

## Synthesis and Structural Characterisation of Some *Triangulo*-Platinum Clusters containing Isocyanide Ligands†

Clive E. Briant, David I. Gilmour, D. Michael P. Mingos,\* and Robert W. M. Wardle  
*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR*

The compound  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  reacts with 3 and 5 mol of 2,6-xylyl isocyanide,  $\text{CNC}_6\text{H}_9$ , to give  $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-CNC}_6\text{H}_9)_2(\text{CNC}_6\text{H}_9)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$  (1) and  $[\text{Pt}_3(\mu\text{-CNC}_6\text{H}_9)_3(\text{CNC}_6\text{H}_9)_2\text{-}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  (2) respectively. The molecular structures of both compounds have been determined by single-crystal *X*-ray techniques using diffractometer data. Compound (1) crystallises in the monoclinic space group  $P2_1/n$  with four units of formula  $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-CNC}_6\text{H}_9)_2(\text{CNC}_6\text{H}_9)\text{-}\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]\cdot 0.5\text{C}_6\text{H}_6$  in a cell of dimensions  $a = 15.431(5)$ ,  $b = 15.810(3)$ ,  $c = 28.489(19)$  Å, and  $\beta = 95.22(4)^\circ$  and (2) in the monoclinic space group  $P2_1/a$  with four formula units in a cell of dimensions  $a = 16.412(2)$ ,  $b = 18.444(2)$ ,  $c = 24.383(2)$  Å, and  $\beta = 90.155(9)^\circ$ . The structures of both molecules are approximately equilateral triangles of Pt atoms with Pt–Pt distances in the range 2.618(1)–2.654(1) Å. The bonded ligand atoms are approximately coplanar with the metal triangles and  $^{31}\text{P}\text{-}\{^1\text{H}\}$  and  $^{195}\text{Pt}\text{-}\{^1\text{H}\}$  n.m.r. studies suggest that both solid-state structures are retained in solution. When intermediate mol ratios of isocyanide were added to  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  then mixtures of (1), (2), and starting material only were obtained. No evidence for the formation of symmetrical products of the type  $[\text{Pt}_3(\mu\text{-CNC}_6\text{H}_9)_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  was obtained. Examination of the molecular structures of (1) and (2) has formed a basis for rationalising the observed stoichiometries. The bridging isocyanide ligands are severely bent about the nitrogen atoms and their steric requirements are incompatible with the presence of  $\text{P}(\text{C}_6\text{H}_{11})_3$  ligands on both of the metal atoms being bridged. Consequently, replacement of bridging CO by the isocyanide labilises an adjacent terminal  $\text{P}(\text{C}_6\text{H}_{11})_3$  ligand. Compound (2) has also been synthesised by sodium-amalgam reduction of  $[\text{Pt}(\text{CO})\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  in the presence of an excess of isocyanide ligand.

Although a large number of 42- and 44-electron *triangulo*-platinum clusters have been characterised<sup>1</sup> their substitution chemistry has not been extensively investigated. In previous papers we have discussed the displacement of the carbonyl ligands in  $[\text{Pt}_3(\mu\text{-CO})_3(\text{PPh}_3)_3]$  by  $\text{SO}_2$  to give  $[\text{Pt}_3(\mu\text{-SO}_2)_3(\text{PPh}_3)_3]$  (ref. 2) and the characterisation of  $[\text{Pt}_3(\mu\text{-SO}_2)_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2(\text{dppp})]$  [dppp = 1,3-bis(diphenylphosphino)propane] which was obtained from  $[\text{Pt}_3(\mu\text{-SO}_2)_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  and dppp.<sup>3</sup> In this paper we describe the reactions of  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  with 2,6-xylyl isocyanide. Isocyanide cluster compounds of platinum of the type  $[\text{Pt}_3(\mu\text{-CNR})_3(\text{CNR})_3]$  have been described previously by Stone and co-workers,<sup>4</sup> but mixed isocyanide–phosphine *triangulo*-platinum clusters have not been reported.

### Results and Discussion

The reactions of 2,6-xylyl isocyanide with  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  are summarised in Scheme 1. These reactions occurred immediately the reagents were mixed and the resultant products were obtained in high yield (>70%) as crystalline solids. Pure products were isolated only when 3 and 5 mol of isocyanide were used. If 1 or 2 mol of isocyanide were added then mixtures of  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  and (1) were obtained. If 4 mol of isocyanide were added then a mixture of complexes (1) and (2) was obtained. When an additional mol of isocyanide was added to (2) and the solution refluxed for 0.5 h in an attempt to convert it into the fully substituted derivative,

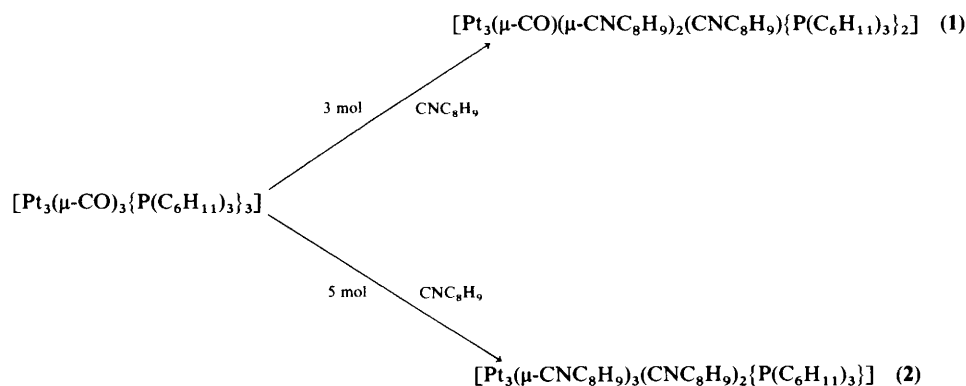
$[\text{Pt}_3(\mu\text{-CNC}_6\text{H}_9)_3(\text{CNC}_6\text{H}_9)_3]$ , complex (2) and unreacted isocyanide were recovered quantitatively. When an excess of isocyanide was added to  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  then cluster degradation products were obtained. The complexes (1) and (2) are red in solution and crystallise as brown solids.

