

*Journal of Organometallic Chemistry*, 181 (1979) 255–269  
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## PLATINUM-PROMOTED CYCLIZATION REACTIONS OF AMINO OLEFINS

### II \*. REGIO- AND STEREOSELECTIVITY IN THE CYCLIZATION REACTIONS OF C-METHYL SUBSTITUTED PENT-4-ENYLAMINES

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(Received June 1st, 1979)

#### Summary

The compounds 1-, 2- and 3-methylpent-4-enylamine cyclize, in a reaction medium containing  $[\text{PtCl}_4]^{2-}$ , to the corresponding *cis*- and *trans*-dimethylpyrrolidines showing marked regio and stereoselectivity effects. The following cyclization reactions are also reported: a) that of hex-4-enylamine which gives a mixture of 2-ethylpyrrolidine and 2-methylpiperidine, b) that of 2,2-dimethylpent-4-enylamine which produces 2,4,4-trimethylpyrrolidine and c) that of 2,2-dimethylhex-4-enylamine which results in the formation of 2-ethyl-4,4-dimethylpyrrolidine and 2-methyl-5,5-dimethylpiperidine.

The X-ray crystal structures of *trans*- $[\text{PtCl}_2(\text{amine})(\text{Et}_3\text{P})]$  (amine = *cis*-2,4-dimethylpyrrolidine and *cis*-2,3-dimethylpyrrolidine) are reported.

#### Introduction

It has recently been shown [1] that 5-amino-pent-1-ene,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_2-\text{CH}_2\text{NH}_2$ , (I), in acid solution in the presence of  $[\text{PtCl}_4]^{2-}$ , undergoes a cycliza-

\* Part I: see [1].

\*\* Dedicated to Joseph Chatt on the occasion of his 65th birthday. I wonder if he remembers that he introduced me to platinum-olefin chemistry on my very first day in his laboratory back in 1952. As he can see, this and many other interests he kindled during the following four years are still a source of inspiration to me.

TABLE I  
CYCLIZATION REACTIONS OF AMINO OLEFINS

Starting Material <sup>a</sup>	Medium	Reaction time (days)	Product(s)	Overall Yield (%)	Ratio of Products
II $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ (racemic)	1	11	{ VIII $\text{cis-HNCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CHCH}_3$ IX $\text{trans-HNCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CHCH}_3$ }	90	40 60
III $\text{CH}_2=\text{CHCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}_2$ (racemic)	1	8	{ X $\text{cis-HNCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CHCH}_3$ XI $\text{trans-HNCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CHCH}_3$ }	85	62 38
IV $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2$ (racemic)	1	21	{ XII $\text{cis-HNCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CHCH}_3$ XIII $\text{trans-HNCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CHCH}_3$ }	85	12 88
V $E\text{-CH}_3\text{CH}=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	2	67	{ XIV $\text{HNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ XV $\text{HNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3$ }	67	9 91
VI $\text{CH}_2=\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$	1	1-2	XVI $\text{HNCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CHCH}_3$	77	
VII $E\text{-CH}_3\text{CH}=\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$	1	25	{ XVII $\text{HNCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CHCH}_2\text{CH}_3$ XVIII $\text{HNCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CHCH}_3$ }	58	60 40

<sup>a</sup> When the same cyclization reactions were carried out starting from the pre-formed olefin complexes slightly shorter reaction times were observed.

tion reaction with formation of 2-methylpyrrolidine. Furthermore, it was observed [1] that *N*-alkyl substitution of the above substrate leads to the formation of both pyrrolidines and piperidines. Intramolecular nucleophilic attack of a free amino group on the coordinated double bond has been proposed [1] to explain this reaction course.

Panunzi et al. [2] have demonstrated that nucleophilic attack by an amine on a platinum(II)-olefin complex takes place in a highly stereospecific manner (*trans*-addition). Furthermore, Lazzaroni et al. [3] have shown that coordination of chiral olefins to platinum(II) results in the formation of diastereoisomers and that the extent of asymmetric induction depends on the proximity of the chiral center to the coordinated double bond and on the nature of the substituents on the chiral center.

In order to gain a better understanding of the mechanistic pathway and to evaluate the potential range of synthetic applications of this reaction, a number of *C*-substituted pent-4-enylamines were cyclized in a reaction medium containing  $[\text{PtCl}_4]^{2-}$ .

## Results and discussion

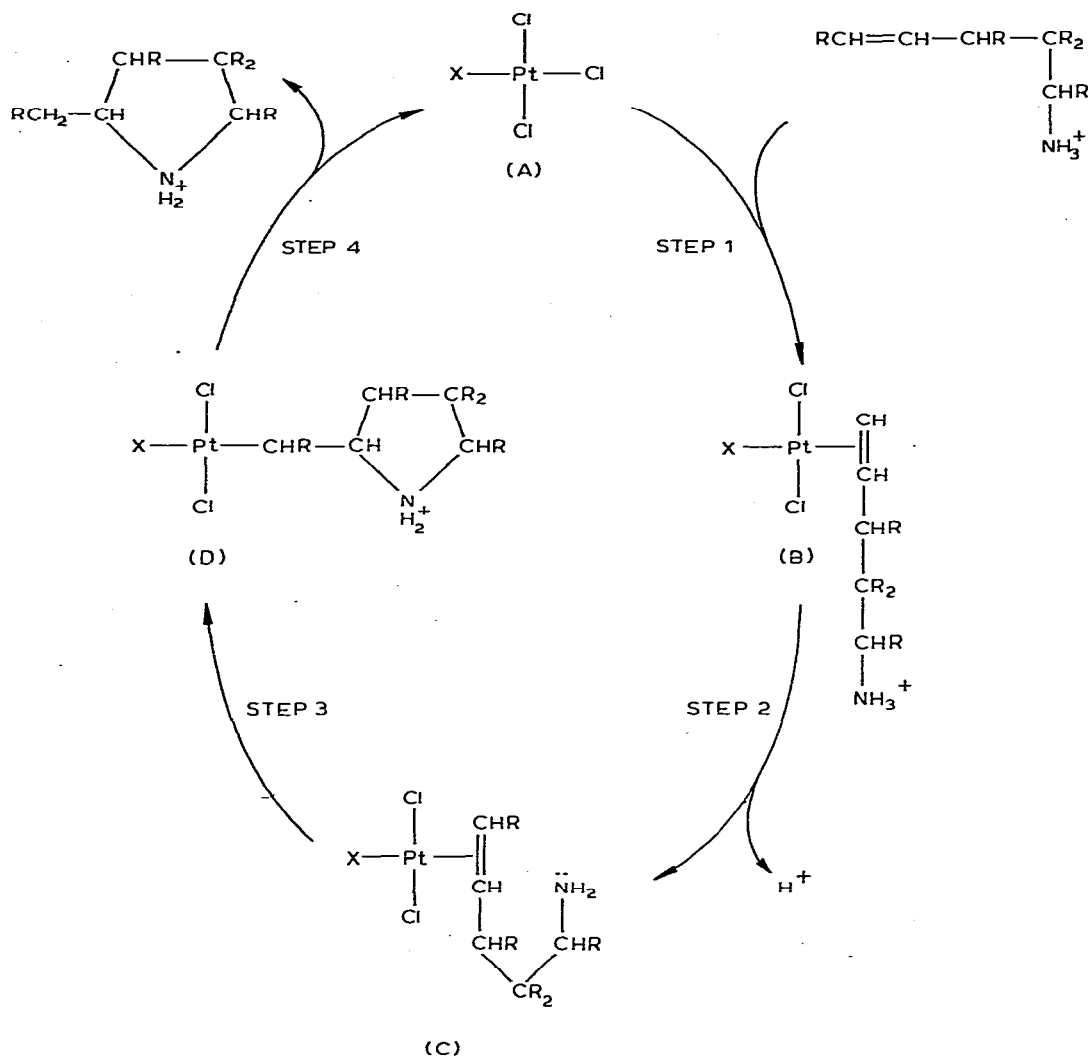
The results of the cyclization reactions on substrates II to VII are shown in table 1. As can be seen, these reactions show marked regio- and stereoselective effects.

