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Synthesis and structure of new 2,6-(diphenylphosphinomethyl)pyridine ruthenium(II) complexes

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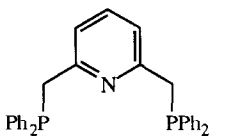
Abstract—The reaction of the tridentate rigid ligand PNP (2,6-bis(diphenylphosphinomethyl)pyridine) with $RuCl_2(PPh_3)_3$ led to the formation of two new ruthenium(II) complexes, $RuCl_2(PNP)(PPh_3)$ (**1**) and $[RuCl(MeCN)(PNP)(PPh_3)]Cl$ (**2**), which were analytically and spectroscopically characterized. The X-ray diffraction study of **1** shows that the PNP ligand coordinates Ru in a meridional mode, and reveals some steric congestion within the complex. Copyright © 1996 Elsevier Science Ltd

Keywords: ruthenium(II) complexes; tridentate ligands; X-ray analysis.

Homogeneous catalysis by transition metal complexes provides mild and selective routes to various chemicals of industrial importance [1] and the search for new efficient catalysts remains an important objective.

Ruthenium complexes have received considerable interest as catalysts for the hydrogenation of various substrates, particularly in the enantioselective reduction of ketones and alkenes [2]. We have been interested in the use of tridentate ligands for such catalytic reactions and have reported recently the synthesis of a family of C_2-symmetric chiral tridentate diphosphine ligands [3]. The coordination chemistry of the simplest achiral member of this family, 2,6-(diphenylphosphinomethyl)pyridine (hereafter designated PNP), has been well studied, but with few applications of the obtained complexes in catalysis [4–7]. As a result of the rigid backbone and fused five membered ring chelation about the metal centre, this PNP ligand should in preference form meridional rather than facial complexes. This is noteworthy because when the chiral C_2-symmetric ligand analogues are used, the C_2 axis can be preserved in the *mer* but not in the *fac* arrangement. This will be important in enantioselective reactions, as the number of diastereoisomeric forms of catalytic intermediates will thus be limited and permit greater stereocontrol of the reaction [8].



PNP

We report here the synthesis and characterization of two new ruthenium(II) complexes bearing the PNP ligand, including a structure analysis by X-ray diffraction methods.

EXPERIMENTAL

General

All experiments were carried out under a nitrogen or argon atmosphere, using a vacuum line or Vacuum Atmospheres glovebox equipped with Dri-Train HE-493 inert gas purifier. Conductivity measurements were performed with a WTW LF535 apparatus. ^1H (300 MHz) and $^{31}P\{^1H\}$ (121.5 MHz, broadband

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decoupled) NMR spectra were recorded in $CDCl_3$ on a Bruker AC300 instrument and referenced to Me_4Si and 85% aqueous H_3PO_4, respectively. FT-IR spectra were recorded on a Perkin-Elmer 1600 Series spectrometer on KBr pellets. FAB MS spectra and elemental analyses were carried out by the corresponding facilities at the Centre de Recherche de Chimie, Université Louis Pasteur, Strasbourg. Methylene chloride and acetonitrile were distilled under nitrogen over calcium hydride, and pentane over sodium. PNP [4] and $RuCl_2(PPh_3)_3$ [9] were prepared following literature methods.

Preparation of $RuCl_2(PNP)(PPh_3)$ (**1**)

A solution of PNP (100 mg, 0.210 mmol) and $RuCl_2(PPh_3)_3$ (210 mg, 0.219 mmol) in 20 cm^3 CH_2Cl_2 was refluxed for 15 min. The orange solution obtained was left at 0°C for 24 h, and **1** precipitated as orange crystals that were collected by filtration, washed with pentane and dried *in vacuo*. Yield: 94%. FAB MS *m/z* (assignment, relative intensity): 909.0 (M^+, 66%), 874.0 ([M—Cl]$^+$, 45%), 838.1 [M—2Cl—H]$^+$, 28%), 647.0 ([M—PPh_3]$^+$, 100%), 612.0 ([M—Cl—PPh_3]$^+$, 59%), 576.0 ([M—2Cl—H—PPh_3]$^+$, 72%). ^1H NMR δ (ppm): 7.57–7.00 and 6.90–6.83 (m, 38 H, $H_{arom.}$), 4.54 (t, 4H, CH_2).