The cluster (2) has also been synthesised in low yield (<25%) by the sodium-amalgam reduction of  $[\text{Pt}(\text{CO})\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  in the presence of an excess of 2,6-xylyl isocyanide.

The i.r. spectrum of complex (1) shows the presence of terminal (2 105  $\text{cm}^{-1}$ ) and bridging (1 730, 1 695, and 1 590  $\text{cm}^{-1}$ ) isocyanide ligands and also bridging carbonyl (1 815  $\text{cm}^{-1}$ ). The  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r. spectrum shows a complex multiplet centred at 64.4 p.p.m. with respect to (trimethyl phosphate) [see Figure 1(a)]. The spectrum has been satisfactorily simulated using a computer analysis based on a system comprising the isotopomers  $A_2$  (no  $^{195}\text{Pt}$  nuclei),  $AA'X$  (one  $^{195}\text{Pt}$  nucleus, X),  $A_2Y$  (one  $^{195}\text{Pt}$  nucleus, Y),  $AA'XY$  (two  $^{195}\text{Pt}$  nuclei, X and Y),  $AA'XX'$  (two  $^{195}\text{Pt}$  nuclei, X and X'), and  $AA'XX'Y$  (three  $^{195}\text{Pt}$  nuclei, X, X', and Y). The  $^{195}\text{Pt}\text{-}\{^1\text{H}\}$  n.m.r. spectrum shows two resonances at –4 300 p.p.m. [essentially a doublet,  $^1J(\text{Pt-P})$  4 113 Hz, with other fine structure; see Figure 1(b)] and –3 870 p.p.m. (broad singlet) with respect to  $\text{Na}_2\text{PtCl}_6$ . The former arises from the two platinum atoms with  $\text{P}(\text{C}_6\text{H}_{11})_3$  ligands co-ordinated and the latter from the platinum with the co-ordinated isocyanide. This was analysed using the spin system described above and is consistent with a structure where the  $\text{P}(\text{C}_6\text{H}_{11})_3$  phosphorus atoms lie in the plane of the triangle in a molecule of  $C_{2v}$  symmetry. The coupling constants derived from the computer simulations of the  $^{31}\text{P}\text{-}\{^1\text{H}\}$  and  $^{195}\text{Pt}\text{-}\{^1\text{H}\}$  spectra are given in Table 1.

The i.r. spectrum of complex (2) also shows the presence of terminal (2 120 and 2 090  $\text{cm}^{-1}$ ) and bridging (1 860, 1 800, 1 720, and 1 587  $\text{cm}^{-1}$ ) isocyanide ligands. Its  $^{31}\text{P}\text{-}\{^1\text{H}\}$  n.m.r.

† Supplementary data available (No. SUP 56256, 6 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.



Scheme 1.

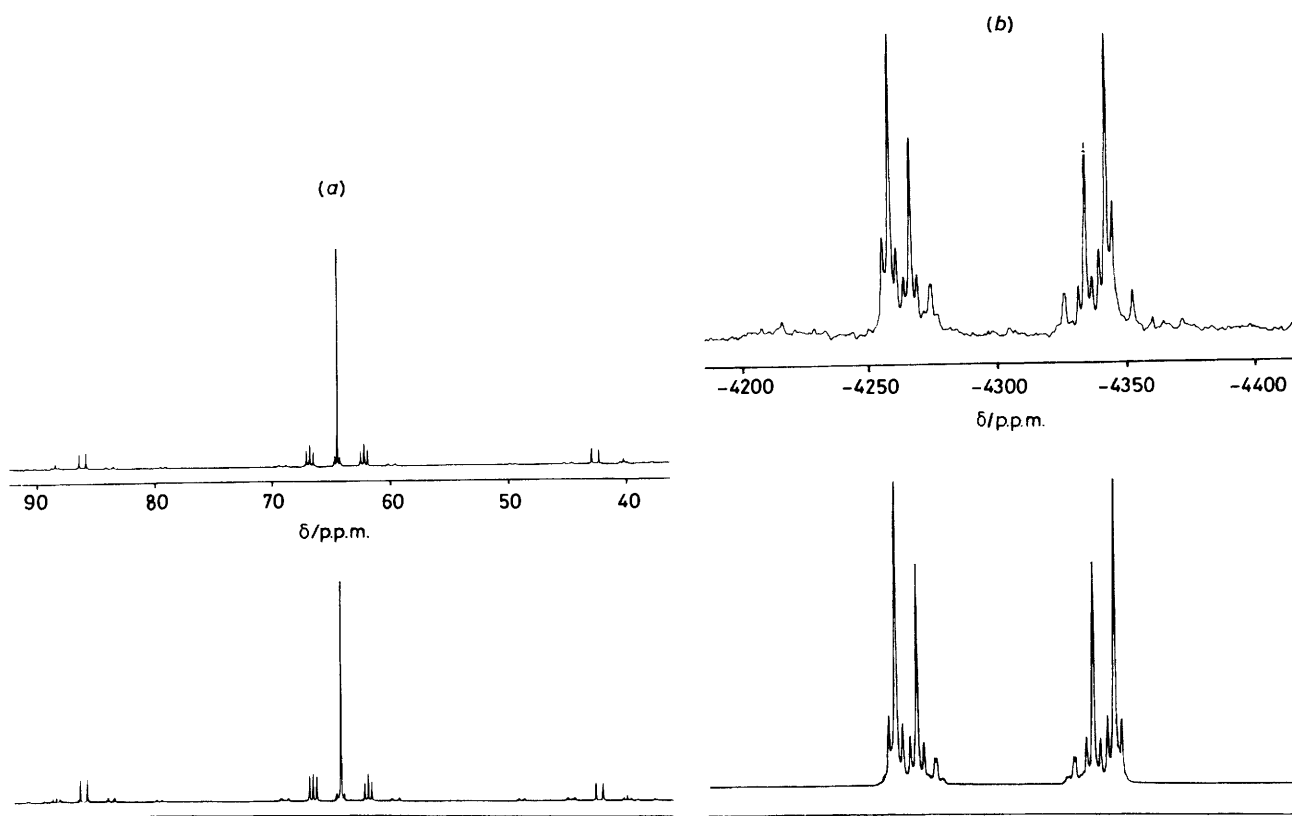


Figure 1. (a) Observed (upper) and calculated  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra for  $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-CNC}_8\text{H}_9)_2(\text{CNC}_8\text{H}_9)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$ . (b) Observed and calculated resonances for the  $\text{Pt}^2, \text{Pt}^{2'}$  part of the corresponding  $^{195}\text{Pt}\{-^1\text{H}\}$  spectrum (see Table 1 for atom labelling)

