Low-valent Isocyanide Complexes and Clusters of Palladium and Platinum. Crystal Structure of $[Pt\{C(=NR)N(R)C(=NR\}(RNC)_2]$ ($R = 2,6\text{-}Me_2C_6H_3$)†‡

Yasuhiro Yamamoto *
Toho University, Faculty of Science, Funabashi, Chiba 274, Japan
Hiroshi Yamazaki
RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama, 351-01, Japan

Reduction of $[PtCl_2(RNC)_2]$ ($R = 2,6\text{-}Me_2C_6H_3$) with sodium amalgam in the presence of isocyanide gave two clusters, $[Pt_3(RNC)_6]$ (**1a**) and $[HgPt_6(RNC)_{12}]$ (**2a**), and two metallocycles, $[Pt\{C(=NR)NR\}(RNC)_2]$ (**3a**) and $[Pt\{C(=NR)N(R)C(=NR)\}(RNC)_2]$ (**4a**). In (**2a**) the six Pt atoms define a trigonal prism whose edges are associated with bridging and terminal isocyanide groups and the mercury atom is sandwiched by the two triangular Pt_3 cores. The structure of (**4a**) was determined by *X*-ray analysis: space group *Pbcn*, $a = 18.542(11)$, $b = 22.702(5)$, $c = 22.197(5)$ Å, and $Z = 8$. In a similar reaction of $[PdCl_2(2,6\text{-}Me_2C_6H_3NC)_2]$, palladium analogues of (**1a**) and (**4a**) were isolated. Reduction of $[MCl_2(RNC)_2]$ ($M = Pt$ or Pd) having bulky R groups $2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2$ or $2,4,6\text{-}Bu^t_3C_6H_2$ gave the corresponding triangular trimetallic complexes $[M_3(RNC)_6]$. Six isocyanide molecules are bound to the metals as terminal and bridging ligands in the 2,4-di-t-butyl-6-methylphenyl isocyanide complex, and as only terminal isocyanide ligand in the 2,4,6-tri-t-butylphenyl isocyanide. Emission spectra of (**2a**) and the triangular palladium complexes were measured at 77 K; the former showed a fluorescence band at *ca.* 720 nm and the latter a phosphorescence band at *ca.* 640 nm.

Metal clusters are of interest in connection with homogeneous and heterogeneous catalytic reactions.[1] Many metal carbonyl clusters are known,[2] however clusters containing only isocyanide molecules as ligands have been limited to nickel,[3] palladium,[4] and platinum.[5] Recently[6] we reported the preparation and crystallographic structure of the high nuclearity isocyanide cluster $[Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}]$. In the cluster framework five Pt atoms comprise a distorted trigonal-bipyramidal unit and two other Pt atoms adopt edge-bridging positions between the same equatorial Pt atom and an apical Pt atom.

We report here the preparation and charactetisation of a mixed-metal cluster and related clusters containing only isocyanide ligands. A preliminary account of this work has already appeared.[7]

Results and Discussion

2,6-*Xylyl isocyanide.*—Treatment of a mixture of $[PtCl_2(RNC)_2]$ and 2,6-xylyl isocyanide (RNC) with sodium amalgam in tetrahydrofuran (thf) gave a dark green solution. Chromatographic separation of the mixture on deactivated alumina gave four complexes, formulated as $[Pt_3(RNC)_6]$ (**1a**) (brown), $[HgPt_6(RNC)_{12}]$ (**2a**) (dark green), $[Pt\{C(=NR) + NR\}(RNC)_2]$ (**3a**) (pale yellow), and $[Pt\{C(=NR)N(R)C(=NR)\}(RNC)_2]$ (**4a**) (pale yellow), respectively. Complex (**1a**) was identified as triangular by spectroscopic comparison with the known complex.[5b,c]

It was determined by an *X*-ray crystallographic analysis that the molecular structure of (**2a**) has a slightly distorted D_{3h} structure in which the mercury atom is sandwiched by two triangular Pt_3 cores, associated with bridging and terminal isocyanides (Figure 1).[7] The i.r. and ^1H n.m.r. spectroscopic data were in good agreement with the structure.

Two possible electronic configurations for complex (**2a**) can be considered. In the first the mercury is present as Hg^{2+} having no *s* electrons, and the platinum triangles are present as $[Pt_6(RNC)_{12}]^{2-}$, *cf.* $[Pt_6(CO)_{12}]^{2-}$.[8] In the second mercury is neutral with a filled *s* orbital, and the complex is composed of Hg and two neutral $[Pt_3(RNC)_6]$ units. This electronic configuration is supported by electronic spectroscopy for chemical analysis (ESCA) which showed that the oxidation states of the Hg and Pt atoms are close to neutral.§

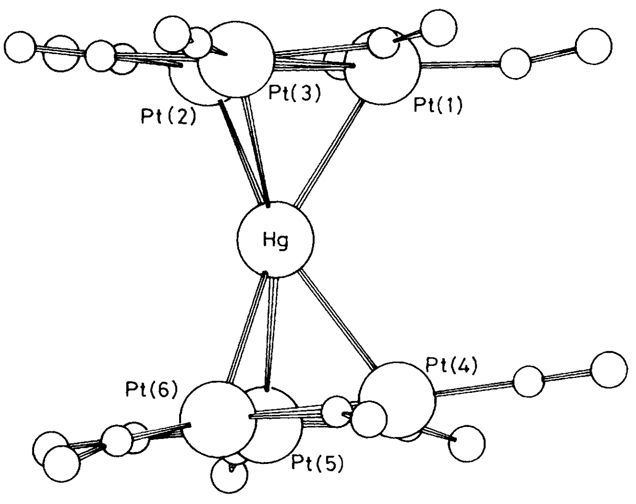


Figure 1. Structure of $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$ (**2a**) with 2,6-xylyl groups omitted for clarity

---

† Taken to be 'Studies on the Interaction of Isocyanide of with Transition-metal Complexes. Part 33. Part 32, Y. Iltaka, T. Oohama, M. Shiina, T. Takizawa, Y. Yamamoto, and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1987, 853.

