazoline. After 3 h, a pale yellow precipitate formed. The solution was taken to dryness and treated with Et_2O (20 mL).

The product was filtered, washed with Et_2O (2 × 5 mL), and identified as $[(Ph_2PCH_2CH_2PPh_2)_2Pt](Cl)_2$. Yield: 250 mg (70%). Anal. Calcd for $C_{48}H_{48}P_4Cl_2Pt$: C, 56.81; H, 4.76; Cl, 6.99. Found: C, 56.02; H, 4.53; Cl, 6.80. $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 47.9 s, $^1J_{PPt}$ = 2333 Hz. The Et_2O solution was taken to dryness, and the oily residue was analyzed by GC/MS. The column was OV1, 25 m, with a 0.25 mm internal diameter, and the temperature was ramped from 100 to 200 °C at 10°/min. The He flow rate was 1 mL/min, and the retention time of free 2-phenyloxazoline was 1.37 min. 2-Phenyloxazoline was identified by its MS spectrum ($[M]^+$, *m/e* 147; $[M - CH_2O]^+$, *m/e* 117), by ^1H NMR spectroscopy (CD_2Cl_2) ($-OCH_2-$ δ 4.41 t, $^3J_{HH}$ = 9.6 Hz; $-NCH_2-$ δ 4.02 t), and by ^{13}C NMR spectroscopy (CD_2Cl_2) ($-OCH_2-$ δ 68.0, $^1J_{CH}$ = 151 Hz; $-NCH_2-$ δ 55.4, $^1J_{CH}$ = 146 Hz). Analytical data for 2-phenyloxazoline, prepared by other methods, have been reported.[10]

Reaction of 2 with *cis*-Bis(diphenylphosphino)ethylene (diphoe). The reaction was carried out similarly to the reaction of 1 with diphos, starting from 2 (110 mg, 0.25 mmol) and diphoe (99 mg, 0.25 mmol). The precipitate $[(Ph_2PCHCHPPh_2)_2Pt](Cl)_2$ was recovered in 75% yield (182 mg). $^{31}P\{^1H\}$ NMR: δ 50.6 s, $^1J_{PPt}$ = 2535 Hz. Anal. Calcd for $C_{48}H_{44}P_4Cl_2Pt$: C, 57.02; H, 4.35; Cl, 7.02. Found: C, 57.10; H, 4.30; Cl, 6.95. The solution was analyzed by GC/MS: the retention time of 2-methyloxazoline was 0.90 min. FAB mass spectrum, *m/e*: 85 ($[M]^+$), 55 ([M −

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(9) (a) Hartley, F. R.; Murray, S. G.; McAuliffe, C. A. *Inorg. Chem.* **1979**, *18*, 1394. (b) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1990**, 199.

Table I. Spectroscopic Data for Complexes 1–5

	IR[a]		^{1}H NMR[b]			^{13}C{^{1}H} NMR			
compd	ν(C═N)	Pt—Cl region	δ (OCH$_2$)	δ (NCH$_2$)	δ(other)	δ(OCH$_2$)	δ (NCH$_2$)	δ(C═N)	δ(other)
1	1639 s	333 m, 342 m	3.98 t, $^3J_{HH}$ = 9.4	3.68 t, $^3J_{HH}$ = 9.4	7.60–7.73 m,[c] 8.63–8.66 m[c]	68.79 s, $^3J_{CPt}$ = 32.3	56.72 s, $^2J_{CPt}$ = 21.6	167.81 s	125.6 s, 133.70 s[d]
2	1665 s	330 m, 338 m	4.51 t	3.92 t	2.48 t,[e] $^4J_{HPt}$ = 8.0[g]	69.20 s	55.74 s	171.80 s	15.39 s[f]
3	1615 s	324 m, 357 m	4.64 t, $^3J_{HH}$ = 9.8	4.32 t, $^3J_{HH}$ = 9.8	7.51–7.69 m,[c] 8.88–8.90 m[c]	68.55 s	57.35 s	167.11 s	125.37 s, 133.28 s[d]
4	1661 s	318 m, 355 m	4.45 t, $^3J_{HH}$ = 9.8	3.94 tq, $^3J_{HH}$ = 9.8	2.47 t,[e] $^4J_{HPt}$ = 7.7,[g]	69.07 s, $^3J_{CPt}$ = 31.8	54.77 s, $^2J_{CPt}$ = 22.8	170.88 s, $^2J_{CPt}$ = 54.7	15.08 s[f]
5	1612 s, 1631 s	333 m, 335 m	4.68 t,[h] $^3J_{HH}$ = 4.9; 5.23 t,[k] $^3J_{HH}$ = 4.8; 4.44 t,[k] $^3J_{HH}$ = 5.0; 5.74 t,[l] $^3J_{HH}$ = 5.2		3.85 t,[i,h] $^3J_{HH}$ = 4.9; 3.56,[k] 3.74,[i,k] $^3J_{HH}$ = 5.0; 4.05 t,[i,l] $^3J_{HH}$ = 5.2; 8.68 br,[n] 8.98 br,[n] 9.30 br[n,l]	70.61 s,[h] 71.14 s,[k,j] 70.05 s,[k,j] m			41.82 s,[h,j] 42.87 s,[k,j] 41.70 s,[k,j] m

[a] Nujol mull, cm^{-1}. Abbreviations: s = strong, m = medium. [b] The ^{1}H and ^{13}C NMR spectra were recorded in CD_2Cl_2. 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. J is given in Hz. Abbreviations: s = singlet, t = triplet, q = quartet, m = multiplet, br = broad. [c] C_6H_5 proton resonances (see text). [d] C_6H_5 carbon resonances. [e] CH_3 protons. [f] CH_3 carbon resonance. [g] Coupling observed at 80 MHz (see text). [h] Isomer A (see text). [i] CH_2Cl protons. [j] CH_2Cl carbons. [k] Isomer B (see text). [l] Isomer C (see text). [m] Resonance of too low intensity to be observed. [n] NH resonances.