In Part I a mechanistic pathway similar to that shown in scheme 1 was proposed. While there is no direct evidence to show whether in species A to D the reactive form is that with  $\text{X} = \text{Cl}^-$  or  $\text{H}_2\text{O}$ , it is presumed that the nucleophilic attack postulated in step 3 occurs more easily when complex C has the lower ionic charge [4].

Semi-quantitative studies of cyclization rates, starting either from  $[\text{PtCl}_4]^{2-}$  or from the pre-formed olefin complex of type B, indicate that step 1 is likely to be significantly faster than step 3. Furthermore, spectrophotometric data collected during the course of the reactions show the absence in solution of significant amounts of species of type D. As we expect step 2 to occur at speeds close to diffusion control, it appears likely that stereoselection occurs during step 3.

As shown in table 1, the cyclization of the terminal unsaturated substrates II, III, IV and VI takes place regiospecifically, only the pyrrolidine derivatives being formed in fair to high yields. Similar high regioselectivity has been observed in the attack of a nucleophile on the substituted carbon atom of a terminal olefin, e.g., in the reaction of amines with platinum(II) olefin complexes [5] and in the Wacker type oxidation of higher olefins [6]. These results are in agreement with the influence of the polarity of the double bond [7] and with the greater ease of formation of five membered rings [8]. It has also been observed that the sensitivity to steric effects in our system appears to be lower than that reported for the reaction of the platinum complexes mentioned above [5]. This is deduced from the observation that IV gives only pyrrolidines XII and XIII. This difference is likely to be due to the presence, in complexes of type C, of only small ligands (Cl and X) in addition to the olefin. Furthermore, the observation that the cyclization of pent-4-enylamine I [9] gives only

**SCHEME 1.** X = Cl<sup>-</sup> or H<sub>2</sub>O; R = H or CH<sub>3</sub>; the ionic of the complexes have been omitted for clarity.



2-methylpyrrolidine shows that the replacement of a hydrogen atom by one methyl group in positions 1, 2 or 3 does not alter the regioselectivity of the nucleophilic attack. On the other hand, the presence of a methyl group in position 5, i.e., on going from I to V or from VI to VII, drastically changes the regioselectivity of the attack which, in the case of V, is actually reversed. This inversion is likely to be due to a significant reduction in polarity of the double bond consequent upon terminal substitution which leaves steric control as the dominant factor.

The stereoselectivity of the cyclization reactions of II, III and IV will mainly depend upon:

- (i) the stereoselectivity of the nucleophilic attack,
- (ii) the diastereoface discrimination and

(iii) the relative activation energies for the cyclization reactions.

It seems reasonable to assume that the observed stereoselectivity does not arise from stereoselectivity in the nucleophilic attack. It has been shown [10] that nucleophilic attack of a free amine on an olefinic ligand in a complex of the type used in this work is stereospecific and corresponds to a *trans*-attack. More generally, *trans*-stereochemistry is a characteristic feature of hydroxy- [11] and alkoxypalladation reactions [12]. With regard to the diastereoface discrimination [13] arising from the presence of a chiral center in the substrate, one can interpret the lack of isomerization of *cis*-2,5-dimethylpyrrolidine, when left for days under the reaction conditions used for cyclization, as demonstrating the kinetic control of the composition of the reaction products. Thus, if the deductions about relative rates made earlier are correct, the diastereomeric composition of the species generated after step 2 should correspond to an equilibrium mixture. Support for this view is provided by the report [3] that diastereoface discrimination has been observed in complexes *cis*- or *trans*-[PtCl<sub>2</sub>-(PhCH<sub>2</sub>NH<sub>2</sub>)(olefin)] (olefin = chiral olefin), where thermodynamic equilibrium between diastereoisomers is rapidly achieved.

Furthermore, diastereoface discrimination, in this type of complex, decreases as the distance between the chirality center and the double bond increases [3]. In fact substrate IV, in which the chiral carbon atom is directly bound to the unsaturated carbon atom, undergoes cyclization with 88% stereoselectivity towards the *trans*-isomer XIII. For the other two substrates, II and III, stereoselectivity is much less pronounced and is in the opposite sense.

Unfortunately the very low solubility of complexes of the type [PtCl<sub>3</sub>(amino-olefin)]<sup>-</sup> prevents an NMR study which could establish the extent of diastereoface discrimination (e.g., see ref. 3).