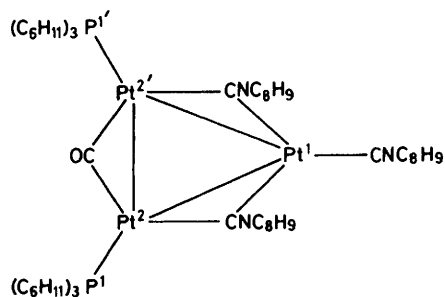
spectrum shows a complex multiplet centred at 51.9 p.p.m. with respect to trimethyl phosphate (see Figure 2) which was analysed in terms of the sum of the isotopomers A (no  $^{195}\text{Pt}$  nuclei), AX (one  $^{195}\text{Pt}$  nucleus, X), AY (one  $^{195}\text{Pt}$  nucleus, Y), AXY (two  $^{195}\text{Pt}$  nuclei, X and Y),  $\text{AY}_2$  (two  $^{195}\text{Pt}$  nuclei, Y), and  $\text{AXY}_2$  (three  $^{195}\text{Pt}$  nuclei, X and 2Y). The  $^{195}\text{Pt}\{-^1\text{H}\}$  n.m.r. spectrum, also analysed in terms of this spin system, shows two resonances at  $-4\ 632$  p.p.m. [doublet,  $^1J(\text{Pt-P})$  3 893 Hz] and  $-3\ 863$  p.p.m. [doublet,  $^2J(\text{Pt-P})$  452 Hz] with respect to  $\text{Na}_2\text{PtCl}_6$ . This is consistent with a structure where one  $\text{P}(\text{C}_6\text{H}_{11})_3$  group is attached to the  $\text{Pt}_3$  triangle giving a molecule of  $\text{C}_{2v}$  symmetry. It did not prove possible to estimate values for  $J(\text{PtPt})$  for this molecule since the resonances from the less-abundant isotopomers were not observed.

In order to confirm the structures of the clusters single-crystal

X-ray crystallographic analyses on (1) and (2) were carried out. Selected intramolecular bond lengths and angles for both molecules are given in Tables 2 and 3, respectively. Fractional co-ordinates of the non-hydrogen atoms in Tables 4 and 5, and the structures are illustrated in Figures 3 and 4.

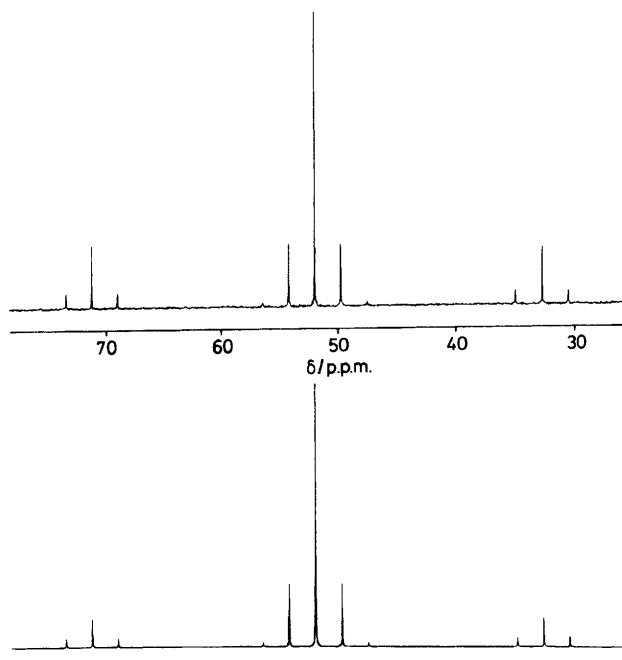
The platinum atoms form approximately equilateral triangles with Pt-Pt distances of 2.648(1), 2.625(1), and 2.627(1) Å in complex (1) and 2.618(1), 2.626(1), and 2.654(1) Å in complex (2). These distances lie around the lower limit of the range found in comparable trinuclear platinum cluster compounds. This may be attributed in part to the small radius of the bridging carbon atoms since Pt-Pt distances in such clusters are found to depend approximately on the size of the atoms of the bridging ligands.

The metal-bound ligand atoms are all approximately

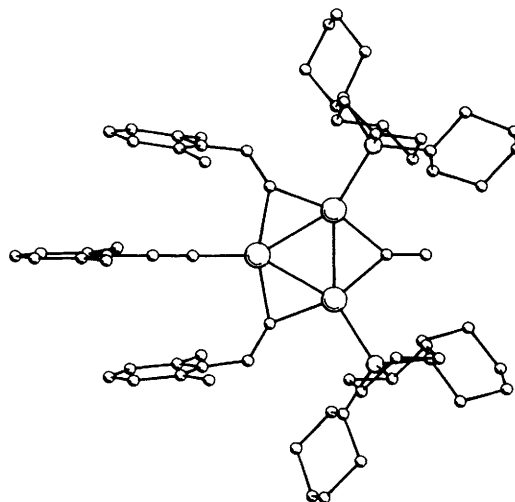
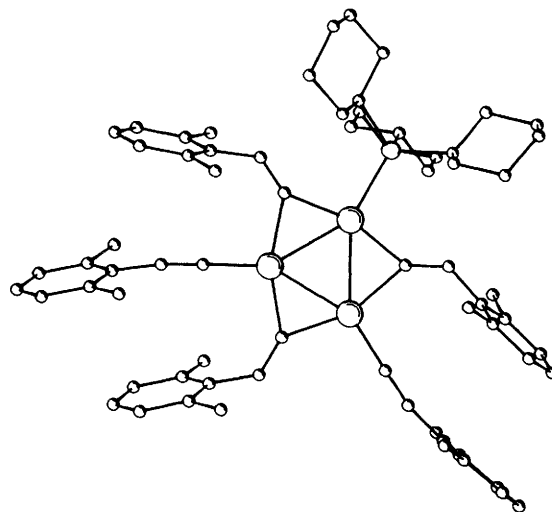
**Table 1.** Chemical shifts and coupling constants for  $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-CNC}_6\text{H}_9)_2(\text{CNC}_6\text{H}_9)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$  (1)