Table II. Crystallographic Data for cis-$Cl_2Pt[\overline{N{=}C(Ph)OCH_2CH_2}]_2$ (1)

formula	$PtCl_2N_2O_2C_{18}H_{18}$
M	560.4
space group (No.)	$P2_1/c$ (14)
a/Å	16.242 (3)
b/Å	9.438 (2)
c/Å	12.679 (2)
β/deg	95.65 (4)
V/Å^3	1934 (1)
Z	4
ρ(calcd)/g cm^{-3}	1.92
λ(Mo Kα radiation)/Å	0.71069
T/°C	22
$R = R(F_o)$	0.023
$R_w = R_w(F_o)$	0.025
μ(Mo Kα)/cm^{-1}	72.5
transm coeff (rel)	72–100
no. of rflns measd	4227
no. of rflns with $I \geq 2.5\sigma(I)$	3248
GOF	1.31

Table III. Atomic Coordinates (×10^4) for Non-Hydrogen Atoms and U Equivalent Isotropic Thermal Parameters (Å × 10^3) with Esd's in Parentheses for cis-$Cl_2Pt[\overline{NC(Ph)OCH_2CH_2}]_2$ (1)

atom	x/a	y/b	z/c	U_{eq}[a]
Pt	7545.8 (1)	6103.0 (2)	583.9 (1)	30.6 (1)
Cl(1)	7858.5 (9)	3876 (1)	−5 (1)	51.3 (4)
Cl(2)	7365.3 (8)	6958 (1)	−1116.1 (9)	49.8 (4)
N(1)	7663 (2)	5334 (4)	2073 (3)	35 (1)
C(1)	6960 (3)	4552 (5)	2452 (4)	49 (2)
O(1)	8112 (2)	4680 (3)	3710 (3)	47 (1)
C(2)	7242 (3)	4292 (6)	3603 (4)	54 (2)
C(3)	8260 (3)	5327 (4)	2808 (3)	38 (1)
C(4)	9094 (3)	5918 (5)	2779 (4)	43 (2)
C(5)	9504 (4)	6429 (8)	3708 (6)	79 (3)
C(6)	10277 (4)	6996 (9)	3707 (7)	97 (3)
C(7)	10646 (3)	7101 (6)	2809 (6)	73 (2)
C(8)	10259 (4)	6573 (8)	1856 (6)	81 (3)
C(9)	9475 (3)	5998 (6)	1855 (5)	65 (2)
C(10)	7976 (3)	9106 (4)	1331 (4)	43 (2)
N(2)	7308 (2)	8052 (3)	1119 (3)	32 (1)
O(2)	6649 (2)	9937 (3)	1657 (3)	52 (1)
C(11)	7512 (3)	10384 (5)	1747 (4)	51 (2)
C(12)	6621 (3)	8587 (4)	1327 (3)	38 (1)
C(13)	5806 (3)	7895 (5)	1265 (4)	42 (2)
C(14)	5410 (3)	7780 (7)	2166 (5)	62 (2)
C(15)	4668 (4)	7043 (7)	2168 (6)	75 (3)
C(16)	4308 (4)	6476 (7)	1245 (6)	70 (3)
C(17)	4694 (5)	6628 (10)	349 (7)	108 (4)
C(18)	5457 (4)	7287 (9)	366 (5)	87 (3)

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

$CH_2O]^+$). ^{1}H NMR: $-NCH_2-$ δ 3.73 tq, $^3J_{HH}$ = 9.2 Hz, $^5J_{HH}$ = 1.4 Hz; $-OCH_2-$ δ 4.14 t; CH_3 δ 1.90 t. ^{13}C NMR: $-NCH_2-$ δ 55.0 t, $^1J_{CH}$ = 143 Hz; $-OCH_2-$ δ 67.6 t, $^1J_{CH}$ = 150 Hz; CH_3 δ 13.78 q, $^1J_{CH}$ = 139 Hz). Analytical data for 2-methyloxazoline, prepared by other methods, have been reported.[10]

X-ray Measurements and Structure Determination for 1. The crystal and refinement data for $PtCl_2N_2O_2C_{18}H_{18}$ (pale yellow transparent prisms from $CHCl_3$/MeOH mixture) are summarized in Table II. A prismatic single crystal of 0.46 × 0.28 × 0.16 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 and varying each of the orientation angles χ and φ over a range of 120°, with $5 \leq \vartheta \leq 8°$. For the determination of precise lattice parameters, 25 strong reflections with $10 \leq \vartheta \leq 14$ were considered. Integrated intensities for khl reflections with $l > 0$ were measured, and two standard reflections, −2,4,2 and 231, were monitored every 180 min. There was no significant fluctuation of intensities other than that expected from Poisson statistics.

The intensity data were corrected for Lorentz–polarization effects, for absorption, following the method of North et al.,[11] and for extinction. The structure was solved by using three-dimensional Patterson and Fourier techniques and refined with full-matrix least squares with anisotropic thermal parameters assigned to all the non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement (d_{C-H} = 0.98 Å and U_{iso} = 0.06 Å^2). The function minimized was $\sum w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$. The anomalous dispersion terms[11] for Pt were taken into account in the refinement. Atomic scattering factors were taken from ref 12. Data processing and computation were carried out by using the SHELX 76 program package[13] and ORTEP[14] for drawings. The refinement of the complex reached convergency at R = 0.023, R_w = 0.025, and GOF = 1.31 [$w = (\sigma^2F_o + 0.000349F_o^2)^{-1}$]. The atomic coordinates are reported in Table III.