‡ [1,3-Bis(2′,6′-xylylimino)-3-(2′,6′-xylyl)-2-azapropane-1,3-diyl]bis-(2′,6′-xylyl isocyanide) platinum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

§ In the *X*-ray photoelectron spectrum of $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$ the binding energies (b.e.s) of the Pt $4f_{\frac{7}{2}}$ and Pt $4d_{\frac{5}{2}}$ core levels were in good agreement with those of $[Pt_3(RNC)_6]$ ($R = 2,4,6\text{-}Bu^t_3C_6H_2$ or $2,4\text{-}Bu^t\text{-}6\text{-}MeC_6H_2$). The b.e. of the Hg $4f_{\frac{7}{2}}$ core level is also similar to that of mercury metal.

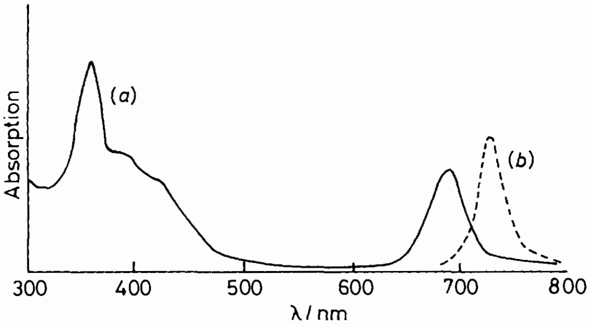


Figure 2. Absorption (*a*) and emission (*b*) spectra (excited at 670 nm) of complex (**2a**) in mthf at 77 K

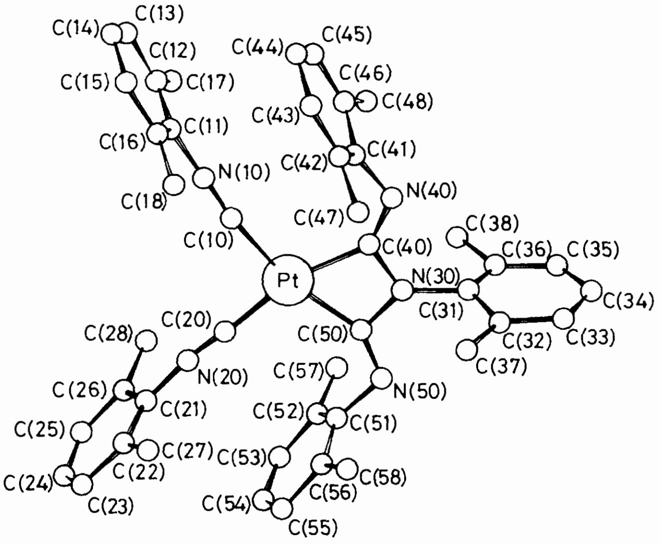
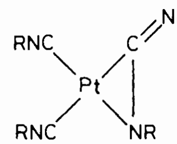


Figure 3. Structure of complex (**4a**)

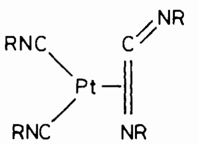
The u.v.-visible absorption and emission spectra of a degassed methyltetrahydrofuran (mthf) solution of complex (**2a**) at 77 K are shown in Figure 2. The emission upon excitation at 670 nm in the absorption spectrum showed an intense band at 718 nm with a lifetime of 2.1 ns, corresponding to the fluorescence band. As the lowest-energy band at 690 nm of (**2a**) was assigned as the transition from the highest occupied molecular orbital (h.o.m.o.), consisting of the d_{z^2} orbitals of the platinum triangles and the *s* orbital of the mercury, to the lowest unoccupied molecular orbital (l.u.m.o.), consisting of the *p* orbitals of the Pt atoms and the π^* orbitals of the C≡N-groups,† the intense fluorescence band at 718 nm was most likely derived from this transition.

The i.r. spectrum of complex (**3a**) showed two peaks at 2 163 and 1 654 cm^{-1}, assignable to the C-N triple and double bonds, respectively. The ^{1}H n.m.r. spectrum showed the four kinds of *o*-methyl resonances at δ 1.85, 2.10, 2.32, and 2.45 in a 1:1:1:1 ratio. From the spectroscopic data and comparison with the structure of (**4a**) (see below), the structure of (**3a**) was assigned as in (**A**) or (**B**).

The i.r. spectrum of complex (**4a**) showed two bands at *ca.* 2 170 and two bands at *ca.* 1 600 cm^{-1}, assignable to the C-N triple and double bonds, respectively. The ^{1}H n.m.r. spectrum showed three bands at δ 2.18, 2.22, and 2.58 in a 2:2:1 ratio. By an *X*-ray analysis, the structure was determined as a platina-3-azacyclobutene derivative (Figure 3). The structures of complexes (**3a**) and (**4a**) showed that cleavage of a C≡N triple bond had occurred in an isocyanide molecule. The fate of the carbon atom is unknown. A precedent is the complex [Fe(dppe)(CO)(RNC){C(=NR)N(R)C(=NR)}] [R = 4-MeC$_6$H$_4$; dppe = Ph$_2$P(CH$_2$)$_2$PPh$_2$] obtained from the reaction of [Fe(dppe)(RNC)$_4$][ClO$_4$]$_2$ with KOH.[9] Another cleavage of a C≡N triple bond has been observed in the pyrolysis of [Ru$_5$(CO)$_{14}$(Bu^{t}NC)(η^5-Bu^{t}NC)].[10] The C≡O triple bond cleavage of carbon monoxide has often been observed for carbonyl complexes, and is considered as a model for a step in the Fischer–Tropsch process.



(**A**)



(**B**)

Reduction of [PdCl$_2$(RNC)$_2$] (R = 2,6-Me$_2$C$_6$H$_3$) with sodium amalgam gave a green solution, suggesting the formation of [HgPd$_6$(RNC)$_{12}$], as observed in the case of the platinum complex. However, during an attempted isolation the green solution changed to reddish brown. The work-up of the solution gave [Pd$_3$(RNC)$_6$] (**5a**)^{5c} and [Pd{C(=NR)N(R)C(=NR)}(RNC)$_2$] (**6a**). No Hg–Pd complex was isolated, suggesting that the Hg–Pd cluster is less stable than the Hg–Pt one.