Furthermore, the lack of the literature data on the relative thermodynamic stabilities of the *cis*- and *trans*-isomeric pairs of the dimethylpyrrolidines, does not permit the analysis of models for possible "product like" transition states. For these reasons a discussion concerning the relative influence of factors (ii) and (iii) on the stereoselectivity of the cyclization reactions of substrates II, III and IV appears at present unwarranted. It is, however, worthy of note that while, in the mercury promoted [14] cyclization reactions of substrates II and III, the degree of stereoselectivity is almost identical with that of the platinum promoted reactions, the mercury promoted reaction of substrate IV shows only a very low stereoselectivity (57% of the *trans*-isomer).

Despite the potentially catalytic nature of this platinum promoted cyclization reaction, the preparative application is, at present, limited by the rather long reaction times. Cyclization rates, however, strongly depend on the substrate. Taking pent-4-enylamine I as reference [1], methyl substitution at position 5 slows down the reaction, whereas substitution at position 1 has almost no influence. An increase in reaction rate by a factor of 2-3 is observed on going from V to VII. Likewise, in the series I, III and VI mono- or disubstitution at position 2 causes an increase in reaction rate by factors of 2 and 8 respectively. The effect of methyl substitution at the internal carbon atoms on rates of ring closure is well established and known as the Thorpe-Ingold effect [15].

Qualitative conformational analysis around the C(2)-C(3) bond in I (fig. 1) suggests that the energy minimum should correspond to conformer  $\gamma$ ; this,

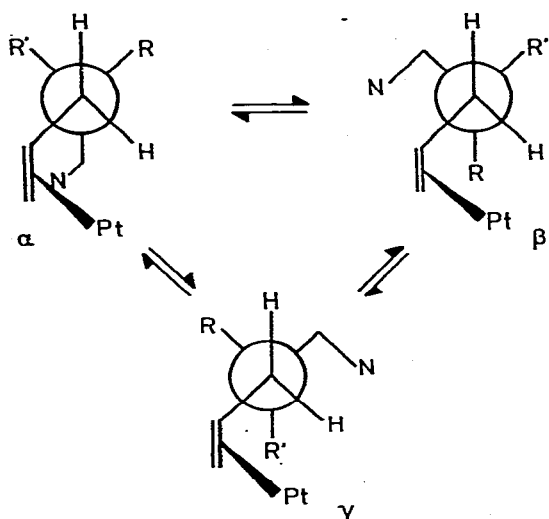


Fig. 1. Newman projections of some conformations of complexes  $[\text{PtCl}_3(\text{CH}_2=\text{CH}-\text{CH}_2-\text{CRR}'-\text{CH}_2-\text{NH}_3^+)]$  (The group  $\text{PtCl}_3$  is indicated as Pt).  $\text{R} = \text{R}' = \text{H}$  (I);  $\text{R} = \text{H}$ ,  $\text{R}' = \text{CH}_3$  (III);  $\text{R} = \text{R}' = \text{CH}_3$  (VI).

however, has the most unfavourable conformation for cyclization. On the other hand, in VI energy differences between conformers should be smaller and for conformers  $\alpha$  and  $\beta$  cyclization is favoured. The situation is less clear for III, for which, because of the existence of a chiral center in the olefinic ligand, the existence of two diastereomers must be taken into account. However, if one considers one diastereoface of the olefin, e.g., that given in fig. 1, which gives rise to the formation of the more abundant pyrrolidine X, one can envisage, also in this case, the conformer  $\beta$  as having the lowest energy as well as being favoured for cyclization. The *cis*- and *trans*-isomeric forms of 2,5-dimethylpyrrolidine, VIII and IX respectively, were identified through their  $^1\text{H}$  NMR spectra (see Experimental Section). As it did not prove possible to assign *cis* or *trans* configurations to the pair of products 2,3-dimethylpyrrolidine, X and XI respectively, and of 2,4-dimethylpyrrolidine, XII and XIII respectively, one of the fractions of the first pair and one of the second pair were reacted with *sym-trans*- $[\text{Pt}_2\text{Cl}_4(\text{Et}_3\text{P})_2]$  and crystal structures of the complexes obtained determined by X-ray diffraction. The two complexes proved to be *trans*- $[\text{PtCl}_2(\text{Et}_3\text{P})(\text{cis-2,3-dimethylpyrrolidine})]$ , XIX, and *trans*- $[\text{PtCl}_2(\text{Et}_3\text{P})(\text{cis-2,4-dimethylpyrrolidine})]$ , XX.

Perspective views of the two molecules are shown in fig. 2. Interatomic bond lengths and angles are given in table 2.

In both molecules the platinum atom has square planar coordination with the donor atoms being the two chlorine atoms in *trans* positions, the phosphorus atom of the triethylphosphine ligand and the nitrogen atom of the pyrrolidine ligand. In both compounds the individual donor atoms are displaced by less than  $0.06 \text{ \AA}$  from the coordination plane of the platinum atom, and the more significant deviation from a regular square-planar arrangement concerns the  $\text{Cl}-\text{Pt}-\text{Cl}$  angle ( $174^\circ$ ).

Corresponding bond lengths and valence angles in XIX and XX agree well and

TABLE 2

INTERATOMIC BOND LENGTHS (Å) AND ANGLES (°) FOR COMPLEXES XIX AND XX  
(Standard deviations are given in parentheses)