$\delta/\text{p.p.m.}$		
P <sup>1</sup>	Pt <sup>1</sup>	Pt <sup>2</sup>
64.4	-3 870	-4 300

	$J/\text{Hz}$			
	Pt <sup>2'</sup>	Pt <sup>2</sup>	Pt <sup>1</sup>	P <sup>1</sup>
P <sup>1'</sup>	4 113	442	441	57
P <sup>1</sup>	442	4 113	441	
Pt <sup>1</sup>	290	290		
Pt <sup>2</sup>	884			

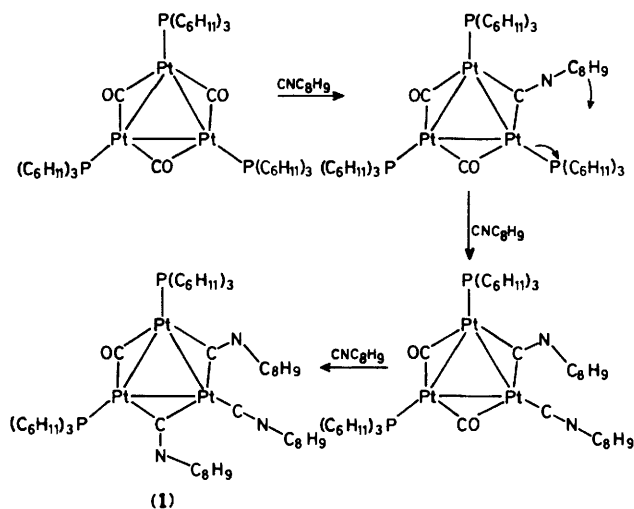
**Figure 2.** Observed (upper) and calculated  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectra for  $[\text{Pt}_3(\mu\text{-CNC}_6\text{H}_9)_3(\text{CNC}_6\text{H}_9)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ 

coplanar with the metal triangle in both complexes and the metal-ligand distances are comparable to those found in other platinum cluster compounds. The terminal isocyanides are effectively linear [C-N-C 178(2)° in (1) and mean C-N-C 170(3)° in (2)] and the bridging isocyanides are bent [mean C-N-C 128.5(5)° in (1) and 132.0(6)° in (2)], an effect accompanied by a lengthening of their C-N bonds and observed

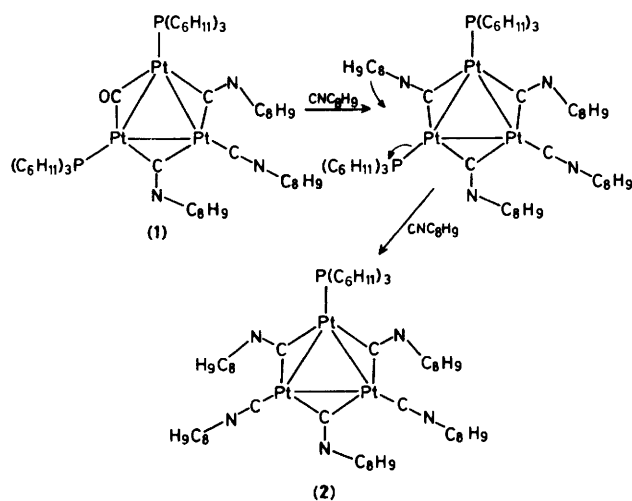
**Figure 3.** The molecular geometry of  $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-CNC}_6\text{H}_9)_2(\text{CNC}_6\text{H}_9)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$ **Figure 4.** The molecular geometry of  $[\text{Pt}_3(\mu\text{-CNC}_6\text{H}_9)_3(\text{CNC}_6\text{H}_9)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ 

previously in molecules such as  $[\text{Fe}_2(\mu\text{-CNMe})_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$ .<sup>5</sup>

Inspection of the molecular structures of (1) and (2) (Figures 3 and 4) provides a basis for understanding why these compounds are formed in preference to the more symmetrically substituted derivatives. In particular, the structures highlight the large difference in the steric requirements of terminal and bridging isocyanides. The terminal isocyanides remain linear about nitrogen and therefore can slot into the molecule and occupy much less space than the tricyclohexylphosphine ligands, particularly if the phenyl rings are orientated perpendicular to the cluster plane. In contrast, the coordination of an isocyanide in a bridging position results in a large change in the bond angle at the nitrogen from around 175° to *ca.* 130°. It is evident from Figures 3 and 4 that it is sterically unfavourable to locate a bridging isocyanide ligand across a  $\text{Pt}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2$  moiety. The replacement of the first bridging carbonyl ligand by  $\text{CNC}_6\text{H}_9$  may be accompanied by the substitution of a terminal  $\text{P}(\text{C}_6\text{H}_{11})_3$  by  $\text{CNC}_6\text{H}_9$ . A sequence of reactions which represents this sequence of events is shown in



Scheme 2.



Scheme 3.