Preparation of [RuCl(MeCN)(PNP)PPh_3)]Cl (**2**)

A solution of PNP (100 mg, 0.210 mmol) and $RuCl_2(PPh_3)_3$ (210 mg, 0.219 mmol) in 20 cm^3 CH_3CN was refluxed for 30 min. The dark yellow solution obtained was left at 0°C for 24 h, and a small crop of crystals of **1** precipitated. After filtration, the filtrate was concentrated and left again for 24 h at 0°C. Fine yellow crystals were collected by filtration, washed with pentane and dried *in vacuo*. Yield: 85%. Found: C, 64.2; H, 4.6; N, 2.8. Calc. for $C_{51}H_{45}N_2P_3Cl_2Ru$: C, 64.4; H, 4.8; N, 2.9%. FAB MS *m/z* (assignment, relative intensity): 915.1 [M—Cl]$^+$, 19%), 874.1 ([M—Cl—CH_3CN]$^+$, 100%), 838.1 ([M—H—2Cl—CH_3CN]$^+$, 46%), 612.0 ([M—Cl—CH_3CN—PPh_3]$^+$, 73%), 576.0 ([M—H—2Cl—CH_3CN—PPh_3]$^+$, 87%). ^1H NMR δ (ppm): 7.75–7.09 and 6.90–6.84 (m, 38 H, $H_{arom.}$), 4.86 and 4.53 (2dt, 2 × 2H, CH_2), 1.73 (s, 3H, CH_3CN).

RESULTS AND DISCUSSION

The reaction of PNP with a slight excess of $RuCl_2(PPh_3)_3$ in refluxing methylene chloride leads to the neutral complex $RuCl_2(PNP)(PPh_3)$ (**1**) as an orange, air-stable, diamagnetic crystalline solid in excellent yield. Two IR bands (KBr pellet) are observed at 1599 and 1565 cm^{-1} which are characteristic of a coordinated pyridine [4]. In addition, a weak band at 328 cm^{-1} is indicative of two mutually *trans* chlorides, according to the interpretation given by Bianchini and coworkers for an analogous ruthenium complex [10]. The $^{31}P\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ exhibits a doublet at 35.3 ppm and a triplet at 41.8 ppm ($^2J_{PP}$ = 28.6 Hz), these chemical shifts falling in the range expected for coordinated PNP and PPh_3 ligands [7,11]. The two PNP phosphorus atoms are thus chemically equivalent and coupled to the phosphorus of a triphenylphosphine located in a *cis* position, as indicated by the magnitude of the coupling constant.

The ^1H NMR spectrum shows a triplet at 4.54 ppm attributed to the methylene protons (Fig. 1(a)). This is typical of an $A_2A'_2XX'$ system where each proton is virtually coupled to the two equivalent phosphorus nuclei ($|{}^2J_{HP}+{}^4J_{HP'}| = 9.7$ Hz). Such a situation has been frequently described in the literature concerning other PNP coordination compounds [6, 7] and is characteristic of a meridional coordination, where the two protons of each CH_2 moiety are chemically equivalent. Therefore the molecule possesses a plane of symmetry that comprises the three donor atoms of PNP, so that PPh_3 necessarily lies *trans* to the pyridine nitrogen.

The X-ray diffraction study of **1** · CH_3CN confirms this interpretation (Fig. 2) [12]. Selected bond distances and angles are given in Table 1. **1** appears as a monomeric complex with a somewhat distorted octahedral geometry around the ruthenium. Importantly, it is confirmed that the PNP ligand coordinates the metallic center in a tridentate meridional mode, with the triphenylphosphine ligand *trans* to pyridine. It is probable that the alternative *cis* configuration would be unstable because of an increased steric hindrance between the phenyl groups on the three phosphorus atoms.