	XIX	XX
Pt—Cl(1)	2.306(3)	2.294(2)
Pt—Cl(2)	2.296(4)	2.293(2)
Pt—P	2.242(4)	2.238(2)
Pt—N	2.139(12)	2.133(7)
N—C(1)	1.44(2)	1.48(1)
C(1)—C(2)	1.58(3)	1.51(1)
C(2)—C(3)	1.55(2)	1.54(1)
C(3)—C(4)	1.44(3)	1.55(2)
C(4)—N	1.59(2)	1.47(1)
C(1)—C(5)	1.48(3)	1.52(1)
C(2)—C(6)	1.42(3)	—
C(3)—C(6)	—	1.51(2)
P—C(7)	1.806(12)	1.817(8)
P—C(9)	1.816(13)	1.817(9)
P—C(11)	1.818(14)	1.824(9)
C(7)—C(8)	1.51(2)	1.53(1)
C(9)—C(10)	1.48(2)	1.54(1)
C(11)—C(12)	1.51(2)	1.51(2)
Cl(1)—Pt—Cl(2)	173.8(1)	173.9(1)
Cl(1)—Pt—P	93.4(1)	92.6(1)
Cl(1)—Pt—N	89.3(3)	89.1(2)
Cl(2)—Pt—P	90.8(1)	91.7(1)
Cl(2)—Pt—N	86.6(3)	86.6(2)
P—Pt—N	177.3(3)	178.3(2)
Pt—N—C(1)	117.6(10)	117.0(5)
Pt—N—C(4)	115.1(8)	117.4(6)
Pt—P—C(7)	115.3(5)	115.9(3)
Pt—P—C(9)	112.2(5)	112.9(3)
Pt—P—C(11)	114.5(5)	113.9(3)
C(7)—P—C(9)	102.2(6)	102.1(4)
C(7)—P—C(11)	104.8(6)	104.6(4)
C(9)—P—C(11)	106.9(7)	106.3(4)
P—C(7)—C(8)	115.7(9)	114.6(6)
P—C(9)—C(10)	115.5(11)	113.4(6)
P—C(11)—C(12)	115.9(10)	117.5(6)
N—C(1)—C(2)	107.7(12)	103.4(7)
C(1)—C(2)—C(3)	104.6(14)	103.9(8)
C(2)—C(3)—C(4)	105.7(14)	102.4(7)
C(3)—C(4)—N	105.2(12)	108.1(7)
C(4)—N—C(1)	104.8(11)	106.1(7)
N—C(1)—C(5)	109.3(15)	110.5(7)
C(5)—C(1)—C(2)	114.1(17)	114.8(9)
C(1)—C(2)—C(6)	119.0(17)	—
C(6)—C(2)—C(3)	113.9(17)	—
C(2)—C(3)—C(6)	—	113.6(9)
C(6)—C(3)—C(4)	—	112.0(8)

their values appear to be normal. The interbond angles at the phosphorus atom show the usual departures from the ideal tetrahedral value. The P—C—C as well as the Pt—N—C angles are greater than  $109^{\circ}28'$ , presumably because of intramolecular overcrowding. The same effect is likely to be responsible for the large deviation in the C(1)—C(2)—C(6) angle in XIX since C(5) and C(6) are nearly eclipsed (vide infra).

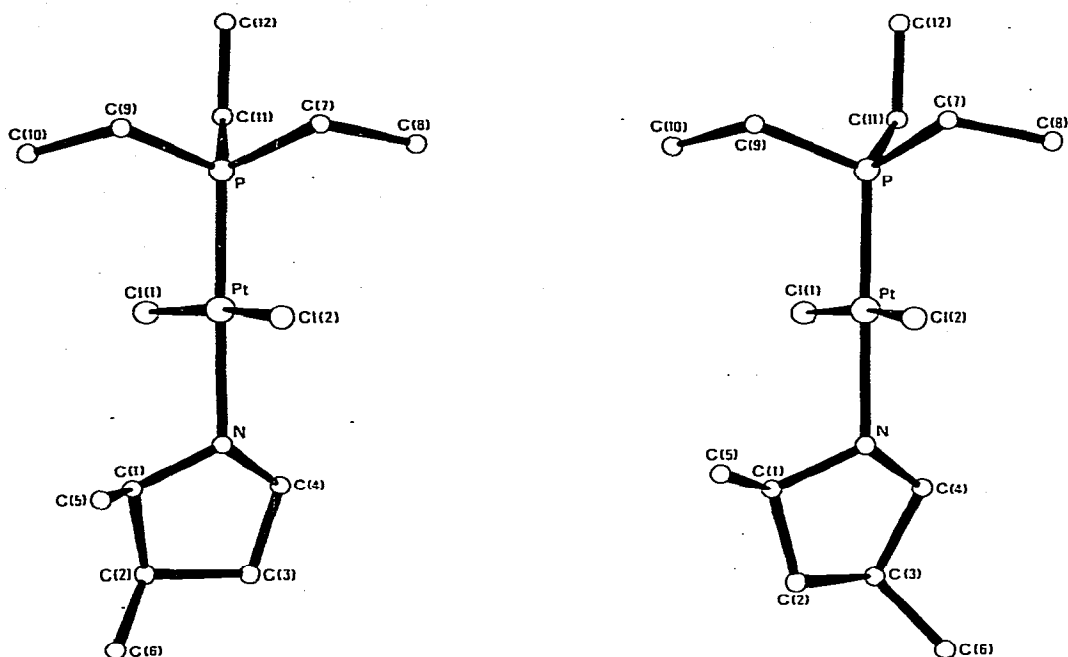


Fig. 2. Computer generated drawings of the molecules of *trans*-[PtCl<sub>2</sub>(*cis*-2,3-dimethylpyrrolidine)(Et<sub>3</sub>P)], XIX, and *trans*-[PtCl<sub>2</sub>(*cis*-2,4-dimethylpyrrolidine)(Et<sub>3</sub>P)], XX.

The arrangements of the triethylphosphine and pyrrolidine ligands are rather similar in XIX and XX as seen from the values of the torsion angles reported in table 3.

The *cis* isomeric forms of 2,3- and 3-4-dimethylpyrrolidine are present in complexes XIX and XX respectively. In both structures the two methyl substituents are in *trans* position to the PtCl<sub>2</sub>(PEt<sub>3</sub>) moiety which is in the equatorial position. There are, however, significant conformational differences in the pyrrolidine ligands in the two complexes.

The torsion angles concerning the pyrrolidine derivatives are reported in table 4, together with some ring torsion angles of the molecule of cyclopentane [16]. The three sets of values A, B and C of Table 4 correspond to the symmetric conformations of cyclopentane which are closer to those found in the two pyrrolidine derivatives.

The *cis*-2,3-dimethylpyrrolidine ligand in XIX has an envelope-like conformation with C(4) at the flap-tip. The atoms N, C(1), C(2) and C(3) are almost exactly coplanar while C(4) is 0.5 Å out of their best plane; this plane makes a dihedral angle of 34° with the plane through C(3), C(4) and N. The *cis*-2,4-dimethylpyrrolidine ligand in XX has a conformation which could be regarded as intermediate between an envelope form with C(1) at the tip and a chair-like form with maximum puckering occurring at the carbon atoms C(1) and C(2). These two atoms are 0.4 and 0.2 Å out of the plane through C(3), C(4), N, lying on opposite sides.