**Table 2.** Selected molecular dimensions (distances in Å, angles in °) for  $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-CNC}_8\text{H}_9)_2(\text{CNC}_8\text{H}_9)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$  with estimated standard deviations in parentheses

Pt(1)–Pt(2)	2.648(1)	Pt(1)–Pt(3)–Pt(2)	60.56(2)
Pt(1)–Pt(3)	2.625(1)	Pt(1)–Pt(2)–Pt(3)	59.68(2)
Pt(2)–Pt(3)	2.627(1)	Pt(2)–Pt(1)–Pt(3)	59.76(2)
Pt(1)–P(1)	2.278(4)	C(1)–Pt(1)–C(4)	160.3(7)
Pt(2)–P(2)	2.268(5)	P(1)–Pt(1)–C(1)	98.3(4)
Pt(3)–C(2)	1.92(2)	P(1)–Pt(1)–C(4)	101.4(6)
Pt(1)–C(1)	2.05(1)	C(1)–Pt(2)–C(3)	160.5(6)
Pt(2)–C(1)	2.06(2)	P(2)–Pt(2)–C(1)	98.4(4)
Pt(2)–C(3)	2.03(2)	P(2)–Pt(2)–C(3)	100.8(5)
Pt(3)–C(3)	2.09(2)	C(3)–Pt(3)–C(4)	159.8(7)
Pt(1)–C(4)	2.05(2)	C(2)–Pt(3)–C(3)	100.4(7)
Pt(3)–C(4)	2.06(2)	C(2)–Pt(3)–C(4)	99.7(8)
C(1)–O(1)	1.17(2)	C(2)–N(2)–C(20)	178(2)
C(2)–N(2)	1.18(2)	C(3)–N(3)–C(30)	129(2)
C(3)–N(3)	1.27(2)	C(4)–N(4)–C(40)	128(2)
C(4)–N(4)	1.27(3)		

Scheme 2. After the first two steps, the second bridging carbonyl may readily be replaced because the incoming  $\text{CNC}_8\text{H}_9$  ligand can also bend towards the single terminal  $\text{CNC}_8\text{H}_9$ . Compound (1) results from this sequence of reactions. The remaining bridging carbonyl ligand can only be replaced if an adjacent  $\text{P}(\text{C}_6\text{H}_{11})_3$  is also lost making room for its bending distortion. Compound (2) may result from such a sequence of reactions (Scheme 3).

If the bridged metal–metal bonds are ignored then these clusters can be viewed in terms of three T-shaped  $\text{ML}_3$  fragments sharing common bridging groups similar to the structures  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  and  $[\text{Pt}_3(\mu\text{-SO}_2)_3(\text{PPh}_3)_3]$ . This analysis of the bonding was discussed in detail by us in a previous paper.<sup>3</sup>

### Experimental

Reactions were routinely carried out, using standard Schlenk-line procedures, under an atmosphere of pure, dry  $\text{N}_2$  and using dry  $\text{O}_2$ -free solvents. Microanalyses (C, H, and N) were carried out by Mr. M. Gascoyne and his staff of this laboratory.

**Table 3.** Selected molecular dimensions (distances in Å, angles in °) for  $[\text{Pt}_3(\mu\text{-CNC}_8\text{H}_9)_3(\text{CNC}_8\text{H}_9)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  with estimated standard deviations in parentheses

Pt(1)–Pt(2)	2.654(1)	Pt(1)–Pt(3)–Pt(2)	60.81(2)
Pt(1)–Pt(3)	2.618(1)	Pt(1)–Pt(2)–Pt(3)	59.44(2)
Pt(2)–Pt(3)	2.626(1)	Pt(2)–Pt(1)–Pt(3)	59.75(2)
Pt(1)–C(1)	1.89(2)	C(2)–Pt(1)–C(5)	157.8(5)
Pt(2)–P(1)	2.287(3)	C(1)–Pt(1)–C(2)	102.9(6)
Pt(3)–C(3)	1.89(1)	C(1)–Pt(1)–C(5)	99.3(6)
Pt(1)–C(2)	2.03(2)	C(4)–Pt(2)–C(5)	162.1(5)
Pt(3)–C(2)	2.04(2)	P(1)–Pt(2)–C(4)	98.1(4)
Pt(2)–C(4)	2.02(1)	P(1)–Pt(2)–C(5)	99.8(4)
Pt(3)–C(4)	2.11(1)	C(2)–Pt(3)–C(4)	159.5(6)
Pt(1)–C(5)	2.08(1)	C(3)–Pt(3)–C(2)	100.7(6)
Pt(2)–C(5)	2.00(1)	C(3)–Pt(3)–C(4)	99.8(6)
C(1)–N(1)	1.18(2)	C(1)–N(1)–C(11)	167(1)
C(2)–N(2)	1.24(2)	C(2)–N(2)–C(21)	131(1)
C(3)–N(3)	1.18(2)	C(3)–N(3)–C(31)	173(1)
C(4)–N(4)	1.22(2)	C(4)–N(4)–C(41)	132(1)
C(5)–N(5)	1.22(2)	C(5)–N(5)–C(51)	133(1)

Infrared spectra were recorded for Nujol mulls using a Pye-Unicam SP2000 spectrometer.

The  $^{31}\text{P}\{-^1\text{H}\}$  and  $^{195}\text{Pt}\{-^1\text{H}\}$  n.m.r. spectra were recorded using a Bruker AM-250 spectrometer, and referenced to  $\text{PO}(\text{OMe})_3\text{-D}_2\text{O}$  and  $\text{Na}_2\text{PtCl}_6\text{-D}_2\text{O}$  respectively. The machine operating frequencies were 101.26 MHz for  $^{31}\text{P}$  and 53.55 MHz for  $^{195}\text{Pt}$ . All samples were run in deuteriated solvents. N.m.r. computer simulations were carried out using the Oxford University VAX computer system utilising a program developed by Dr. R. K. Harris of the University of East Anglia and adapted for use at Oxford by Dr. A. E. Derome.

The complex  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]$  was synthesised by the method of Clark *et al.*<sup>6</sup> from *trans*- $[\text{PtH}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$  and CO and *cis*- $[\text{Pt}(\text{CO})\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  also by a method of Clark and co-workers<sup>7</sup> from  $[\text{PtCl}_2(\text{cod})]$  (cod = cyclo-octa-1,5-diene), CO, and  $\text{P}(\text{C}_6\text{H}_{11})_3$ .