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(10) (a) Seeliger, W.; Thier, W. *Justus Liebigs Ann. Chem.* **1966**, *698*, 158. (b) *Dictionary of Organic Compounds*, 5th ed.; Buckingham, J., Donaghi, S. M., Eds.; Chapman and Hall: New York, 1982; Vol. 2.

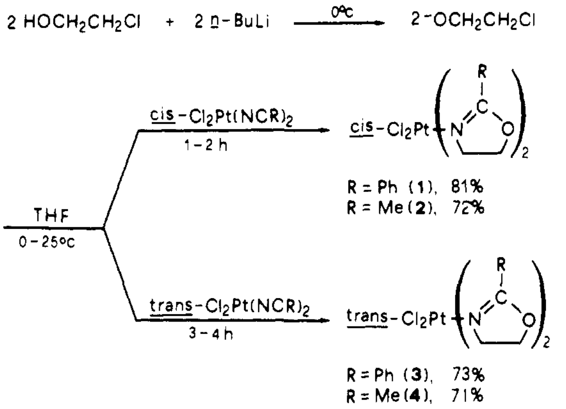
(11) North, A. C. T.; Philips, D. C.; Matheus, F. *Acta Crystallogr.* **1968**, *A24*, 351.

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

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

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

Scheme I



Results

Reactions with 2-Chloroethanol/Base. Both nitrile ligands in *cis*- and *trans*-$Cl_2Pt(NCR)_2$ (R = Ph, Me) complexes react in THF at room temperature or below with 2 equiv of $^-OCH_2CH_2Cl$ to give the corresponding oxazoline ligands in good yield, as reported in Scheme I. These reactions do not occur without added base even upon heating the nitrile complexes in 2-chloroethanol at 80 °C for several hours. The most convenient base is *n*-BuLi, which presumably gives *n*-BuH as the other product. However, these reactions also proceed, but in lower yields and longer reaction times, with crystalline NaH.

Under the experimental conditions used for the reactions leading to 1, 3, and 4, the solution IR spectra show the fast disappearance (10–15 min) of the $\nu(C{\equiv}N)$ band of the starting nitrile complexes accompanied by the simultaneous growth of the $\nu(C{=}N)$ absorption at ca. 1630–1650 cm^{-1}. For 2, the reaction is completed in ca. 2 h. There is no infrared evidence during the course of these reactions for imidoyl intermediates (see eq 1). It presumably cyclizes rapidly to the oxazoline ligand under the reaction conditions.

Compounds 1–4 are pale yellow solids, air-stable in the solid state and in solution. They are soluble in DMSO, slightly soluble in CH_2Cl_2, and insoluble in saturated hydrocarbons. The spectral data for 1–4, which are collected in Table I, indicate that (i) no cis–trans isomerization at the metal center occurs in the reactions reported in Scheme I and (ii) they provide evidence for the cyclic structure of the reaction products. This latter feature is unambiguously confirmed by an X-ray structural determination carried out for 1 (see below).

The trans or cis stereogeometry of dichloro complexes of Pt(II) can usually be deduced by the presence of one or two bands, respectively, in the Pt–Cl region.[15] This is found, for example, in the *trans*- and *cis*-bis(imido esters) of Pt(II) derived from nucleophilic attack of MeOH on the coordinated benzonitrile ligands in *trans*- and *cis*-$Cl_2Pt(NCPh)_2$.[2b] For the bis(oxazoline) derivatives 1–4 both the cis and trans isomers display two absorptions in the Pt–Cl region. Although not perhaps of diagnostic use for the identification of the stereoisomers, we have observed, for several repetitive preparations of 1–4, that for each set of isomers the difference between the frequencies of the two bands is always lower for the cis isomers 1 and 2 (ca. 10 cm^{-1}) than for the trans species 3 and 4 (ca. 35 cm^{-1}). It is also worth noting that the uncommon IR pattern in the Pt–Cl region shown by 3 and 4 somewhat resembles that of *trans*-$Cl_2Pt(NCPh)_2$, which displays three bands in this region.[2,3]

The oxazoline compounds display also the characteristic C=N stretching vibration as a strong absorption in the range 1615–1665 cm^{-1}. Similar values have been reported for acyclic imido esters of Pt(II).[16] An increase in the value of the $\nu(C{=}N)$ band by ca. 20–45 cm^{-1} is observed as one passes from the aryloxazolines in compounds 1 and 3 to the alkyloxazolines in complexes 2 and 4. On the other hand, $\nu(C{=}N)$ of Pt(II)-coordinated oxazolines are somewhat lower than those of the corresponding free oxazolines [2-methyloxazoline 1676 cm^{-1}, 2-phenyloxazoline 1646 cm^{-1} (THF solutions)].