The two complexes, which have three chiral atoms (N, C(1) and C(2) in XIX and N, C(1) and C(3) in XX), are present in the crystals in the racemic forms,



TABLE 3

RELEVANT TORSION ANGLES DEFINING THE ARRANGEMENTS OF THE LIGANDS IN XIX AND XX

	XIX	XX
Cl(1)—Pt—P—C(7)	+148.7(5)	+157.8(3)
Cl(1)—Pt—P—C(9)	-95.2(5)	-85.0(3)
Cl(1)—Pt—P—C(11)	+27.0(6)	+36.4(4)
Cl(2)—Pt—P—C(7)	-35.9(5)	-26.6(3)
Cl(2)—Pt—P—C(9)	+80.3(5)	+90.6(3)
Cl(2)—Pt—P—C(11)	-157.6(6)	-147.9(4)
Pt—P—C(7)—C(8)	-61.0(10)	-61.1(7)
Pt—P—C(9)—C(10)	+56.8(11)	+62.4(6)
Pt—P—C(11)—C(12)	+178.5(10)	+179.7(6)
Cl(1)—Pt—N—C(1)	+63.0(10)	+68.0(5)
Cl(1)—Pt—N—C(4)	-61.2(9)	-59.9(6)
Cl(2)—Pt—N—C(1)	-112.4(10)	-107.6(5)
Cl(2)—Pt—N—C(4)	+123.4(9)	+124.5(6)

the two enantiomers in each case being related by the crystallographic centre of symmetry. Coordinates and torsion angle signs [17] given in the tables refer to the N(S) : C(1)(S) : C(2)(S) configuration for XIX and to the N(S) : C(1)(S) : C(3)(R) configuration for XX [18].

Short contacts are observed between atoms of centrosymmetrically related molecules both of XIX and XX: Cl(2)⋯N = 3.440(11) Å in the crystal of XIX; Cl(2)⋯N' = 3.495(8) Å in the crystal of XX. These short contacts are probably due to Cl⋯H—N hydrogen bonds. The packings for XIX and XX are shown in Fig. 3.

TABLE 4

TORSION ANGLES CONCERNING THE TWO DIMETHYLPYRROLIDINES (DMP) X AND XII<sup>a</sup>

	X	XII	A	B	C
N—C(1)—C(2)—C(3)	-1.0(16)	+40.5(9)	0.0	+40.3	+42.3
C(1)—C(2)—C(3)—C(4)	+22.5(17)	-28.8(9)	+25.0	-25.0	-34.3
C(2)—C(3)—C(4)—N	-33.9(15)	+7.3(9)	-40.3	0.0	+13.2
C(3)—C(4)—N—C(1)	+33.6(15)	+17.7(8)	+40.3	+25.0	+13.2
C(4)—N—C(1)—C(2)	-18.6(14)	-36.1(8)	-25.0	-40.3	-34.3
Pt—N—C(1)—C(2)	-147.8(9)	-169.3(5)			
Pt—N—C(1)—C(5)	+87.7(15)	+67.4(8)			
C(4)—N—C(1)—C(5)	-143.1(14)	-159.4(7)			
C(5)—C(1)—C(2)—C(3)	+120.5(18)	+160.9(9)			
N—C(1)—C(2)—C(6)	-129.5(19)	—			
C(5)—C(1)—C(2)—C(6)	-8.0(27)	—			
C(1)—C(2)—C(3)—C(6)	—	-149.9(9)			
C(6)—C(2)—C(3)—C(4)	+154.0(17)	—			
C(6)—C(3)—C(4)—N	—	+129.4(8)			
C(3)—C(4)—N—Pt	+164.2(10)	+150.7(5)			

<sup>a</sup> Ring torsion angles of the symmetric forms, envelope ( $C_s$  symmetry) and half-chair ( $C_2$ -symmetry), encountered along the strain-free pseudorotation circuit of cyclopentane [16] closer to those experimentally found, are also reported for comparison: (obviously the molecule of cyclopentane would have a fifth carbon atom in place of nitrogen) A, envelope with C(4) at the tip; B, envelope with C(1) at the tip; C, half-chair with maximum puckering at C(1)—C(2).

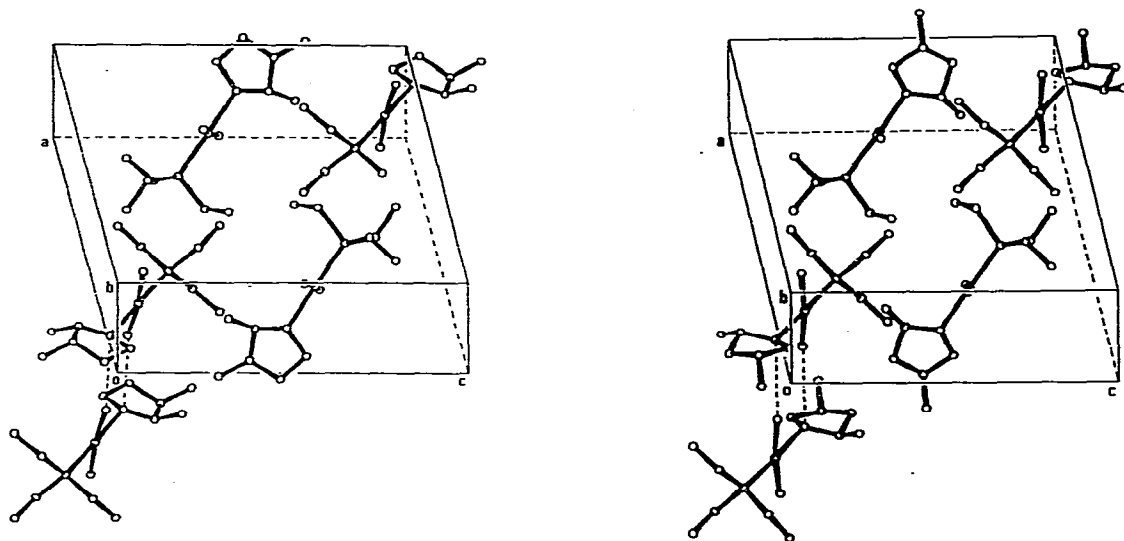


Fig. 3. Packing of the molecules in the structures of XIX and XX. The hydrogen bonds  $\text{NH}\cdots\text{Cl}$  are shown by broken lines.