*Synthesis of*  $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-CNC}_8\text{H}_9)_2(\text{CNC}_8\text{H}_9)\{\text{P}(\text{C}_6\text{H}_{11})_3\}_2]$  (1).—2,6-Xylyl isocyanide (0.051 g, 0.39 mmol)

**Table 4.** Final fractional co-ordinates for non-hydrogen atoms in compound (1) with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pt(1)	-0.136 65(4)	0.122 31(4)	0.104 57(2)	C(111)	-0.382(1)	0.173(1)	0.066 8(7)
Pt(2)	-0.004 98(4)	0.122 11(4)	0.171 02(2)	C(112)	-0.467(1)	0.123(1)	0.058 8(7)
Pt(3)	-0.112 99(4)	-0.006 52(4)	0.162 42(2)	C(113)	-0.513(1)	0.138(2)	0.009 3(7)
P(1)	-0.208 9(3)	0.189 1(3)	0.041 8(1)	C(114)	-0.452(1)	0.117(1)	-0.029 1(7)
P(2)	0.115 2(3)	0.188 2(3)	0.205 1(2)	C(115)	-0.367(1)	0.169(1)	-0.021 3(6)
C(1)	-0.038 6(9)	0.208 7(9)	0.118 6(5)	C(120)	-0.205(1)	0.305(1)	0.047 1(5)
O(1)	-0.013(1)	0.271(1)	0.102 7(6)	C(121)	-0.252(1)	0.356(1)	0.006 1(6)
C(2)	-0.151(1)	-0.114(1)	0.184 4(7)	C(122)	-0.232(2)	0.452(1)	0.013 7(7)
N(2)	-0.171(1)	-0.182(1)	0.197 4(6)	C(123)	-0.259(2)	0.481(1)	0.062 5(7)
C(20)	-0.196 8(7)	-0.257 9(9)	0.213 4(4)	C(124)	-0.215(2)	0.427(1)	0.102 8(7)
C(21)	-0.252 0(8)	-0.255(1)	0.249 4(4)	C(125)	-0.237(1)	0.333(1)	0.094 7(6)
C(22)	-0.281 6(8)	-0.331(1)	0.266 8(5)	C(130)	-0.155 0(9)	0.169 6(9)	-0.013 4(6)
C(23)	-0.254 8(9)	-0.406(1)	0.247 4(5)	C(131)	-0.146(1)	0.073(1)	-0.019 6(7)
C(24)	-0.199 6(9)	-0.409(1)	0.211 1(5)	C(132)	-0.101(1)	0.051(1)	-0.065 1(7)
C(25)	-0.169 7(8)	-0.333(1)	0.193 5(5)	C(133)	-0.011(1)	0.096(1)	-0.063 2(8)
C(26)	-0.110(2)	-0.328(2)	0.154(1)	C(134)	-0.024(1)	0.192(1)	-0.057 6(7)
C(27)	-0.275(2)	-0.171(2)	0.271(1)	C(135)	-0.065(1)	0.211(1)	-0.011 9(7)
C(3)	-0.004(1)	0.014 4(9)	0.209 6(5)	C(210)	0.215(1)	0.156(1)	0.177 7(7)
N(3)	0.032(1)	-0.021(1)	0.246 2(6)	C(211)	0.225(1)	0.059(1)	0.181 7(8)
C(30)	0.018 4(7)	-0.100(1)	0.263 4(5)	C(212)	0.311(2)	0.032(2)	0.161 3(9)
C(31)	0.049 1(7)	-0.171(1)	0.241 4(5)	C(213)	0.311(2)	0.063(1)	0.109 4(9)
C(32)	0.036 5(9)	-0.251(1)	0.260 8(7)	C(214)	0.300(2)	0.159(2)	0.107(1)
C(33)	-0.006 5(9)	-0.259(1)	0.301 6(7)	C(215)	0.213(2)	0.184(2)	0.125 3(8)
C(34)	-0.037 1(8)	-0.187(1)	0.323 3(6)	C(220)	0.138(1)	0.161(1)	0.269 0(6)
C(35)	-0.024 8(8)	-0.107(1)	0.304 1(5)	C(221)	0.065(1)	0.190(2)	0.298 1(9)
C(36)	-0.070(2)	-0.028(2)	0.327(1)	C(222)	0.081(2)	0.155(2)	0.348 3(9)
C(37)	0.089(2)	-0.162(2)	0.196(1)	C(223)	0.168(2)	0.191(2)	0.371 0(9)
C(4)	-0.211(1)	0.016(1)	0.109 5(8)	C(224)	0.243(2)	0.162(2)	0.342 7(9)
N(4)	-0.277(1)	-0.021(1)	0.088 6(6)	C(225)	0.228(1)	0.192(2)	0.291 1(8)
C(40)	-0.308 5(8)	-0.100(1)	0.098 1(5)	C(230)	0.111(1)	0.304(1)	0.197 7(7)
C(41)	-0.362 2(8)	-0.109(1)	0.134 6(5)	C(231)	0.028(1)	0.347(1)	0.213 3(9)
C(42)	-0.393 0(9)	-0.189(1)	0.144 9(6)	C(232)	0.019(2)	0.438(2)	0.193(1)
C(43)	-0.370(1)	-0.258(1)	0.118 3(7)	C(233)	0.104(2)	0.491(2)	0.204(1)
C(44)	-0.317(1)	-0.250(1)	0.081 6(6)	C(234)	0.182(2)	0.446(2)	0.186(1)
C(45)	-0.286 3(8)	-0.169(1)	0.071 6(5)	C(235)	0.194(1)	0.358(1)	0.211 0(9)
C(46)	-0.232(2)	-0.156(2)	0.032(1)	C(50)	-0.013(2)	0.568(2)	0.029(1)
C(47)	-0.387(2)	-0.032(2)	0.162(1)	C(51)	0.027(2)	0.496(3)	0.047 8(7)
C(110)	-0.322(1)	0.151(1)	0.028 1(5)	C(52)	0.037(1)	0.425(2)	0.020(2)

was added with stirring to a solution of  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}_3]\cdot\text{C}_6\text{H}_6$  (0.20 g, 0.13 mmol) in dichloromethane (20 cm<sup>3</sup>). The deep red solution immediately lightened slightly in colour and stirring was continued for a further 15 min. The resulting solution was concentrated *in vacuo* and methanol added to precipitate the product as orange-brown microcrystals. Large red crystals of 1,2- $\mu$ -carbonyl-1,2-bis(tricyclohexylphosphine)-1,3,2,3-bis( $\mu$ -2',6'-xylyl isocyanide)-3-(2',6'-xylyl isocyanide)-triangulo-triplatinum (0.17 g, 86%) suitable for X-ray crystallography were obtained by layering from benzene-methanol (Found: C, 50.3; H, 6.0; N, 2.6.  $\text{C}_{67}\text{H}_{96}\text{N}_3\text{OP}_2\text{Pt}_3$  requires C, 50.1; H, 6.0; N, 2.6%);  $\nu(\text{CN})$  at 2 105s, 1 730s, 1 695s, and 1 590s cm<sup>-1</sup> and  $\nu(\text{CO})$  at 1 815 cm<sup>-1</sup>.