All Ru—P (2.340–2.368 Å), Ru—Cl (2.412, 2.426 Å) and Ru—N (2.168(2) Å) distances lie within the normal range [13]; in particular, the ruthenium–phosphorus and ruthenium–chloride bond lengths compare well with the corresponding bond lengths observed by Bianchini *et al.* in the closely related complex *mer*-$RuCl_2[nPrN(CH_2CH_2PPh_2)_2](PPh_3)$ [14]. The values of the P(1)—Ru—N and P(2)—Ru—N bond angles (78.60, 79.31°) are also very close to Bianchini's data (79.45, 80.69°), or to the value of 80.3(1)° found by DuBois *et al.* [7] for the N—Pd—P angle in the cationic complex $[Pd(PNP)(PEt_3)]^{2+}$. The ruthenium atom lies approximately in the plane defined by the nitrogen and the three phosphorus atoms, with a deviation of only 0.018 Å. The four ligands *cis* to PPh_3 are all bent away from PPh_3, as illustrated by the reduced Cl(1)—Ru—Cl(2) angle (171.81(3)°) and the even smaller P(1)—Ru—P(2) angle (157.90(3)°). A large Cl(2)—Ru—P(2) angle of 95.49(3)° is observed, while the Cl(1)—Ru—P(2) angle is normal (88.17(3)°). The reason for this is probably that Cl(2) is sterically hindered by C(49) and therefore bent away from P(2). These considerations of the bond distances and angles in $RuCl_2(PNP)(PPh_3)$ show that the molecule is sterically congested, as seven phenyl groups and two chlorides are forced together in close proximity. In comparison, the $RuCl_2[nPrN(CH_2CH_2PPh_2)_2](PPh_3)$ and $[Pd(PNP)(PEt_3)]^{2+}$ complexes suffer less steric

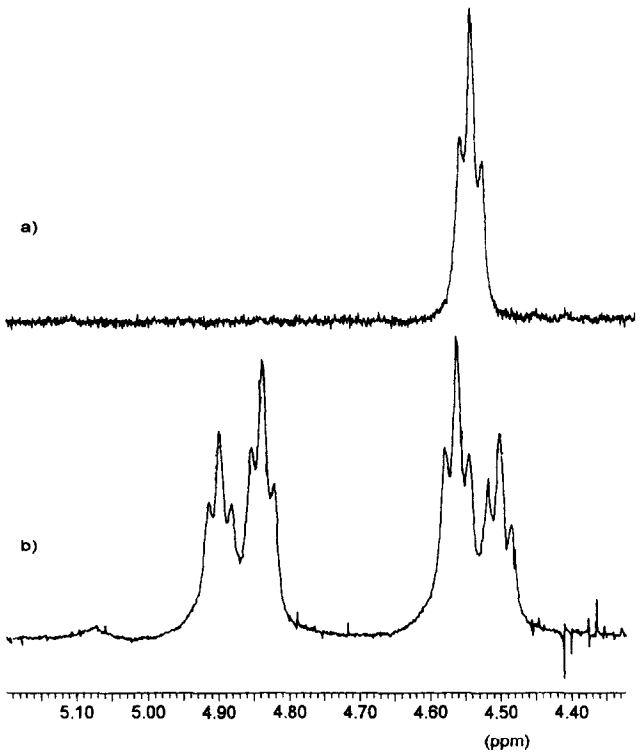


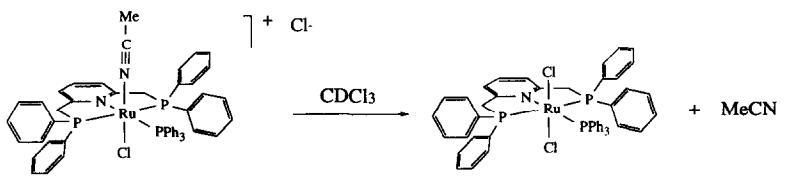
Fig. 1. ^{1}H NMR signals of the PNP methylene protons in $CDCl_3$; (a) complex **1**; (b) complex **2**.

hindrance, probably because in the first case nPrN($CH_2CH_2PPh_2$)$_2$ is more flexible than PNP, and in the second PEt_3 is less bulky than PPh_3 and further, the complex bears no axial ligand.