The i.r. spectrum of complex (**6a**) showed the N≡C triple bond at 2 176 and 2 160 cm^{-1}, and the C=N double bond at 1 616 and 1 582 cm^{-1}. The ^{1}H n.m.r. spectrum indicated three singlets at δ 2.21, 2.28, and 2.61 in a 2:2:1 ratio for *o*-methyl groups. Since these spectroscopic results were in good agreement with those of (**4a**), complex (**6a**) was assigned as the palladium analogue of (**4a**). No carbodi-imide derivatives were obtained.

6-Methyl-2,4-di-t-butylphenyl and 2,4,6-tri-t-butylphenyl Isocyanide.—When [PtCl$_2$(2,4-Bu$^t{}_2$-6-MeC$_6$H$_2$NC)$_2$] was treated with Na–Hg in the presence of 6-methyl-2,4-di-t-butylphenyl isocyanide, a green colour developed, suggesting the formation of a Hg–Pt cluster, but the only complex isolated was brown (**1b**), formulated as '[Pt(2,4-Bu$^t{}_2$-6-MeC$_6$H$_2$NC)$_2$].' The presence of terminal and bridging isocyanide groups was shown by the bands at 2 108, 2 088, and 1 720 cm^{-1} in the i.r. spectrum. The ^{1}H n.m.r. spectrum showed six singlets in the range δ 1.0—3.0 due to the *o*-methyl, *o*- and *p*-t-butyl groups, suggesting the presence of two kinds of isocyanide ligands in a 1:1 ratio. They were assigned to the bridging and terminal isocyanides. From these spectral data, (**1b**) has a triangular structure.

A similar reaction using bulky 2,4,6-tri-t-butylphenyl isocyanide gave a brown complex (**1c**) having the formula '[Pt(2,4,6-Bu$^t{}_3$C$_6$H$_2$NC)$_2$].' The green colour reminiscent of a Hg–Pt cluster was not observed in this case. The i.r. spectrum showed two bands at 2 099 and 1 826 cm^{-1}. Since the ^{1}H n.m.r. spectrum indicated the presence of only one kind of isocyanide ligand at ambient temperature and even at low temperature, the two peaks in the i.r. spectrum were assigned to the terminal isocyanide groups. The low frequency near 1 830 cm^{-1} due to the C≡N triple bonds may be due to substantial bending at the nitrogen atoms of the RNC ligands. Similar low stretching frequencies have been observed for [Ru(Bu^{t}NC)$_5$] (1 815 cm^{-1})[11] and [Fe(Bu^{t}NC)$_5$] (1 830 cm^{-1}).[12] Their bent angles at the nitrogen atoms have been confirmed by *X*-ray analyses.

The palladium complex (**5c**) of formula '[Pd(2,4,6-Bu$^t{}_3$C$_6$H$_2$NC)$_2$]' was formed by reduction of [PdCl$_2$(2,4,6-Bu$^t{}_3$C$_6$H$_2$NC)$_2$] with sodium amalgam. The formation of Hg–M (M =

---

† The extended-Hückel m.o. (EHMO) studies will be reported elsewhere.

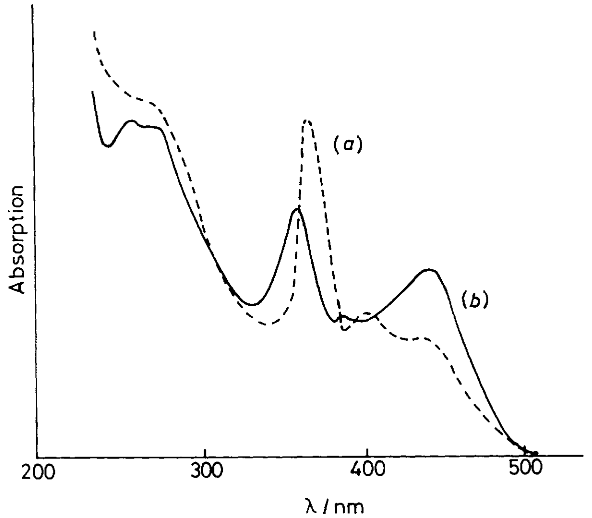


Figure 4. Electronic spectra of [$Pt_3(RNC)_6$] in CH_2Cl_2: R = 2,4-Bu^t_2-6-MeC_6H_2 (*a*) and 2,4,6-$Bu^t_3C_6H_2$ (*b*)

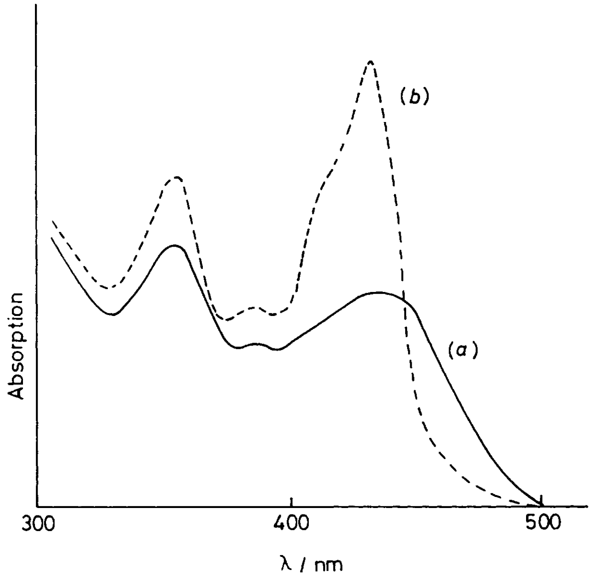


Figure 5. Room-temperature (*a*) and 77 K (*b*) absorption spectra of [$Pt_3(2,4,6\text{-}Bu^t_3C_6H_2NC)_6$] in mthf