The ^1H NMR spectra are reported in Table I. On the basis of assignments of protons in 2-oxazoline and related systems,[7a,8a,17] the methylene protons adjacent to the oxygen are assigned to lower field resonances, which are approximately 0.3–0.7 ppm from the methylene protons adjacent to the nitrogen. The $-OCH_2-$ protons appear as triplets (3.98–4.64 ppm) due to coupling with the $-NCH_2-$ protons ($^3J_{HH}$ = 9.4–9.8 Hz). The $-NCH_2-$ protons are also triplets at δ 3.69 and 4.32 for 1 and 3, respectively; for 2 and 4, the $-NCH_2-$ protons appear as triplets of quartets at δ 3.92 and 3.94, respectively, owing to the long-range coupling with the methyl group ($^5J_{HH}$ = ca. 1 Hz). At 80 MHz (but not at 400 MHz) the methyl resonance in 2 and 4 is flanked by ^{195}Pt satellites ($^4J_{HPt}$ = ca. 8 Hz). The loss of ^{195}Pt coupling at higher magnetic fields may be due to relatively short T_1 relaxation times, as reported for other platinum(II) complexes.[18] In 1 and 3 the ortho protons of the phenyl group, which are cis to platinum, are shifted downfield (δ 8.6–8.9) due to a deshielding effect of the metal. A similar effect has been noted in related Pt(II)–imido esters having cis-metal–phenyl conformations.[2b] No $J_{PtH(ortho)}$ coupling is observed even at 80 MHz, presumably owing to the relatively free rotation about the phenyl–oxazoline bond.[19]

The ^{13}C NMR spectra of 1–4 show singlets for $-OCH_2-$ carbons in the range δ 68.5–69.2 with a $^3J_{CPt}$ of ca. 30 Hz for 1 and 4. This latter value is comparable to those reported for a series of platinum(II)–carbene derivatives such as *trans*-$\{(CH_3)Pt(PMe_2Ph)_2[C(CH_3)N(CH_3)_2]\}PF_6$ having an $N{-}CH_3$ group trans to the metal.[20a] The $-NCH_2-$ carbons appear as singlets at higher field (δ 54.8–57.3) with a $^2J_{PtC}$ of ca. 20 Hz for 1 and 4. It is observed that for these complexes the $^2J_{PtC}$ are lower than the $^3J_{PtC}$ values. This trend is consistent with that found for saturated hydrocarbon ligands coordinated to Pt(II).[20b] The $-N{=}C(R)-$ carbons of 1–4 appear as singlets in the range 167.1–171.8 ppm. Only for the more soluble compound 4 are ^{195}Pt satellites observed ($^2J_{PtC}$ = 54.7 Hz). The cyclic structure of the oxazoline ligand in 1–4 is confirmed by comparison with the coupled ^{13}C NMR spectra of free oxazolines (i.e. 2-methyloxazoline: $-NCH_2-$ δ 55.0 t, $^1J_{CH}$ = 143 Hz;

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(15) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986.

(16) Ros, R.; Renaud, J.; Roulet, R. *J. Organomet. Chem.* **1976**, *104*, 271.

(17) (a) Lambert, R. F.; Christofferson, C. E. *J. Org. Chem.* **1965**, *30*, 3938. (b) Pretsch, E.; Clerc, T.; Seible, J.; Simon, W. In *Strukturaufklärung Organischer Verbindungen*; Springer Verlag: Berlin, 1976. (c) Zanotto, L.; Bertani, R.; Michelin, R. A. *Inorg. Chem.* **1990**, *29*, 3265.

(18) (a) Lellemand, J. Y.; Soulvè, J.; Chottard, J. C. *J. Chem. Soc., Chem. Commun.* **1980**, 436. (b) Anklin, C. G.; Pregosin, P. S. *Magn. Reson. Chem.* **1985**, *23*, 671.

(19) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1990**, *29*, 1812 and references therein.

(20) (a) Chisholm, M. H.; Clark, H. C.; Ward, J. E. H.; Yasufuku, K. *Inorg. Chem.* **1975**, *14*, 893. (b) Kalinowki, H. O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; J. Wiley & Sons: Chichester, U.K., 1988. (c) Mann, E. B.; Taylor, F. B. *^{13}C NMR Data for Organometallic Compounds*; Maitlis, P. M., Ed.; Academic Press: London, 1981.

Table IV. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for *cis*-$Cl_2Pt[NC(Ph)OCH_2CH_2]_2$ (1)

Pt–Cl(1)	2.304 (1)	Pt–Cl(2)	2.293 (1)
Pt–N(1)	2.014 (3)	Pt–N(2)	2.011 (3)
N(1)–C(1)	1.480 (6)	N(1)–C(3)	1.277 (5)
C(1)–C(2)	1.507 (7)	O(1)–C(2)	1.452 (6)
O(1)–C(3)	1.339 (6)	C(3)–C(4)	1.469 (7)
C(4)–C(5)	1.382 (8)	C(4)–C(9)	1.379 (8)
C(5)–C(6)	1.365 (10)	C(6)–C(7)	1.341 (10)
C(7)–C(8)	1.398 (10)	C(8)–C(9)	1.384 (9)
C(10)–N(2)	1.476 (6)	C(10)–C(11)	1.542 (7)
N(2)–C(12)	1.276 (6)	O(2)–C(11)	1.458 (6)
O(2)–C(12)	1.341 (5)	C(12)–C(13)	1.471 (6)
C(13)–C(14)	1.369 (8)	C(13)–C(18)	1.350 (8)
C(14)–C(15)	1.392 (8)	C(15)–C(16)	1.364 (10)
C(16)–C(17)	1.357 (11)	C(17)–C(18)	1.384 (10)
N(1)–Pt–N(2)	91.0 (1)	Cl(2)–Pt–N(2)	89.1 (1)
Cl(2)–Pt–N(1)	178.1 (1)	Cl(1)–Pt–N(2)	178.3 (1)
Cl(1)–Pt–N(1)	88.3 (1)	Cl(1)–Pt–Cl(2)	91.6 (1)
Pt–N(1)–C(3)	132.9 (3)	Pt–N(1)–C(1)	118.6 (3)
C(1)–N(1)–C(3)	108.4 (4)	N(1)–C(1)–C(2)	103.0 (4)
C(2)–O(1)–C(3)	106.9 (4)	C(1)–C(2)–O(1)	104.5 (4)
N(1)–C(3)–O(1)	116.0 (4)	O(1)–C(3)–C(4)	116.0 (4)
N(1)–C(3)–C(4)	128.0 (4)	C(3)–C(4)–C(9)	122.3 (5)
C(3)–C(4)–C(5)	118.6 (5)	C(5)–C(4)–C(9)	119.1 (5)
C(4)–C(5)–C(6)	120.1 (6)	C(5)–C(6)–C(7)	121.2 (7)
C(6)–C(7)–C(8)	120.4 (6)	C(7)–C(8)–C(9)	118.4 (7)
C(4)–C(9)–C(8)	120.7 (6)	N(2)–C(10)–C(11)	102.4 (4)
Pt–N(2)–C(10)	121.1 (3)	C(10)–N(2)–C(12)	109.7 (3)
Pt–N(2)–C(12)	129.2 (3)	C(11)–O(2)–C(12)	107.6 (4)
C(10)–C(11)–O(2)	104.2 (4)	N(2)–C(12)–O(2)	115.9 (4)
O(2)–C(12)–C(13)	116.2 (4)	N(2)–C(12)–C(13)	127.9 (4)
C(12)–C(13)–C(18)	122.3 (5)	C(12)–C(13)–C(14)	119.0 (4)
C(14)–C(13)–C(18)	118.6 (5)	C(13)–C(14)–C(15)	121.2 (5)
C(14)–C(15)–C(16)	119.5 (6)	C(15)–C(16)–C(17)	118.9 (6)
C(16)–C(17)–C(18)	121.4 (7)	C(13)–C(18)–C(17)	120.3 (6)