## Experimental section

Physical measurements and gas-chromatographic separations were carried out as described previously [1].

The following organic compounds were prepared either as indicated in the appropriate reference or as described below.

*1-Methylpent-4-enylamine, II*, (b. pt. 115–116°C) was prepared from 1-hexen-5-one (Fluka product, purum), via the corresponding oxime, according to the procedures described by Vogel [19]. IR ( $\text{cm}^{-1}$ )  $\nu(\text{NH}) = 3340\text{m}, 3270\text{m}; \nu(\text{C}=\text{C}) = 1630\text{s}$ .  $^1\text{H}$  NMR. ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 6.2–5.5 (m, 1 H), 5.2–4.8 (m, 2 H), 2.9 (sextet 1 H,  $J$  6.0 Hz), 2.4–1.9 (m, 2 H), 1.8–1.0 (m, 7 H) which includes 1.15 (d, 3 H,  $J$  6.0 Hz), and 1.0 (s, 2 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 138.56, 114.56, 46.40, 38.80, 30.68, 23.27.

*2-Methylpent-4-enylamine, III*, (b. pt. 115–116°C) was prepared by the procedure described by Cottin [20] starting from ethyl 2-cyanopropanoate (Fluka product, pract.). IR ( $\text{cm}^{-1}$ )  $\nu(\text{NH}) = 3350\text{m}, 3260\text{m}; \nu(\text{C}=\text{C}) = 1625\text{s}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 6.15–5.45 (m, 1 H), 5.2–4.8 (m, 2 H), 2.85–1.2 (m, 5 H), 1.1 (s, 2 H), 0.9 (d, 3 H,  $J$  6.0 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 136.74, 116.20, 46.99, 38.86, 34.90, 17.29.

*3-Methylpent-4-enylamine, IV*, (b. pt. 115–116°C) was prepared from 3-methyl-pent-4-enal, obtained as described by Vig et al. [21], via the corresponding oxime as described for II. IR ( $\text{cm}^{-1}$ )  $\nu(\text{NH}) = 3360\text{ m}, 3280\text{m}; \nu(\text{C}=\text{C}) = 1635\text{s}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 6.1–5.4 (m, 1 H), 5.2–4.75 (m, 2 H), 2.7 (t, 2 H,  $J$  7.3 Hz), 2.25 (quintet, 1 H,  $J$  7.3 Hz), 1.7–1.2 (m, 4 H) which included 1.3 (s, 2 H), and 1.0 (d, 3 H,  $J$  7.2 Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 144.41, 112.69, 40.75, 40.16, 35.74, 20.41.

*E-Hex-4-enylamine, V*, (b. pt. 29°C/11 mm) was prepared starting from *trans*-hex-4-en-1-ol, prepared by the method of Crombie and Harper [22], via

the Gabriel synthesis on the tosylate [23]; the unsaturated amine being liberated by standard procedures [24]. IR ( $\text{cm}^{-1}$ )  $\nu(\text{NH}) = 3360\text{m}, 3280\text{m}; \nu(\text{C}=\text{C}) = 1675\text{m}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 5.9–5.1 (m, 2 H), 2.7 (t, 2 H,  $J$  6.7 Hz), 2.3–1.2 (m, 7 H), 1.05 (s, 2 H).

*2,2-Dimethylpent-4-enylamine*, VI, [9] was prepared by the  $\text{LiAlH}_4$  reduction [25] of the corresponding nitrile obtained from isobutyronitrile condensation with allyl chloride according to the procedure of Ziegler and Ohlinger [26].

IR ( $\text{cm}^{-1}$ )  $\nu(\text{NH}) = 3370\text{w}, 3290\text{w}; \nu(\text{C}=\text{C}) = 1635\text{m}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 6.2–5.5 (m, 1 H), 5.3–4.9 (m, 2 H), 2.5 (s, 2 H), 2.0 (m, 2 H), 1.05 (s, 2 H), 0.9 (s, 6 H).  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 134.4, 118.9, 49.5, 43.8, 32.8, 24.0.

*E-2,2-Dimethylhex-4-enylamine*, VII, (b.pt. 52–53°C/10 mm) was prepared as above using *E*-crotylchloride. IR ( $\text{cm}^{-1}$ )  $\nu(\text{NH}) = 3390\text{w}, 3110\text{w}; \nu(\text{C}=\text{C}) = 1620$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta(\text{ppm})$ ): 5.7–5.2 (m, 2 H), 2.4 (s, 2 H), 2.1–1.1 (m, 5 H), 0.95 (s, 2 H), 0.8 (s, 6 H).

*cis- and trans-2,5-Dimethylpyrrolidine*, VIII and IX, were obtained in pure form from the commercial products (Aldrich) by rectification on an auto-annular still, Perkin-Elmer 251. The *cis*-isomer, which has the shorter retention time by gas-chromatography on a 4m Polyglycol 4000-KOH on Kieselgur column, was identified by NMR spectroscopy of its *N*-benzyl derivative [27]. VIII,  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 56.9, 30.8, 17.6. IX,  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 56.1, 32.4, 17.9.

*cis-2,4-Dimethylpyrrolidine*, X, was obtained by hydrogenation [28] of the corresponding pyrrole [29] and identified through X-ray diffraction of its complex *trans*- $[\text{PtCl}_2(\text{amine})(\text{Et}_3\text{P})]$  (see below). This isomer has a shorter retention time than the *trans* compound by GC as described above.  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 57.5, 51.5, 40.6, 33.1, 17.5, 17.2.

*trans-2,4-Dimethylpyrrolidine*, XI, was not isolated in a preparative experiment. It was obtained as a mixture with the *cis* isomer in cyclization experiments and the two isomers were separated by gas chromatography.  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 56.3, 52.3, 39.4, 31.8, 18.2, 18.0.