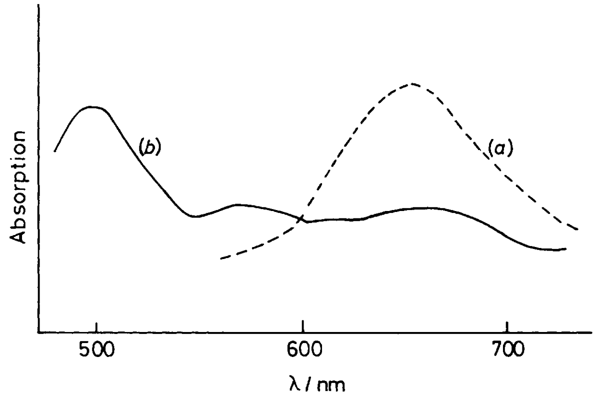


Figure 6. Emission (*a*) (excitation at 430 nm) and transient absorption (*b*) (excitation at 355 nm) spectra of [$Pd_3(2,4,6\text{-}Bu^t_3C_6H_2NC)_6$] in toluene

Table 1. Spectral data for [$HgPt_6(RNC)_{12}$] and [$Pd_3(RNC)_6$]

Complex	Emission[a]		Absorption[b]
	$\lambda_{max.}$/nm	(τ/μs)	$\lambda_{max.}$/nm
(**2a**) [$HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}$]	718	(2.1)[c]	669 (685)[d]
(**5a**) [$Pd_3(2,6\text{-}Me_2C_6H_3NC)_6$]	642	50	442
(**5c**) [$Pd_3(2,4,6\text{-}Bu^t_3C_6H_2NC)_6$]	647	31	448

[a] Excitation at 430 nm for (**5**) in toluene and at 670 nm for (**2a**) in mthf, measured at 77 K. [b] Measured at *ca.* 300 K; assigned to the σ–σ* transition. [c] τ (ns). [d] Measured at 77 K.

Pt or Pd) clusters in these reactions was not observed, preventing incorporation of a mercury atom between two triangular cores containing sterically bulky substituents such as t-butyl. No metallacyclic compounds were observed.

The i.r. and ^1H n.m.r. spectroscopic data for (**5c**) were in good agreement with those of (**1c**). The electronic spectrum of (**1c**) has a similar pattern to that of (**1b**) which possesses a triangular core (Figure 4). Although we cannot exclude the possibility that complex (**1c**) has an extremely low energy in bridge–terminal RNC exchange, we assume that the structures of (**1c**) and (**5c**) have a triangular core with only terminal isocyanide ligands, according to their i.r. spectra, in which the geometry around platinum and palladium is either planar or tetrahedral.

It was predicted by Dedieu and Hoffmann[13] that the favourable geometry of the complex [$Pt_3(PR_3)_6$] having only terminal ligands, if it exists, will be tetrahedral around the Pt atoms. Thus, the geometry around platinum or palladium in (**1c**) and (**5c**) is possibly tetrahedral. However, an accurate structure must wait an *X*-ray analysis.

The electronic spectra of complex (**1c**) at 300 and 77 K in mthf are shown in Figure 5. The band at 438 nm sharpened and shifted to higher energy upon cooling, in agreement with a σ–σ* transition. Such behaviour has been observed in related bi- and tri-nuclear metal carbonyls with metal–metal bonds.[14] The band near 430 nm of (**1b**) showed a similar temperature dependence to that of (**1c**), also assignable to a σ–σ* transition. Since the position of a σ–σ* transition is known to shift to higher energy with increasing M–M bond strength, the metal–metal bond of (**1b**) is stronger than that of (**1c**).

The low-temperature emission spectrum of the tripalladium complex (**5c**) in mthf is shown in Figure 6. Excitation at 430 nm resulted in phosphorescence at 647 nm (τ = 30—50 μs) (Table 1). As the band at 448 nm in the absorption spectrum is assigned as σ–σ*, the intense phosphorescence band is likely derived from this state. By using a Nd:YAG laser as the excitation source, the transient absorption spectrum of (**5c**) in toluene was measured at 77 K (Figure 6). The spectral pattern of the excited state was similar to that of the ground state, indicating that the framework of the active species was not significantly different from that in the ground state. The band at *ca.* 650 nm is assigned to a σ–σ* transition in the excited state in comparison with that in the ground state. A red shift of a σ–σ* transition showed that the metal–metal bond distances in the excited state are slightly longer than those in the ground state.

Crystal Structure of Complex (**4a**).—The molecule of (**4a**) consists of a four-membered ring containing platinum metal (Figure 3). Bond lengths and angles are given Table 2. The geometry around the platinum atom is almost planar. The Pt–C(10) length is 2.03(4) Å and the Pt–C(20) one is 1.95(4) Å, slightly longer than the corresponding bond lengths, 1.88(2) and 1.91(2) Å, in *cis*-[$PtCl_2(PhNC)_2$].[15] The Pt–C(40) and Pt–C(50) single bonds [2.04(4) and 2.05(4) Å], C(40)–N(40) and C(50)–N(50) double bonds [1.25(5) and 1.30(5) Å] are

Table 2. Selected bond lengths (Å) and angles (°)

Pt–C(10)	2.03(4)	Pt–C(20)	1.95(4)
Pt–C(40)	2.04(4)	Pt–C(50)	2.05(4)
C(10)–N(10)	1.16(5)	C(20)–N(20)	1.14(5)
C(40)–N(30)	1.42(5)	C(40)–N(40)	1.25(5)
C(50)–N(30)	1.41(5)	C(50)–N(50)	1.30(5)
C(10)–Pt–C(20)	96.5(16)	C(10)–Pt–C(40)	99.1(17)
C(10)–Pt–C(50)	166.4(16)	C(20)–Pt–C(40)	164.4(17)
C(20)–Pt–C(50)	97.2(16)	C(40)–Pt–C(50)	67.3(17)
Pt–C(10)–N(10)	172.5(33)	C(10)–N(10)–C(11)	173.6(33)
Pt–C(20)–N(20)	175.6(34)	C(20)–N(20)–C(21)	172.4(36)
C(40)–N(40)–C(50)	67.3(17)	C(31)–N(30)–C(40)	124.7(30)
C(31)–N(30)–C(50)	128.1(30)	Pt–C(40)–N(30)	93.1(25)
Pt–C(40)–N(40)	141.7(34)	N(30)–C(40)–N(40)	124.8(38)
C(40)–N(40)–C(41)	121.3(35)	Pt–C(50)–N(30)	93.0(24)
Pt–C(50)–N(50)	148.7(31)	N(30)–C(50)–N(50)	117.9(34)
C(50)–N(50)–C(51)	115.3(31)		