**Synthesis of  $[\text{Pt}_3(\mu\text{-CNC}_8\text{H}_9)_3(\text{CNC}_8\text{H}_9)_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  (2).**—*Method (a)* 2,6-Xylyl isocyanide (0.085 g, 0.65 mmol) was added with stirring to a solution of  $[\text{Pt}_3(\mu\text{-CO})_3\{\text{P}(\text{C}_6\text{H}_{11})_3\}]\cdot\text{C}_6\text{H}_6$  (0.20 g, 0.13 mmol) in dichloromethane (20 cm<sup>3</sup>). The reaction mixture was worked up in a similar manner as for (1) and large red crystals of 1-tricyclohexylphosphine-1,2,1,3,2,3-tris( $\mu$ -2',6'-xylyl isocyanide)-2,3-bis(2',6'-xylyl isocyanide)-triangulo-triplatinum were obtained by recrystallisation from dichloromethane-methanol by slow evaporation (0.15 g, 78%) (Found: C, 49.7; H, 5.1; N, 4.6.  $\text{C}_{63}\text{H}_{78}\text{N}_3\text{PPT}_3$  requires C, 49.7; H, 5.1; N, 4.6%);  $\nu(\text{CN})$  at 2 120s, 2 090s, 1 860w, 1 800m, 1 720s, and 1 587s cm<sup>-1</sup>.

*Method (b)* A solution of  $[\text{Pt}(\text{CO})\text{Cl}_2\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$  (0.20 g, 0.35 mmol) in dried tetrahydrofuran (20 cm<sup>3</sup>) was shaken with 1% sodium amalgam (5 cm<sup>3</sup>) for 1 h in the presence of an excess of 2,6-xylyl isocyanide (0.20 g, 1.53 mmol). The resulting red solution was filtered and evaporated to dryness *in vacuo*. The product was extracted with benzene (20 cm<sup>3</sup>) and precipitated from solution as an orange-brown microcrystalline solid with light petroleum. Recrystallisation from benzene-methanol by layering afforded deep red single crystals of compound (2) suitable for X-ray crystallography (0.02 g, 11%) (Found: C, 49.9; H, 4.4; N, 4.6%). The i.r. spectrum was identical to that of the product from Method (a).

**Crystal Data for Compound (1).**— $\text{C}_{64}\text{H}_{93}\text{N}_3\text{OP}_2\text{Pt}_3\cdot 0.5\text{C}_6\text{H}_6$ ,  $M = 1\ 606.5$ , monoclinic,  $a = 15.431(5)$ ,  $b = 15.810(3)$ ,  $c = 28.489(19)$  Å,  $\beta = 95.22(4)^\circ$ ,  $U = 6\ 922$  Å<sup>3</sup> (by least-squares refinement of diffractometer angles for 25 automatically centred reflections,  $\lambda = 0.710\ 69$  Å), space group  $P2_1/n$ ,  $D_m = 1.58$  g cm<sup>-3</sup>,  $Z = 4$ ,  $D_c = 1.54$  g cm<sup>-3</sup>,  $F(000) = 3\ 164$ . Red crystals grown from benzene-methanol and mounted in a 1.5 mm Lindemann capillary tube. Crystal dimensions 1.0 × 0.8 × 0.5 mm,  $\mu(\text{Mo-K}\alpha) = 64.5$  cm<sup>-1</sup>.

Geometric diffraction data were collected on a CAD4 diffractometer,  $\omega$ -2 $\theta$  scan with  $\omega$  scan width = 0.9°, graphite-monochromated Mo-K $\alpha$  radiation; 15 351 reflections measured ( $1 < \theta < 25^\circ$ ), 7 896 unique reflections with  $I \geq 3\sigma(I)$ , merging