*cis- and trans-2,3-Dimethylpyrrolidine*, XII and XIII, were obtained, as a mixture, by the cyclization reaction described by Cottin [30]. The pure isomers were isolated by preparative gas-chromatography on a 4.5 m, Polyglycol 4000-KOH column, the *cis* isomer showing the shorter retention time. The *cis* isomer was identified by X-ray diffraction of its complex *trans*- $[\text{PtCl}_2(\text{amine})(\text{Et}_3\text{P})]$  (see later). XII,  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 57.1, 43.9, 36.2, 32.9, 14.7, 14.2. XIII,  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 61.7, 44.1, 41.2, 33.8, 17.7, 17.9.

*2-Ethylpyrrolidine*, XIV, was prepared by the mercury promoted cyclization of *E*-hex-4-enylamine, V, [14] and identified by its NMR and mass spectral data.  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 62.7, 45.5, 29.6, 25.2, 23.4, 10.7.

*2-Methylpiperidine*, XV, the commercial product (Fluka, purum) was used.  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 53.6, 45.0, 30.7, 22.2, 19.4.

*2,4,4-Trimethylpyrrolidine*, XVI, was prepared from 2,2-dimethylpent-4-enylamine VI as described for 2-ethylpyrrolidine [14] and purified by preparative gas-chromatography.  $^1\text{H NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 4.05–3.65 (m, 1 H), 3.05 (s, 2 H), 2.05 (quartet, 1 H,  $J$  7.8 Hz,  $J'$  14.4 Hz), 1.55 (quartet, 1 H,  $J$  11.7 Hz,  $J'$  14.4 Hz), 1.4 (d, 3 H,  $J$  7.2 Hz), 1.15 (s, 3 H), 1.1 (s, 3 H).  $^{13}\text{C NMR}$  ( $\text{D}_2\text{O}/\text{DCl}$ ,  $\delta(\text{ppm})$ ): 56.9, 56.4, 46.7, 38.7, 26.5, 17.5.

TABLE 5

DECOMPOSITION POINTS, YIELDS AND ANALYTICAL DATA FOR COMPLEXES [PtCl<sub>3</sub>(amineH)<sup>+</sup>]<sup>+</sup>

Amine	Decomp. pt. (°C)	Yield (%)	C(%) found (calcd.)	H(%) found (calcd.)	N(%) found (calcd.)	Cl(%) found (calcd.)
II	175	82	17.71 (17.94)	3.55 (3.51)	3.56 (3.49)	
III	160	72	18.13 (17.94)	3.52 (3.51)	3.51 (3.49)	26.08 (26.48)
IV	165	50	17.91 (17.94)	3.50 (3.51)	3.41 (3.49)	
V	180	88	18.07 (17.94)	3.54 (3.51)	3.39 (3.49)	
VI	135	50	20.09 (20.23)	4.04 (3.88)	3.25 (3.37)	
VII	180	73	22.46 (22.36)	4.33 (4.22)	3.25 (3.26)	24.61 (24.75)

*2-Ethyl-4,4-dimethylpyrrolidine, XVII*, was prepared from *E*-2,2-dimethylhex-4-enylamine and purified by preparative gas-chromatography. <sup>13</sup>C NMR (D<sub>2</sub>O/DCl, δ(ppm)): 62.3, 57.3, 44.3, 38.3, 26.3, 25.9, 10.7.

*2-Methyl-5,5-dimethylpiperidine, XVIII*, was identified by its <sup>13</sup>C NMR spectrum in the mixture obtained from the cyclization reaction of substrate VII. This structural assignment is also supported by a gas-chromatographic/mass-spectral study of the reaction mixture. <sup>13</sup>C NMR (D<sub>2</sub>O/DCl, δ(ppm)): 54.5, 53.4, 35.2, 29.9, 28.5, 27.3, 23.2, 18.7.

The complexes [PtCl<sub>3</sub>(amino olefinH)] (amino olefinH = protonated II, III or IV) were prepared as described elsewhere [31]. The yields and analytical data are given in table 5. Some IR data on these complexes are given in table 6.

The complex *trans*-[PtCl<sub>2</sub>(amine)(Et<sub>3</sub>P)<sub>2</sub>], amine = *cis*-2,4-dimethylpyrrolidine and *cis*-2,3-dimethylpyrrolidine, were prepared from *sym-trans*-[Pt<sub>2</sub>Cl<sub>4</sub>(Et<sub>3</sub>P)<sub>2</sub>] [32], and the appropriate amine as described elsewhere [33]. Analytical data are as follows: for the *cis*-2,4-dimethylpyrrolidine complex found: C, 29.95; H, 5.72; Cl, 14.00; N, 2.96, for the *cis*-2,3-dimethylpyrrolidine complex, found: C, 29.93; H, 5.74; Cl, 14.82; N, 2.94. C<sub>19</sub>H<sub>43</sub>Cl<sub>2</sub>NP<sub>2</sub>Pt calcd.: C, 29.88; H, 5.64; Cl, 14.70; N, 2.90.

TABLE 6

IR DATA FOR THE TRICHLORO(ALKENYLAMMONIUM)PLATINUM(II) COMPLEXES

Amine	-NH <sub>3</sub> <sup>+</sup> or -NH <sub>2</sub> <sup>+</sup> (cm <sup>-1</sup> )	C=C coord. (cm <sup>-1</sup> )	-CH <sub>2</sub> - in -(CH <sub>2</sub> ) <sub>2</sub>	Pt-Cl (cm <sup>-1</sup> )
II	1600m 1565m	1495m(sh) 1480s	745m 735m	
III	1585m 1565s	1490m(sh) 1480s	<sup>a</sup>	335s 285s
IV	1590s 1575m	1490m	760m	335s 295s
V	1595m 1570m	1490m	740m	
VI	1590s(br)	1500s		
VII	1580s	1495m(sh) <sup>b</sup> 1470s		325s 275s

<sup>a</sup> Not observed. <sup>b</sup> sh = shoulder.