comparable with Pt–C [2.03(1) Å] and C–N [1.29(2) Å] in *trans*-[PtI{C(Me)=NC$_6$H$_4$Cl-4}(PPh$_3$)$_2$].[16] The average C–N single-bond distance in the four-membered ring is 1.415 Å, compared with the usual C–N bond length of 1.47 Å. The three C–Pt–C angles, except C(40)–Pt–C(50) 67.3(17)°, exhibit similar values (98°). The Pt–C–N and C–N–C bond angles of the terminal isocyanides are nearly linear. The C(40)–N(40)–C(41) and C(50)–N(50)–C(51) bond angles are 121.3(35) and 115.3(31)°, and the iminophenyl groups bend towards the platinum atom. The dihedral angles between the PtC$_4$N plane and five phenyl rings are nearly perpendicular (87.7—91.5°). The dihedral angles between the phenyl rings C(11)—C(16) and C(41)—C(46) and C(21)—C(26) and C(51)—C(56) are 2 and 5°, respectively. This conformation minimises steric interactions.

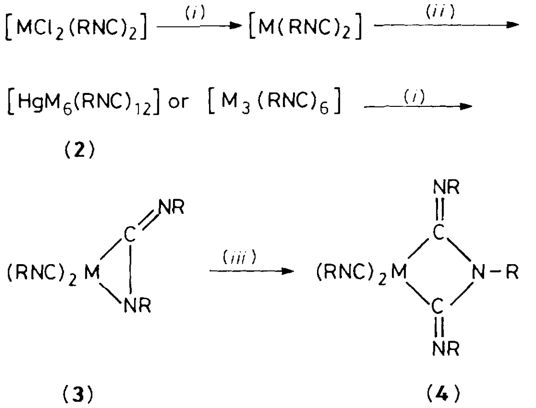
Reaction Mechanism.—We have reported that coulometric electrolysis of [PtCl$_2$(RNC)$_2$] at a mercury electrode at −1.70 V *vs.* saturated calomel electrode (s.c.e.) gives [HgPt$_6$(RNC)$_{12}$] or [Pt$_3$(RNC)$_6$].[17] This electrochemical reaction was initiated by two-electron reduction to give an 18-electron species, followed by elimination of Cl$^-$ to afford a 14-electron species [Pt(RNC)$_2$]. The reaction was completed by trimerisation of the 14-electron species to produce the final complexes (Scheme 1).

$$[PtCl_2(RNC)_2] \xrightarrow{2e} [PtCl_2(RNC)_2]^{2-} \xrightarrow{-2Cl^-} [Pt(RNC)_2] \longrightarrow [HgPt_6(RNC)_{12}] \text{ or } [Pt_3(RNC)_6]$$

Scheme 1.

Since the reduction potential of sodium amalgam is estimated as *ca.* −1.85 *vs.* s.c.e.,* we can assume that a similar process to the electrochemical reaction occurred in the chemical reduction with sodium amalgam.

Since the reaction of [Pt$_3$(μ-CO)$_3$(PEt$_3$)$_4$] with metallic mercury gives [HgPt$_6$(μ-CO)$_6$(PEt$_3$)$_6$],[18] the reaction of (**1a**) with metallic mercury in the presence of 2,6-xylyl isocyanide was attempted, and (**1a**) was recovered quantitatively. However the reaction with Na–Hg afforded the Hg–Pt cluster (**2a**). The driving force for the incorporation of a mercury atom between two triplatinum cores is assumed to be due to the interaction of mercury activated by sodium amalgam with the triangular platinum complex (**1a**). The further continuous reduction changed the solution from dark green to pale yellow, from which (**3a**) and (**4a**) were obtained. The reaction of complex (**3a**) with 2,6-xylyl isocyanide readily led to an insertion of isocyanide into the metal–nitrogen bond to give (**4a**), suggesting that (**3a**) is a precursor of (**4a**). The d.c. polarogram of the finally isolated complex (**4a**) showed an irreversible two-electron reductive wave at $E_{\frac{1}{2}} = -2.25$ V *vs.* s.c.e. showing that there is no further reduction of (**4a**) with sodium amalgam. There is no information on the mechanism of the cleavage of the C≡N triple bond which will occur during these reactions.



Scheme 2. (*i*) Na–Hg; (*ii*) trimerisation; (*iii*) RNC

Experimental

The reactions were carried out under an atmosphere of nitrogen. Electronic spectra were recorded on a Hitachi 330 spectrometer. The d.c. polarograms were measured on a HUSO model 321 Potential Scanning Unit. A platinum-wire counter electrode and a Ag–AgNO$_3$–MeCN reference electrode were used. Potentials are with reference to the saturated calomel electrode (s.c.e.) N.m.r. spectra were recorded on a JEOL FX100 spectrometer. Samples for the laser flash photolysis and low-temperature electronic spectra were loaded into a round-bottomed flask connected to a quartz cuvette (1.0 cm path length) by glass tubing. The solutions were freeze–pump–thaw degassed three times and then sealed in a degassed condition.

2,6-Xylyl, 6-methyl-2,4-di-t-butylphenyl, and 2,4,6-tri-t-butylphenyl isocyanides were prepared by procedures described in the literature.[19,20] The complex [PdCl$_2$(RNC)$_2$] was synthesised by a literature procedure;[21] [PtCl$_2$(RNC)$_2$] was prepared by the reaction of [PtCl$_2$(cod)] (cod = cyclo-octa-1,5-diene) with isocyanide.