When the reaction of PNP on $RuCl_2(PPh_3)_3$ is performed in acetonitrile instead of methylene chloride and at higher temperature (MeCN reflux), yellow crystals of **2** are obtained in good yield, **1** now being present as a by-product. Like **1**, **2** is diamagnetic and stable in the air. Its elemental analysis is consistent with the formula $RuCl_2(MeCN)(PNP)(PPh_3)$. The value of the molar conductivity of **2** in acetonitrile is 106 Ω^{-1} cm^2 mol^{-1} at a 2×10^{-3} M concentration, which falls within the expected range (92–199 Ω^{-1} cm^2 mol^{-1}) for a 1:1 electrolyte in this solvent [15]. The FAB-MS spectrum of **2** (NBA matrix) exhibits a signal at m/z 915.1; this value and the isotope profile structure fit a molecular peak [M—Cl]$^+$ formulated as $RuCl(MeCN)(PNP)(PPh_3)^+$. The IR spectrum of **2** shows two bands at 2276 and 2351 cm^{-1} characteristic of an end-on coordination of the acetonitrile ligand [7, 16]. Further, the bands in the 1500 1600 cm^{-1} region are very similar to those displayed in the spectrum of **1** (1598 and 1562 cm^{-1}), indicative of a coordination of Ru^{II} by the central pyridine moiety.

The $^{31}P\{^1H\}$ NMR spectrum of **2** resembles very much that of **1** (doublet at 31.3 ppm and triplet at 42.0 ppm; $^2J_{PP}$ = 26.5 Hz). However the PNP methylene signals now appear in the ^{1}H NMR spectrum as a set of two doublets of triplets centered at 4.53 ppm and 4.86 ppm, corresponding to an AA′BB′XX′ system [6a] (Fig. 1(b)). The two methylene protons borne by each carbon are no longer equivalent, and a *gem* coupling constant of 16.9 Hz is observed. Each of them is virtually coupled to the phosporus atoms, with slightly different coupling constants ($|^2J_{HP}+{}^4J_{HP'}| = 8.9$ and 9.4 Hz). The plane of symmetry observed for **1** (*vide supra*) is lost, indicating the presence of two different axial ligands.

When **2** is allowed to stand in $CDCl_3$ for 24 h, the solution turns from yellow to orange and orange crystals form. ^{31}P and ^{1}H NMR analyses indicate that the totality of **2** has been converted into **1**:



2
(hypothetical structure)

1

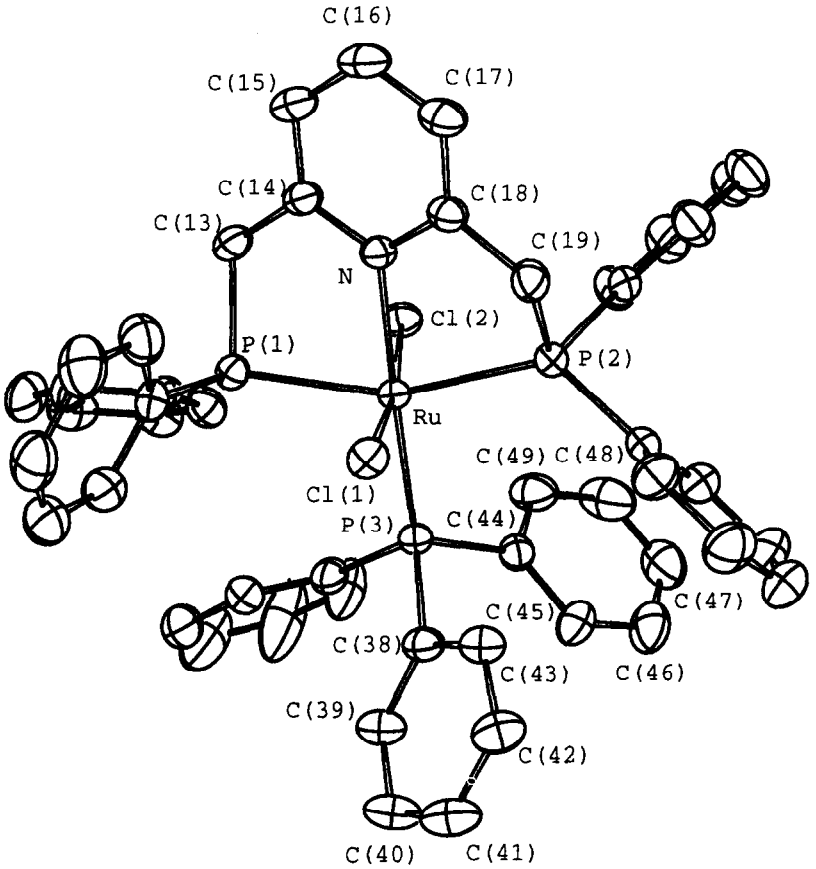


Fig. 2. ORTEP drawing of $RuCl_2(PNP)(PPh_3) \cdot CH_3CN$ showing 30% probability thermal ellipsoids and the atom-numbering scheme. MeCN and hydrogen atoms are omitted for clarity.