TABLE 7  
SUMMARY OF CRYSTAL DATA

Compound	XIX	XX
Formula	$C_{12}H_{28}Cl_2NPt$	
Formula wt (amu)	483.33	
$a$ (Å)	11.296(5)	11.808(7)
$b$ (Å)	11.518(4)	11.484(7)
$c$ (Å)	14.006(5)	13.211(5)
$\beta$ ( $^\circ$ )	103.32(3)	102.42(5)
$V$ (Å <sup>3</sup> )	1773(11)	1749.6(18)
$D_c$ g cm <sup>-3</sup>	1.811	1.834
$D_m$ g cm <sup>-3</sup>	1.81(1)	1.83(1)
$Z$	4	4
$\mu$ (Mo- $K\alpha$ ) (cm <sup>-1</sup> )	83.6	84.7

### Crystal data

Preliminary Weissenberg photographs revealed that the crystals of XIX and XX belong to the monoclinic space group  $P2_1/c$ . Accurate unit cell dimensions were determined from the angular positions of 15 reflections measured with a Syntex  $P2_1$  automated diffractometer using graphite monochromatized  $K\alpha$  radiation. A summary of crystal data is reported in table 7.

*Intensity measurement.* Intensity data for the two compounds were collected on the Syntex  $P2_1$  diffractometer: relevant details for the data collection are given in table 8.

The data were processed to yield values of  $I$  and  $\sigma(I)$  as previously described [34]. In the estimation of  $\sigma(I)$  the uncertainty factor  $p$  was set equal to 0.011 for XIX and 0.010 for XX, as calculated by the variance of the standard reflections [35]. The values of  $I$  and  $\sigma(I)$  were corrected for Lorentz, polarization and shape anisotropy effects. For the latter correction the already published procedure was followed [36,37].

2567 and 2974 independent reflections for XIX and XX respectively, having  $F_o^2 > 3\sigma(F_o^2)$ , were used in all the subsequent calculations.

*Structure analysis and refinement.* The two structures were solved by the usual combination of Patterson and Fourier methods, and refined by full-matrix least-squares procedures. The isotropic refinements converged at  $R = 0.099$  for

TABLE 8  
DATA COLLECTION DETAILS

	XIX	XX
Radiation	Graphite monochromatized Mo- $K\alpha$	
Crystal dimensions	0.12 × 0.20 × 0.40 mm	0.23 × 0.28 × 0.45 mm
Scan mode	$\omega$	$\omega$
Scan speed	1.5—29.3° min <sup>-1</sup>	2.5—29.3 min <sup>-1</sup>
Scan range	1.00°	0.80°
Background counts	For the scan time at $\pm 0.60^\circ$	at $\pm 0.75^\circ$ from the peak
Check reflections	3 every 100 reflections: no decay	
Data collection limits	3.0 ÷ 5.60° in $2\theta$	3.0 ÷ 5.60° in $2\theta$
No. of data	4725	4647

TABLE 9

## POSITIONAL PARAMETERS OF XIX AND XX

Standard deviations are given in parentheses.

	XIX			XX		
	x	y	z	x	y	z
Pt	0.23639(4)	0.15289(4)	0.10439(3)	0.24534(3)	0.13476(2)	0.09219(2)
Cl(1)	0.2953(3)	0.3444(3)	0.1281(3)	0.3243(2)	0.3177(2)	0.0966(2)
Cl(2)	0.1746(3)	-0.0340(3)	0.0631(3)	0.1629(2)	-0.0467(2)	0.0689(2)
P	0.3965(3)	0.0877(3)	0.2176(2)	0.3919(2)	0.0689(2)	0.2155(2)
N	0.0801(9)	0.2070(8)	-0.0040(7)	0.1028(6)	0.1929(6)	-0.0248(5)
C(1)	0.1006(15)	0.2637(17)	-0.0907(12)	0.1273(7)	0.2219(8)	-0.1272(7)
C(2)	-0.0053(14)	0.3544(15)	-0.1256(13)	0.0173(9)	0.2810(8)	-0.1832(7)
C(3)	-0.0869(14)	0.3410(15)	-0.0517(13)	-0.0174(8)	0.3579(8)	-0.0993(8)
C(4)	-0.0104(14)	0.2907(14)	0.0351(11)	0.0330(8)	0.2895(8)	0.0016(8)
C(5)	0.1095(23)	0.1753(18)	-0.1648(15)	0.1593(11)	0.1128(10)	-0.1799(8)
C(6)	-0.0702(25)	0.3537(22)	-0.2250(14)	-0.1470(9)	0.3761(9)	-0.1146(10)
C(7)	0.3694(11)	-0.0420(11)	0.2818(9)	0.3607(8)	-0.0587(7)	0.2862(7)
C(8)	0.2729(14)	-0.0322(13)	0.3398(11)	0.2645(9)	-0.0418(9)	0.3455(8)
C(9)	0.5211(12)	0.0430(13)	0.1639(10)	0.5151(8)	0.0203(7)	0.1646(7)
C(10)	0.5668(16)	0.1331(16)	0.1059(13)	0.5707(9)	0.1183(9)	0.1117(9)
C(11)	0.4586(13)	0.1915(11)	0.3140(9)	0.4480(7)	0.1758(7)	0.3160(7)
C(12)	0.5644(15)	0.1494(14)	0.3928(12)	0.5466(9)	0.1358(9)	0.4026(8)

XIX and  $R = 0.095$  for XX; anisotropic refinements led to  $R = 0.055$  and  $0.044$  for the two compounds respectively. At this stage the fixed contribution of the hydrogen atoms was included in the structure factor calculations. The positions of the hydrogen atoms were idealized and readjusted after each cycle of refinement; each hydrogen atom was assigned the  $B$  value which the nearest atom had at the end of the isotropic refinement. The final  $R$  is  $0.049$  ( $R_w = 0.051$ ) for XIX and  $0.037$  ( $R_w = 0.040$ ) for XX. In both cases the final difference-Fourier synthesis did not reveal any region exceeding  $\pm 3\sigma(\rho)$  [ $\sigma(\rho) = 0.30$  and  $0.25 e \text{ \AA}^{-3}$  for XIX and XX].

The function minimized during the refinements was  $\sum w(|F_o| - |F_c|)^2$  with  $w = 4F_o^2/\sigma^2(F_o^2)$ : this function was not appreciably dependent on either  $\theta$  or  $F_o$ .

Atomic scattering factors and anomalous dispersion terms were taken from well known sources [38]. The calculations were performed, using local programmes, on the UNIVAC 1110 computer of the University of Rome [39] and on the HP 21MS minicomputer of the CNR Research Area [40]. The final positional parameters of the non hydrogen atoms of XIX and XX are given in table 9.

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