Preparation of [PtCl$_2$(2,6-Me$_2$H$_3$NC)$_2$].—A mixture of [PtCl$_2$(cod)] (1.9 g, 2.7 mmol) and 2,6-xylyl isocyanide (0.8 g, 6.1 mmol) in benzene (20 cm^3) was kept for 1 h at room temperature. The white solids were filtered off and washed with hexane to give the required complex (1.36 g, 95%). I.r. (KBr): 2 228 and 2 195 (N≡C) cm^{-1} (Found: C, 41.00; H, 3.50 N, 5.30. Calc. for C$_{18}$H$_{18}$Cl$_2$N$_2$Pt: C, 40.90; H, 3.45; N, 5.30%).

The following complexes were prepared by a similar procedure.

[PtCl$_2$(2,4,6-Bu^t$_3$C$_6$H$_2$NC)$_2$] (86%). I.r. (KBr): 2 232 and 2 195 (N≡C) cm^{-1} (Found: C, 56.80; H, 7.10; N, 3.40. Calc. for C$_{38}$H$_{58}$Cl$_2$N$_2$Pt: C, 56.80; H, 7.10; N, 3.45%).

[PtCl$_2$(2,4-Bu^t$_2$-6-MeC$_6$H$_2$NC)$_2$] (93%). I.r (KBr): 2 230 and 2 194 (N≡C) cm^{-1}. ^{1}H N.m.r. (CDCl$_3$): δ 1.32 (s, 4 Bu^t), 1.50 (s, 2 Bu^t), 2.41 (s, 6-Me), and *ca.* 7.2 (aromatic protons) (Found: C, 53.00; H, 6.50; N, 3.85. Calc. for C$_{32}$H$_{46}$Cl$_2$N$_2$Pt: C, 53.05; H, 6.40; N, 3.85%).

Reaction of [PtCl$_2$(2,6-Me$_2$C$_6$H$_3$NC)$_2$] *with Sodium Amalgam.*—A mixture of [PtCl$_2$(2,6-Me$_2$C$_6$H$_3$NC)$_2$] (0.6 g,

---

* The potential of Na–Hg was measured in a mixture of *ca.* 2% Na–Hg and 0.1 mol dm^{-3} [NBu^n$_4$][ClO$_4$]–MeCN solution, using a Ag–AgNO$_3$ solution as a reference electrode.

Table 3. Positional parameters (× 10^3) of complex (**4a**)*

Atom	x	y	z	Atom	x	y	y
Pt	1 811(1)	2 447(1)	2 155(1)	C(28)	−6(3)	136(2)	346(3)
C(10)	1 316(30)	3 215(21)	2 084(22)	C(31)	318(3)	161(2)	104(2)
N(10)	916(21)	3 615(16)	1 973(16)	C(32)	395(3)	179(2)	112(3)
C(20)	1 438(28)	2 222(23)	2 920(27)	C(33)	436(3)	148(2)	67(2)
N(20)	1 155(23)	2 078(19)	3 404(20)	C(34)	406(3)	105(2)	26(2)
N(30)	2 740(23)	1 940(18)	1 480(19)	C(35)	333(3)	92(2)	25(2)
C(40)	2 396(26)	2 504(31)	1 373(21)	C(36)	289(3)	120(2)	67(2)
N(40)	2 463(26)	2 775(18)	897(17)	C(37)	423(3)	222(2)	157(3)
C(50)	2 437(33)	1 754(22)	2 056(23)	C(38)	208(3)	107(2)	66(2)
N(50)	2 752(23)	1 263(18)	2 285(20)	C(41)	213(3)	333(2)	85(2)
C(11)	56(3)	412(2)	182(2)	C(42)	247(3)	387(2)	103(2)
C(12)	−12(3)	408(2)	153(2)	C(43)	209(3)	437(2)	82(2)
C(13)	−45(3)	463(2)	135(3)	C(44)	144(3)	442(3)	50(3)
C(14)	−13(3)	519(2)	149(3)	C(45)	112(3)	382(2)	35(3)
C(15)	52(3)	523(2)	180(3)	C(46)	146(3)	325(2)	49(2)
C(16)	93(3)	468(2)	199(2)	C(47)	318(3)	383(2)	133(2)
C(17)	−44(3)	352(2)	141(2)	C(48)	115(3)	260(3)	27(2)
C(18)	166(3)	470(2)	229(3)	C(51)	250(3)	109(2)	289(2)
C(21)	93(3)	188(2)	399(2)	C(52)	191(3)	72(2)	291(3)
C(22)	133(3)	216(2)	447(2)	C(53)	170(4)	47(3)	348(3)
C(23)	105(3)	196(2)	502(3)	C(54)	210(3)	68(3)	392(3)
C(24)	48(3)	158(3)	506(3)	C(55)	272(3)	106(3)	388(3)
C(25)	11(4)	135(3)	461(3)	C(56)	300(3)	134(2)	332(2)
C(26)	32(3)	156(2)	401(2)	C(57)	150(3)	45(2)	343(3)
C(27)	199(3)	255(3)	438(2)	C(58)	365(3)	174(3)	321(3)

* Parameters of Pt to N(50) are multiplied by 10^4.

1.14 mmol) and 2,6-xylyl isocyanide (0.05 g, 0.38 mmol) was treated with Na–Hg in thf (30 cm^3) at room temperature. After 1 h the solvent was removed from the dark green solution under reduced pressure. The residue was chromatographed on deactivated alumina (containing 10% water, column height 3 cm), using benzene and CH_2Cl_2 as eluants. Elution with benzene gave a dark green solution. The solvent was evaporated to *ca.* 5 cm^3 and hexane was added to give dark green crystals of complex (**2a**) (0.19 g). After the dark green crystals had been filtered off the solution changed to brown. Brown crystals of complex (**1a**) (0.04 g) were obtained by further crystallisation from the mother-liquor. Elution with benzene–CH_2Cl_2 (5:1) showed two bands, very pale yellow and pale yellow. The work-up of each band gave pale yellow complexes (**3a**) (0.01 g) and (**4a**) (0.03 g), recrystallised from benzene–hexane.