$-OCH_2-$ δ 67.6 t, $^1J_{CH} = 150$ Hz; CH_3 δ 13.78 q, $^1J_{CH} = 139$ Hz; N=*C*—O δ 165.2; the corresponding data for 2-phenyloxazoline are reported in the Experimental Section). Thus, the ^{1}H-coupled ^{13}C NMR spectrum of 4 shows the $-OCH_2-$ and $-NCH_2-$ carbons as triplets at δ 69.2 ($^1J_{CH} = 154$ Hz) and δ 54.9 ($^1J_{CH} = 147$ Hz), respectively. Similarly, data for 1 are as follows: $-OCH_2-$ δ 68.8, $^1J_{CH} = 154$ Hz; $-NCH_2-$ δ 56.7, $^1J_{CH} = 148$ Hz.

Description of the Structure of *cis*-$Cl_2Pt[N{=}C(Ph)OCH_2CH_2]_2$ (1). The crystal contains *cis*-(dichloro)bis[2-phenyloxazoline]platinum(II) molecules, one of which is represented in Figure 1 with the atom-numbering scheme. Selected bond distances and angles are listed in Table IV. The coordination geometry around Pt(II) is almost square planar, with the nitrogen atoms lying above and below [N(1) 0.056 (4), N(2) −0.051 (4) Å] the least-squares coordination plane defined by the four ligand atoms [Cl(1) −0.010 (2), Cl(2) 0.009 (2), Pt −0.002 (1) Å]. The Cl(1)–Pt–N(2) and Cl(2)–Pt–N(1) systems are "quasi" linear, the angular values being 178.3 (1) and 178.1 (1)°, respectively. The Pt–Cl(1) and Pt–Cl(2) distances of 2.304 (1) and 2.293 (1) Å, respectively, compare well with the corresponding values of 2.286 (6) (trans to amidine) and 2.291 (7) Å (trans to amino group) found in the platinum–amino–amidine metallacycle *cis*-$Cl_2Pt(NH{=}CPhNBu^tCH_2CH_2NHBu^t)$.[21] The Pt–N distances are 2.014 (3) and 2.011 (3) Å for Pt–N(1) and Pt–N(2), respectively. These values may be compared with those found for the aforementioned amino–amidine complex (Pt–N(amidine) 1.961 (15) Å and Pt–N(amine) 2.015 (15) Å) and also with those found in $Pt(NH{=}CPhNBu^tCH_2CH_2NHBu^t)Cl(NHCOPh)$ with Pt–N distances ranging from 2.000 (8) (trans to amidine) to 2.049 (8) Å (trans to benzamidate).[2a] The five-membered rings of the two oxazoline ligands are almost planar: in the oxazoline ring N(2)–C(10)–C(11)–O(2)–C(12) the deviations from its mean plane are N(2) 0.000 (3), C(10) 0.017 (5), C(11) 0.031 (5), C(12) − 0.015 (4), and O(2) 0.016 (4) Å; while in the N(1)–C(1)–C(2)–O(1)–C(3) ring, they are N(1) − 0.015 (4), C(1) 0.067 (5), C(2) −0.089 (6), O(1), 0.025 (3), and C(3) −0.014 (4) Å, with a slightly twisted conformation in the latter. Apparently, these small deviations do not affect the electronic delocalization within the N–C–O moiety of the oxazoline ligands. In fact, the N(1)–C(3) and C(3)–O(1) as well as the N(2)–C(12) and C(12)–O(2) bond lengths are rather short [N–C 1.277 (9) Å (av) and C–O 1.340 (6) Å (av)]. The C(2)–O(1) [1.452 (6) Å] and C(11)–O(2) [1.458 (6) Å] bonds have values typical of C(sp^3)–O bonds in ring systems;[21] also the two N(1)–C(1) [1.480 (6) Å] and N(2)–C(10) [1.476 (6) Å] bonds have values which compare well with that found in the oxazolin-2-ylidene Pt(II) complex *trans*-$\{(PPh_3)_2Pt[CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O]Br\}BF_4$ [1.48 (1) Å].[8a] Finally, the two C(sp^3)–C(sp^3) distances of 1.507 (7) Å for C(1)–C(2) and 1.542 (7) Å for C(10)–C(11) compare well with observed values for similar systems.[8a] The two oxazoline rings intersect the platinum coordination plane at different angles, i.e. 95.7 (1)° for N(1)–C(1)–C(2)–O(1)–C(3) and 88.2 (1)° for N(2)–C(10)–C(11)–O(2)–C(12), probably due to steric requirements. Concerning the conformation of the two organic ligands, we note a different tilting of each phenyl with respect to the corresponding oxazoline ring, i.e. 149.8 (2)° for N(2)–C(10)–C(11)–O(2)–C(12) and 58.8 (2)° for N(1)–C(1)–C(2)–O(1)–C(3). The tilting of 58.8 (2)° is related to a relatively short H(9)···Pt contact of 2.734 (6) Å, which represents also the shortest Pt···H interaction within the molecule. The shortest contact distance with the second ligand is H(18)···Pt of 3.240 (7) Å. Contact distances involving the previously quoted hydrogens and the coordinated chlorines seem to stabilize the two organic ligand conformations: H(9)···Cl(1) 3.019 (6) Å [C(9)–H(9)···Cl(1) 150 (1)°] and H(18)···Cl(2) 2.960 (7) Å [C(18)–H(18)···Cl(2) 144 (1)°]. The phenyls of the two oxazoline ligands are rather parallel to each other (dihedral angle 5.4 (2)°). The molecular packing, shown in Figure 2, is dominated by a parallel arrangement of the phenyls with short intermolecular contacts C(17)···C(17)′ of 3.76 (2) Å (prime = $1 - x$, $1 - y$, $-z$), C(7)···C(9)″ (double prime = $2 - x$, $^1/_2 + y$, $^1/_2 - z$), and C(7)···C(4)″; the latter two are both 3.71 (1) Å, without stacking. The different phenyl contacts together with the intramolecular interactions of H(9) and H(18) with platinum and chlorines affect the different organic ligand conformations.