**Table 5.** Final fractional co-ordinates for non-hydrogen atoms in compound (2) with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pt(1)	0.169 72(3)	-0.022 97(4)	0.223 04(2)	C(41)	0.377 4(6)	0.315 5(7)	0.219 1(4)
Pt(2)	0.221 94(3)	0.103 22(3)	0.291 93(2)	C(42)	0.333 7(8)	0.372 9(7)	0.184 6(4)
Pt(3)	0.265 22(3)	0.106 12(4)	0.188 34(2)	C(43)	0.378 0(9)	0.427 9(8)	0.149 1(5)
P(1)	0.231 6(2)	0.161 0(2)	0.378 7(1)	C(44)	0.462 9(9)	0.424 6(8)	0.148 0(5)
C(1)	0.106 8(9)	-0.128(1)	0.212 7(6)	C(45)	0.506 7(8)	0.366 7(8)	0.182 1(5)
N(1)	0.065 9(8)	-0.192 7(9)	0.206 7(5)	C(46)	0.462 0(7)	0.311 8(7)	0.217 7(4)
C(11)	0.020 9(8)	-0.273 0(8)	0.212 2(4)	C(47)	0.508(1)	0.247(1)	0.255 8(8)
C(12)	0.061 0(8)	-0.351(1)	0.228 4(4)	C(48)	0.243(1)	0.375(1)	0.185 3(8)
C(13)	0.016(1)	-0.430(1)	0.238 7(4)	C(5)	0.148 6(8)	-0.001 8(9)	0.306 3(5)
C(14)	-0.068(1)	-0.428(1)	0.232 9(4)	N(5)	0.109 7(7)	-0.037 8(8)	0.342 9(5)
C(15)	-0.108 2(8)	-0.350(1)	0.216 6(4)	C(51)	0.057 2(7)	-0.113 1(8)	0.343 7(4)
C(16)	-0.063 5(8)	-0.271 6(9)	0.206 1(4)	C(52)	0.086 0(8)	-0.195 0(8)	0.364 3(4)
C(17)	0.156(2)	-0.350(2)	0.237(1)	C(53)	0.032 0(9)	-0.268(1)	0.369 1(4)
C(18)	-0.106(1)	-0.185(1)	0.186 2(9)	C(54)	-0.048 9(9)	-0.256 6(9)	0.333 4(4)
C(2)	0.215 9(9)	-0.000(1)	0.147 2(6)	C(55)	-0.077 6(8)	-0.174 9(9)	0.332 9(4)
N(2)	0.213 0(7)	-0.032 4(8)	0.100 1(5)	C(56)	-0.023 8(7)	-0.101 9(9)	0.327 6(4)
C(21)	0.249 7(7)	-0.003 4(6)	0.050 3(5)	C(57)	-0.054(1)	-0.014(1)	0.306 6(8)
C(22)	0.200 4(8)	0.033 1(6)	0.009 0(5)	C(58)	0.176(1)	-0.204(2)	0.384(1)
C(23)	0.236 8(9)	0.057 8(7)	-0.040 7(5)	C(110)	0.3199	0.1124	0.4147
C(24)	0.320 1(9)	0.045 8(7)	-0.047 6(6)	C(111)	0.309 2(7)	0.010 0(8)	0.419 9(5)
C(25)	0.368 9(9)	0.009 2(7)	-0.006 6(6)	C(112)	0.381 7(8)	-0.033 6(9)	0.449 8(6)
C(26)	0.333 1(7)	-0.015 8(6)	0.043 1(5)	C(113)	0.462 5(8)	-0.011 7(9)	0.420 8(6)
C(27)	0.386(1)	-0.060(1)	0.085 5(9)	C(114)	0.473 1(8)	0.091 2(9)	0.416 4(6)
C(28)	0.109(1)	0.041(2)	0.019(1)	C(115)	0.400 4(7)	0.133(1)	0.384 2(6)
C(3)	0.325 1(8)	0.161 4(9)	0.131 7(6)	C(210)	0.249 7(7)	0.284 6(8)	0.379 4(5)
N(3)	0.363 3(7)	0.193 8(8)	0.095 8(5)	C(211)	0.186 3(8)	0.333 4(8)	0.342 3(5)
C(31)	0.403 5(7)	0.224 0(6)	0.048 9(5)	C(212)	0.208 8(9)	0.434 2(9)	0.336 2(5)
C(32)	0.357 1(7)	0.263 4(6)	0.007 2(5)	C(213)	0.217(1)	0.481(1)	0.392 9(6)
C(33)	0.395 8(8)	0.287 6(7)	-0.041 6(5)	C(214)	0.278 3(9)	0.430 0(9)	0.429 0(6)
C(34)	0.478 9(8)	0.271 9(7)	-0.046 7(6)	C(215)	0.256 2(8)	0.329 6(8)	0.435 5(5)
C(35)	0.524 9(8)	0.233 6(7)	-0.004 9(5)	C(310)	0.146 4(7)	0.130 4(8)	0.424 2(5)
C(36)	0.487 3(7)	0.208 8(6)	0.044 2(5)	C(311)	0.066 0(7)	0.172 6(9)	0.403 1(5)
C(37)	0.535(1)	0.167(1)	0.092 5(9)	C(312)	-0.007 1(9)	0.132(1)	0.434 7(6)
C(38)	0.265(1)	0.279(1)	0.015 2(8)	C(313)	0.002 6(9)	0.146(1)	0.496 4(6)
C(4)	0.294 6(8)	0.193 2(9)	0.253 8(6)	C(314)	0.083 7(8)	0.106(1)	0.517 3(6)
N(4)	0.334 2(7)	0.262 3(7)	0.258 5(4)	C(315)	0.156 7(8)	0.147(1)	0.486 2(5)

$R = 0.0728$ . An empirical absorption correction was applied before refinement with anisotropic thermal parameters using a program DIFABS written by Walker and Stuart.<sup>8</sup>

The structure was solved by standard Patterson and Fourier methods. Refinement by blocked-matrix least squares, Pt and P anisotropic, remaining atoms isotropic. A Chebyshev weighting scheme with coefficients of 1 628.8, 2 201.1, and 602.4 gave satisfactory agreement analyses. Final  $R$  and  $R'$  0.0703 and 0.0963.

**Crystal Data for Compound (2).**— $C_{63}H_{78}N_5PPt_3$ ,  $M = 1\,521.3$ , monoclinic,  $a = 16.412(2)$ ,  $b = 18.444(2)$ ,  $c = 24.383(2)$  Å,  $\beta = 90.155(9)^\circ$ ,  $U = 5\,942$  Å<sup>3</sup> (by least-squares refinement of diffractometer angles for 25 automatically centred reflections,  $\lambda = 0.710\,69$  Å), space group  $P2_1/a$ ,  $D_m = 1.69$  g cm<sup>-3</sup>,  $Z = 4$ ,  $D_c = 1.70$  g cm<sup>-3</sup>,  $F(000) = 2\,960$ . Red crystals grown from benzene-methanol and mounted in a 0.5 mm Lindemann capillary tube. Crystal dimensions  $0.45 \times 0.09 \times 0.04$  mm,  $\mu(\text{Mo-K}\alpha) = 74.8$  cm<sup>-1</sup>.

Data were collected using the same scanning mode as above; 11 113 reflections measured ( $1.5 < \theta < 22.5^\circ$ ), 5 886 unique reflections with  $I \geq 3\sigma(I)$ , merging  $R = 0.0601$ . The crystal faces were measured and an analytical absorption correction was applied.

The structure was solved and refined as above and a Chebyshev weighting scheme with coefficients 1 217.7, 1 661.9, and 536.6 gave satisfactory agreement analyses. Final  $R$  and  $R'$  0.0424 and 0.0600.

Programs and computers used and sources of scattering factor data are given in refs. 9–11.

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