[$HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}$] (**2a**). I.r (Nujol): 2 095 (N≡C) and 1 720 (C=N) cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 2.16 (br s, 6 Me), 2.52 (s, 6 Me), and *ca.* 7.3 (aromatic protons) (Found: C, 44.15; H, 3.70; Hg, 7.05; N, 5.75; Pt, 39.60. Calc. for $C_{108}H_{108}HgN_{12}Pt_6$: C, 44.05; H, 3.70; Hg, 6.80; N, 5.70; Pt, 39.75%).

[Pt{C(=NR)NR}(RNC)$_2$](**3a**;R = $2,6\text{-}Me_2C_6H_3$.I.r.(Nujol): 2 163 (N≡C) and 1 654 (C=N) cm^{-1}. ^{1}H N.m.r. (CD_2Cl_2): δ 1.85 (s, 2 Me), 2.10 (s, 2 Me) 2.32 (s, 2 Me), 2.45 (s, 2 Me), and *ca.* 6.5 (aromatic protons) (Found: C, 59.10; H, 5.07; N, 7.90. Calc. for $C_{35}H_{36}N_4Pt$; C, 59.40; H, 5.15; N, 7.90%).

[Pt{C(=NR)N(R)C(=NR)}(RNC)$_2$] (**4a**; R = $2,6\text{-}Me_2C_6H_3$). I.r. (Nujol): 2 168, 2 176 (N≡C), 1 614 and 1 584 (C=N) cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 2.26 (br s, 4 Me), 2.59 (s, 4 Me), 2.84 (s, 2 Me), and *ca.* 6.5 (aromatic protons) (Found: C, 62.90; H, 5.45; N, 8.30; Pt, 23.10. Calc. for $C_{44}H_{45}N_5Pt$: C, 63.00; H, 5.40; N, 8.35; Pt, 23.45%).

Reaction of [$PtCl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_2$] *with Sodium Amalgam.*—A mixture of [$PtCl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_2$] (0.28 g, 0.39 mmol) and Na–Hg (*ca.* 2%) was stirred for 1 h. The mixture changed from pale yellow to yellow brown *via* yellow green. The solvent was removed and the residue was chromatographed on silica gel (column height *ca.* 3 cm), using benzene as an eluant. The solvent was evaporated to dryness and the residue was crystallised from hexane at −10 °C (0.07 g). [$Pt_3(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_6\cdot0.5C_6H_6$] (**1b**). I.r. (Nujol): 2 108, 2 008 (N≡C), and 1 720 (C=N) cm^{-1}. ^{1}H N.m.r. (C_6D_6): δ 1.00 (s, 4-Bu^t, terminal), 1.15 (s, 2-Bu^t, bridging), 1.41 (s, 2-Bu^t, terminal), 1.56 (s, 2-Bu^t, bridging), 2.30 (s, 2- and 6-Me, terminal), 2.59 (s, 2- and 6-Me, bridging), and *ca.* 7.0 (aromatic protons) (Found: C, 59.70; H, 7.35; N, 4.20. Calc. for $C_{99}H_{141}N_6Pt_3$: C, 59.45; H, 7.10; N, 4.20%).

The complex [$Pt_3(2,4,6\text{-}Bu^t_3C_6H_2NC)_6$] (**1c**) was prepared by a similar procedure. I.r. (Nujol): 2 099 and 1 826 (N≡C) cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 1.32 (s, 2,6-Bu^t), 1.51 (s, 4-Bu^t), and 7.0 (aromatic protons) (Found: C, 61.85; H, 8.00; N, 3.65. Calc. for $C_{114}H_{174}N_6Pt_3$: C, 61.85; H, 7.90; N, 3.80%).

Reaction of [$PdCl_2(2,6\text{-}Me_2C_6H_3NC)_2$] *with Sodium Amalgam.*—A mixture of [$PdCl_2(2,6\text{-}Me_2C_6H_3NC)_2$] (0.96 g, 2.16 mmol) and 2,6-xylyl isocyanide (0.4 g, 3.1 mmol) was treated with Na–Hg in thf (30 cm^3) at room temperature. The solution in the neighbourhood of the surface of the sodium amalgam changed from pale yellow to green. With stirring, the green colour changed rapidly to dark brown. After 1 h the orange solution was separated by decantation. The solvent was evaporated to dryness and the residue chromatographed on deactivated alumina (containing 10% water), using benzene and CH_2Cl_2–ethyl acetate (5:1) as eluants. Elution with benzene gave a yellow-brown solution. Removal of the solvent and crystallisation of the residue from benzene–hexane gave the known complex [$Pd_3(2,6\text{-}Me_2C_6H_3NC)_6$] (0.38 g, 47.8%).[5c] Elution with a mixture of benzene and ethyl acetate gave a pale yellow solution. Work-up of the solution gave 0.055 g of complex (**6a**) as pale yellow crystals. I.r. (Nujol): 2 176, 2 160 (N≡C), 1 616 and 1 582 (N=C) cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 2.21 [s, 2,6-Me(terminal)], 2.28 [s, 2.6-Me(iminoxylyl)], 2.61 [s, 2,6-Me(N-aminoxylyl)], and *ca.* 6.5 (aromatic protons) (Found: C, 70.45; H, 6.15; N, 9.00. Calc. for $C_{44}H_{45}N_5Pd$: C, 70.45; H, 6.05; N, 9.35%).

A mixture of [$PdCl_2(2,4,6\text{-}Bu^t_3C_6H_2NC)_2$] (0.9 g, 1.25

mmol) and 2,4,6-tri-t-butylphenyl isocyanide (0.15 g, 0.55 mmol) was treated with sodium amalgam in thf (25 cm^3). After 1 h, the colour of the reaction mixture changed from orange-yellow to reddish orange. The orange solution was separated by decantation. The solvent was removed to dryness, and the residue was chromatographed on deactivated alumina (containing 10% water), using benzene as an eluant. Removal of the solvent from the reddish brown solution and crystallisation of the residue from hexane at −10 °C gave $[Pd_3(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_6]$ (0.24 g, 30%) as yellow-orange crystals. I.r. (Nujol): 2 082, 1 956, 1 928, ad 1 912 (N≡C) cm^{-1}. ^{1}H N.m.r. (PhCl): δ 1.20 (s, 4-Bu^t) and 1.54 (br s, 2- and 6-Bu^t) (Found: C, 69.45; H, 9.00; N, 4.15. Calc. for $C_{114}H_{174}N_6Pd_3$: C, 70.30; H, 9.00; N, 4.30%).