Reactions with Oxirane/Cl⁻. In the presence of chloride ion, oxirane reacts with both benzonitrile ligands in *cis*-$Cl_2Pt(NCPh)_2$, but the nature of the reaction product appears to be determined by the chloride concentration. All the experiments were carried out by using a nitrile complex concentration of 1.6×10^{-2} M in 2-chloroethanol (30 mL) and oxirane (10 mL) at 0 °C for 3 h and then at room temperature (ca. 25 °C) for 43 h. It is observed that, with LiCl concentrations of 3.33×10^{-2}, 1.75×10^{-2}, 0.95

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(21) Tiripicchio, A.; Tiripicchio Camellini, M.; Maresca, L.; Natile, G. *Acta Crystallogr.* **1990**, *C46*, 549.

(22) Allen, F. H.; Kennard, O.; Waston, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

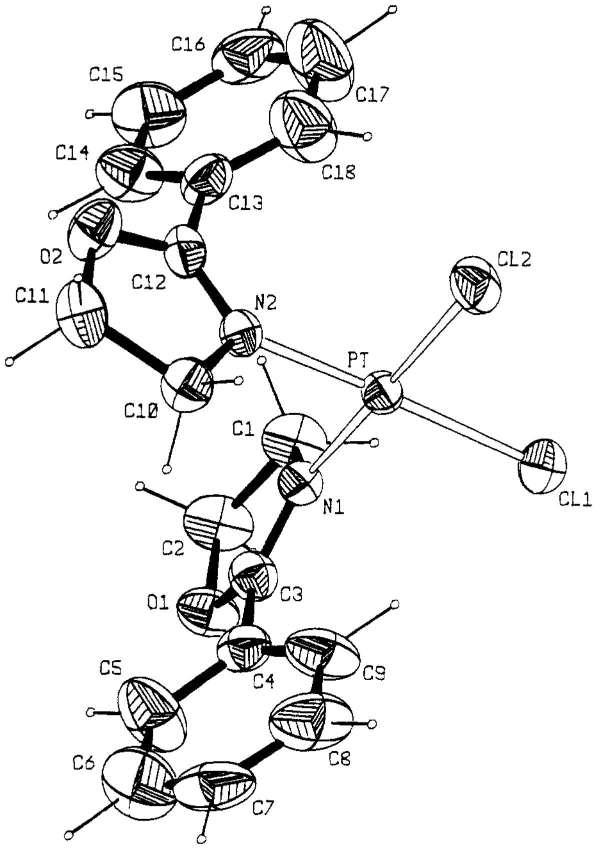
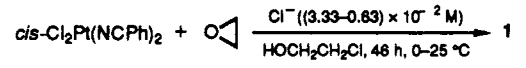


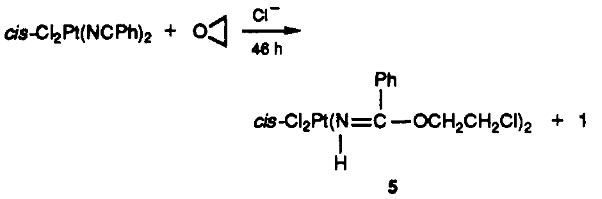
Figure 1. ORTEP view of $cis\text{-}Cl_2Pt[\overline{N{=}C(Ph)OCH_2CH_2}]_2$ (1) with the atomic numbering scheme. (Ellipsoids are at the 50% probability level.)

$\times\ 10^{-2}$, and 0.63×10^{-2} M, compound 1 is formed in ca. 85% isolated yield (eq 2) after 46 h overall reaction time.