Table 1. Selected bond distances (Å) and bond angles (°) for $\mathbf{1} \cdot CH_3CN$

Ru—Cl(1)	2.4122(7)	Ru—N	2.168(2)
Ru—Cl(2)	2.4263(7)	P(1)—C(13)	1.842(3)
Ru—P(1)	2.3682(7)	C(14)—N	1.360(3)
Ru—P(2)	2.3641(7)	N—C(18)	1.355(3)
Ru—P(3)	2.3401(7)	C(19)—P(2)	1.835(3)
Cl(1)—Ru—Cl(2)	171.81(3)	N—Ru—P(2)	78.60(6)
Cl(1)—Ru—P(1)	89.65(3)	N—Ru—P(3)	177.62(6)
Cl(1)—Ru—N	86.24(6)	P(2)—Ru—P(3)	99.17(2)
Cl(1)—Ru—P(2)	88.17(3)	Ru—P(1)—C(13)	98.21(8)
Cl(1)—Ru—P(3)	92.88(2)	Ru—N—C(18)	120.4(2)
Cl(2)—Ru—P(1)	84.20(3)	Ru—P(2)—C(19)	97.32(8)
Cl(2)—Ru—N	87.31(6)	Ru—P(3)—C(38)	118.98(9)
Cl(2)—Ru—P(2)	95.49(3)	P(1)—C(13)—C(14)	112.0(2)
Cl(2)—Ru—P(3)	93.76(3)	C(18)—C(19)—P(2)	108.4(2)
P(1)—Ru—N	79.31(6)	C(13)—C(14)—N	117.0(2)
P(1)—Ru—P(2)	157.90(3)	N—C(18)—C(19)	116.7(2)
P(1)—Ru—P(3)	102.90(2)	C(14)—N—C(18)	118.4(2)

A straightforward interpretation of this observation is that the chloride anion and the acetonitrile compete as a ligand for ruthenium, the competition being in favour of MeCN when it is used as the solvent, and in favour of Cl^- in a solvent of low polarity such as chloroform.

CONCLUSION

We have prepared and characterized two new ruthenium(II) complexes with the PNP ligand where it is found to be bound in a meridional way to the metal. An X-ray crystallographic study has shown

that the presence of triphenylphosphine as an ancillary ligand induces important steric constraints in these complexes. Experiments are under way in our laboratory to study the catalytic properties of these and similar complexes and in particular those of the chiral analogues of the PNP for asymmetric catalysis. It will be of interest to compare our findings with the closely related results reported by Zhang *et al.* in a publication that appeared during the preparation of this manuscript [17].