X-*Ray Structural Determination.*—Pale yellow crystals of complex (**4a**) were obtained from a mixture of CH_2Cl_2 and benzene. *X*-Ray photographic data from Weissenberg photographs show the crystal to be orthorhombic with systematic extinction ($0kl$, $k = 2n$; $h0l$, $l = 2n$, $h + k = 2n$) consistent with the space group *Pbcn*.

Crystal data. $C_{44}H_{45}N_5Pt$, M 839, $a = 18.542(11)$, $b = 22.702(5)$, $c = 22.197(5)$ Å, $U = 9\,346(6)$ Å^3, $Z = 8$, $D_c = 1.193$, $D_m = 1.22$, and $F(000) = 3\,376$.

Data collection was carried out on a Rigaku four-circle diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å) with $2\theta < 45°$ and the ω—2θ ($\geqslant 30°$) and ω ($< 30°$) scan techniques with scan rate of 8° min^{-1}. A total of 2 243 reflections were measured of which 2 083 having $|F_o| > 3\sigma(F_o)$ were used in the calculations. Intensities were corrected for Lorentz and polarisation effects. The linear absorption coefficients was 30.6 cm^{-1}, and no absorption correction was made. The position of the Pt atom was determined by a Patterson map. The remaining atoms were located in succeeding Fourier difference syntheses. The positions of Pt, five N, and four C atoms (two terminal isocyanide carbons and two carbon atoms in a five-membered ring) were refined anisotropically using block-diagonal least-squares methods, and the others isotropically. The final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/F_o{}^2]^{\frac{1}{2}}$ values were 0.073 and 0.091 ($w = 1$), respectively. A final Fourier difference map showed residual peaks at less than 0.7 e Å^{-3}. The atomic scattering factors were taken from ref. 22. Both the f' and f'' components of the anomalous dispersion were included for all non-hydrogen atoms.[23] No attempt to locate hydrogen atoms was made. The calculations were carried out by using the UNICS III system.[24] The final positional parameters are listed in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

We thank Dr. T. Hoshino in the Institute for measurements of an absorption spectrum in the excited state using a Nd:YAG laser and for low-temperature electronic spectra, and also Dr. K. Takahashi in the Institute for measurement of the d.c. polarograms.

References

1 R. Ugo, *Cat. Rev.*, 1975, **11**, 225; E. L. Muetterties, *Bull. Soc. Chim. Belg.*, 1975, **84**, 959; 1976, **85**, 541.
2 B. F. G Johnson and R. E. Benfield, *Top. Stereochem.*, 1981, **12**, 253.
3 M. G. Thomas, W. R. Pretzer, B. F. Beier, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1977, **99**, 743.
4 E. O. Fischer and H. Werner, *Chem. Ber.*, 1962, **95**, 703; S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Am. Chem. Soc.*, 1969, **91**, 6994; L. Malatesta, *J. Chem. Soc.*, 1955, 3924; C. G. Francis, S. I. Khan, and P. R. Morton, *Inorg. Chem.*, 1984, **23**, 3680.
5 (*a*) M. Green, J. A. K. Howard, M. Murray, J. L Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 1509; (*b*) *ibid.*, 1980, 2097; (*c*) A. Christofides, *J. Organomet. Chem.*, 1983, **259**, 355.
6 Y. Yamamoto, K. Aoki, and H. Yamazaki, *Chem. Lett.*, 1979, 391; *Organometallics*, 1983, **2**, 1377.
7 Y. Yamamoto, H. Yamazaki, and T. Sakurai, *J. Am. Chem. Soc.*, 1982, **104**, 2329.
8 J. C. Calabrese, L. F. Dahl, P. Chini, G. Langoini, and S. Martinengo, *J. Am. Chem. Soc.*, 1974, **96**, 2014.
9 V. Rieva, J. Ruiz, A. Tiripicchio, and M. T. Camallini, *J. Organomet. Chem.*, 1987, **327**, C5.
10 R. D. Adams, P. Mathur, and B. E. Segmuller, *Organometallics*, 1983, **2**, 1258.
11 G. K. Barker, A. M. R. Galas, M. Green, J. A. K. Howard, F. G. A. Stone, T. W. Turney, A. J. Welch, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 1977, 256.
12 J. M. Bassett, D. E. Berry, G. K. Barker, M. Green, J. A. K. Howard, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1979, 1003.
13 A. Dedieu and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 2074.
14 R. A. Levenson, H. B. Gray, and G. P. Caeser, *J. Am. Chem. Soc.*, 1970, **92**, 3653; R. A. Levenson and H. B. Gray, *ibid.*, 1975, **97**, 6042; H. B. Abrahamson, C. C. Frazie, D. S. Ginley, H. B. Gray, J. Liliental, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, 1977, **16**, 155.
15 B. Tavnovic, Lj. Manojlovic-Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1972, 1178.
16 K. P. Wagner, P. M. Treichel, and J. C. Calabrese, *J. Organomet. Chem.*, 1974, **71**, 1178.
17 Y. Yamamoto, K. Takahashi, K. Matsuda, and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1987, 1833.
18 A. Albinati, A. Moor, P. S. Pregosin, and L. M. Venanzi, *J. Am. Chem. Soc.*, 1982, **104**, 7672.
19 Y. Yamamoto, K. Aoki, and H. Yamazaki, *Chem. Lett.*, 1985, 201.
20 I. Ugi and R. Meyer, *Chem. Ber.*, 1960, **93**, 239.
21 Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1843; Y. Yamamoto, K. Takahashi, and H. Yamazaki, *ibid.*, 1987, **60**, 2665.
22 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.
23 D. T. Cromer and L. J. Liberman, *Chem. Phys.*, 1971, **52**, 198.
24 T. Sakurai and K. Kobayashi, UNICS SYSTEM III, 1978.

Received 5th April 1989; *Paper* 9/02764E