(2)

On the other hand, with a lower chloride concentration (i.e. 3.2×10^{-3} and 1.6×10^{-3} M) the reactions proceed differently, yielding 1 and the bis(imido ester) complex 5 (eq 3), in approximately 2:1 and 1:1 ratios, respectively, as



(3)

5

established by ^{1}H NMR data. With a "catalytic" amount of Cl$^-$ (1.6×10^{-4} M) a mixture of the starting nitrile complex and 5 (10%), which could not be separated, is formed. Complex 5 (ca. 20%) is also obtained as a mixture with 1 (ca. 5%) and the starting nitrile complex in the reaction without added LiCl after a 93 h of reaction time. It is possible that this latter reaction may be promoted by traces of Cl$^-$ ions due to the presence of HCl in the solvent. It is important to note that no reaction occurs in the absence either of both oxirane and Cl$^-$ ions, the starting complex being recovered unchanged. These results, taken all together, demonstrate that it is the oxirane rather than the 2-chloroethanol solvent that is involved in the nitrile cyclization reactions (2) and (3).

A pure sample of complex 5 (see Experimental Section) was characterized by its elemental analysis and spectroscopic data (Table I). The IR (Nujol mull) spectrum of 5 shows a strong NH absorption at 3206 cm^{-1}, two bands at 1612 and 1631 cm^{-1} due to the C=N stretching vibration and NH deformation, and a medium absorption at 676 cm^{-1} attributable to ν(C–Cl). The presence of two very close bands in the Pt–Cl region (333 and 335 cm^{-1}) indicates its cis stereogeometry. The complexity of the ^{1}H NMR spectrum suggests the presence of several isomers, which can be due to different conformations of the imido ester ligands in the molecule. The three possible arrangements (A, B, and C) are shown, where E and Z in-

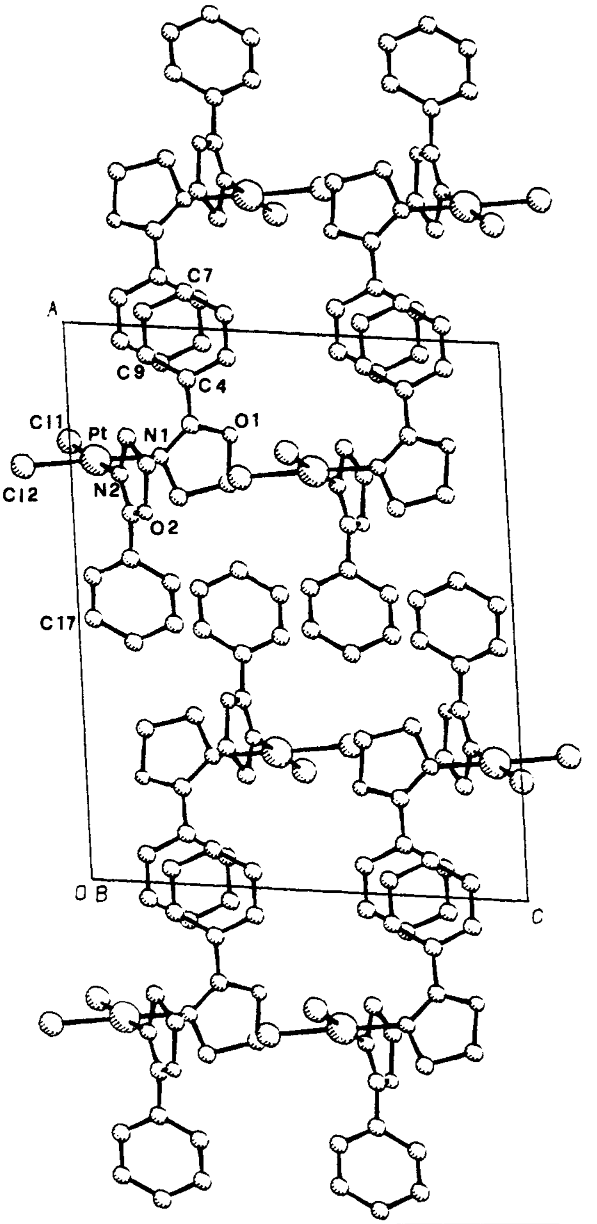
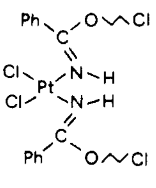
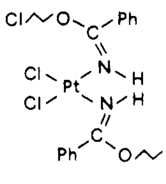


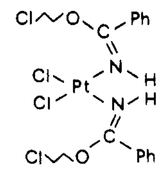
Figure 2. Packing diagram of $cis\text{-}Cl_2Pt[\overline{N{=}C(Ph)OCH_2CH_2}]_2$ (1) as viewed down the crystallographic axis b.



A(E,E)



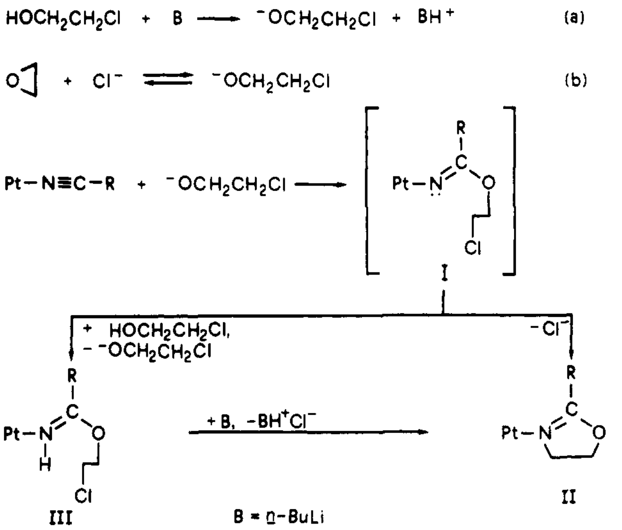
B(E,Z)