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REFERENCES

1. J. M. Brown, *Chem. Soc. Rev.* 1993, **22,** 25.
2. (a) M. A. Bennett and T. W. Matheson, in *Comprehensive Organometallic Chemistry* (Edited by G. Wilkinson, F. G. A. Stone, E. W. Abel), vol. 4, 931 Pergamon Press, Oxford (1986); (b) A. Spencer, in *Comprehensive Coordination Chemistry* (Edited by G. Wilkinson, R. D. Gillard and J. A. McCleverty), vol. 6, p. 229, Pergamon Press, Oxford (1987); (c) R. Noyori, *Asymmetric Catalysis In Organic Synthesis*, J. Wiley & Sons, New York (1994); (d) D. Rose, J. D. Gillett, R. P. Richardson and G. Wilkinson, *J. Chem. Soc.* (*A*) 1969, 2610.
3. (a) R. Sablong, C. Newton, P. Dierkes and J. A. Osborn, *Tetrahedron Lett.* 1996, **37,** 4933; (b) R. Sablong and J. A. Osborn, *Tetrahedron Lett.* 1996, **37,** 4937.
4. W. V. Dahlhoff and S. M. Nelson, *J. Chem. Soc.* (*A*) 1971, 2184.
5. (a) P. Giannoccaro, G. Vasapollo and A. Sacco, *J. Chem. Soc., Chem. Commun.* 1980, 1136; (b) G. Vasapollo, P. Giannoccaro, C. F. Nobile and A. Sacco, *Inorg. Chim. Acta* 1981, **48,** 125; (c) P. Giannoccaro, G. Vasapollo, C. F. Nobile and A. Sacco, *Inorg. Chim. Acta* 1982, **61,** 69; (d) A. Sacco, P. Giannoccaro and G. Vasapollo, *Inorg. Chim. Acta* 1984, **83,** 125.
6. (a) G. Vasapollo, C. F. Nobile and A. Sacco, *J. Organomet. Chem.* 1985, **296,** 435; (b) A. Sacco, G. Vasapollo, C. F. Nobile, A. Piergiovanni, M. A. Pellinghelli and M. Lanfranchi, *J. Organomet. Chem.* 1988, **356,** 397.
7. B. D. Steffey, A. Miedaner, M. L. Maciejewski-Farmer, P. R. Bernatis, A. M. Herring, V. S. Allured, V. Carperos and D. L. DuBois, *Organometallics* 1994, **13,** 4844.
8. (a) C. Newton, Doctorate Thesis, Université Louis Pasteur, Strasbourg, France (1995); (b) J. K. Whitesell, *Chem. Rev.* 1989, **89,** 1581.
9. P. S. Hallman, T. A. Stephenson and G. Wilkinson, *Inorg. Synth.* 1970, **12,** 238.
10. C. Bianchini, P. Innocenti, D. Masi, M. Peruzzini and F. Zanobini, *Gazz. Chim. Ital.* 1992, **122,** 461.
11. J. F. Nixon and A. Pidcock, *Annual Review of NMR Spectroscopy* (Edited by E. F. Mooney), vol. 2, 345. Academic Press, London (1969).
12. Crystal data for $\mathbf{1}\cdot CH_3CN$: $C_{51}H_{45}N_2P_3Cl_2Ru$, $M = 950.8$, triclinic, space group $P\text{-}1$, $a = 10.663$ (3), $b = 13.710$ (4), $c = 17.300$ (5) Å, $\alpha = 68.26$ (2), $\beta = 87.05$ (2), $\gamma = 71.70$ (2)°, $V = 2224.4$ Å^3, $Z = 2$, $r_{calcd} = 1.420$ g cm^{-3}. A total of $10225 + h \pm k \pm l$ reflections was collected on an orange crystal of dimensions $0.40 \times 0.38 \times 0.20$ mm^3, using a Nonius CAD4-F diffractometer, graphite monochromated Mo-K_α ($\lambda = 0.7107$ Å), $\mu = 6.091$ cm^{-1}, $2 < \theta < 26$°, room temperature. 7188 unique reflections having $I > 3\sigma(I)$ were used to determine (heavy atom method) and refine the structure (refinements against $|F|$). Hydrogen atoms were introduced as fixed contributors, C—H = 0.95 Å, B(H) = 1.3*Beqv(C) Å^2. 532 parameters. Final results: $R(F) = 0.030$, $Rw(F) = 0.044$, GOF = 1.084, maximum residual electronic density = 0.14 eÅ^{-3}. For all computations the Enraf-Nonius MolEN (C.K. Fair in *MolEN: An Interactive Intelligent System for Crystal Structure Analysis*. Nonius, Delft, The Netherlands (1990)) package was used running on a DEC Alpha3600S computer. Further details of the crystal structure investigation are available on request from the Director of Cambridge Crystallographic Data Center, 12 Union Road, GB-Cambridge CB2 1EZ (U.K.), on quoting the full journal citation. Complete listings of crystal data, atomic coordinates, thermal parameters, bond distances and angles have been deposited with the Cambridge Crystallographic Data Center.
13. A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.* 1989, S1.
14. C. Bianchini, D. Masi, M. Peruzzini, A. Romerosa and F. Zanobini, *Acta Cryst.* 1995, **C15,** 2514.
15. W. J. Geary, *Coord. Chem. Rev.* 1971, **7,** 81.
16. (a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn, p. 280. J. Wiley & Sons, New York (1986); (b) B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.* 1977, **23,** 1.
17. Q. Jiang, D. Van Plew, S. Murtuza and X. Zhang, *Tetrahedron Lett.* 1996, **37,** 797.