C(Z,Z)

dicate that NH and OCH$_2$CH$_2$Cl are in a cis or trans

Scheme II



position with respect to the C=N double bond. The signal assignments have been made by taking into account the RCH_2Cl methylene resonances (R = alkyl) fall in the range 3.5–3.8 ppm[23] and that $-OCH_2-$ protons are differently shifted depending on the *Z* or *E* conformation of the imido ester ligand, as described for similar systems.[2b] Thus, for the *Z* conformation a downfield shift of the $-OCH_2-$ protons is expected, due to their position close to platinum. Consequently, the downfield resonances are attributed to the B and C species. Furthermore, homodecoupling experiments allowed the identification of each $-OCH_2CH_2Cl$ system. As for B, where the imido ester ligands have *E* and *Z* conformations, two different patterns of signals, integrating 1:1, are present, one for each $-OCH_2CH_2Cl$ moiety, either in the ^1H or in the ^{13}C NMR spectra.

The acyclic imido ester complex 5 can be converted to the oxazoline derivative 1 in 70% yield by reaction with equivalent amounts of *n*-BuLi (eq 4). It is most likely that

$$5 \xrightarrow[\text{THF, 0 °C, 2 h}]{2n\text{-BuLi, }-2n\text{-BuH, }-2\text{LiCl}} 1 \qquad (4)$$

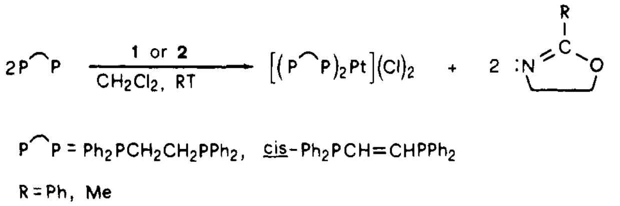
reaction 4 proceeds by deprotonation of the imidic proton to give an imidoyl intermediate (see eq 1), which then cyclizes intramolecularly to give the oxazoline derivative 1.

Discussion

The nitrile–oxazoline conversion may be performed with either 2-chloroethanol/base or oxirane/Cl^- systems. A reasonable mechanism for this transformation may involve for both systems the formation of $^-OCH_2CH_2Cl$ as the reactive species (eqs a and b of Scheme II). While the haloalkoxide ion in eq a is obtained by deprotonation of the alcohol by a strong base, in eq b the 2-chloroethoxide ion is produced by Cl^- attack on oxirane. This latter reaction is supported by other studies in which the halide ion acts as a catalyst to promote ring opening in certain organic reactions.[24] Most of these studies have been carried out in aqueous media,[24b,25] and the results indicate that (i) eq b is an equilibrium and (ii) the reaction proceeds through the formation of 2-chloroethoxide as an intermediate, which eventually reacts with water to give 2-chloroethanol.[24b]

Nucleophilic attack by the haloalkoxide ion on the nitrile carbon affords intermediate I, which may convert to the oxazoline product II, by intramolecular cyclization, or to the acyclic imido ester III, presumably by proton addition from the solvent. The formation of II or III appears to be determined by the lithium chloride concentration. As noted in the Results, the higher LiCl concentration produces completely product II, while at lower LiCl concentration complex III is also formed. This can be explained by assuming that the higher chloride concentration shifts equilibrium b in Scheme II to the right to give a higher chloroethoxide concentration, which in turn increases the rate of deprotonation of the nitrogen in III to give II. The conversion of III to II has been independently confirmed, as reported in eq 4.

The possibility of ring opening of the coordinated oxazoline in II (i.e. conversion of II to III) has also been examined. Although free oxazolines are known to hydrolyze with mineral acids to give ring opening,[26] we do not observe oxazoline ring cleavage upon reaction of 1 with an excess of anhydrous HCl, HCl(aq), or $HBF_4(Et_2O)$ at room temperature, compound 1 being recovered unchanged. Furthermore, the oxazoline ring in 1 is not cleaved by reaction with Cl^- ions or displaced by acetonitrile even at reflux for several hours. On the other hand complexes 1 and 2 react with diphosphines to give the free oxazoline, as outlined in eq 5. It is worth noting that 2 equiv of the diphosphine



(5)

are necessary to complete these reactions. When only 1 equiv is used, some unreacted starting complex is recovered. Attempts to detect any intermediate involved in eq 5 by ^{31}P NMR spectroscopy were unsuccessful. The only observed signals were those due to the bis(diphosphino) cationic complexes (see Experimental Section).

Conclusion

This work has described the synthesis of 2-oxazoline ligands, which are five-membered cyclic imido esters, from metal-coordinated nitriles by reaction with 2-chloroethanol/base or oxirane/Cl^- systems. One synthetic feature of these reactions is that the 2-oxazolines are formed under *basic* conditions. Usually, imido esters are obtained from nitriles and alcohols under *strongly acidic* conditions (Pinner synthesis).[26] In particular, 2-oxazolines are obtained from nitriles by reaction with oxirane using concentrated H_2SO_4.[26] Study of the generality of the metal-mediated synthesis of 2-oxazolines and related heterocyclic compounds such as 1,3-oxazines and imidazolines is in progress.

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Supplementary Material Available: Listings of hydrogen atom coordinates and thermal parameters (2 pages); a list of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(23) Szymanski, H. A.; Yelin, R. E. *NMR Band Handbook*; Plenum Press: New York, 1968.

(24) (a) Bradley, W.; Forrest, J.; Stephenson, O. *J. Chem. Soc.* **1951**, 1589. (b) Buddrus, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1041.

(25) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59*, 737.

(26) Frump, J. A. *Chem. Rev.* **1971**, *71*, 483.