

Synthesis and Crystal and Molecular Structure of Tris- μ -(*t*-butyl isocyanide)-tris(*t*-butyl isocyanide)-triangulo-triplatinum

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Reaction of *t*-butyl isocyanide with bis(cyclo-octa-1,5-diene)platinum gives the orange crystalline complex $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$ in essentially quantitative yield. Methyl, ethyl, and cyclohexyl isocyanides react with $[\text{Pt}(1,5\text{-C}_8\text{H}_{12})_2]$ in a similar manner to give $[\text{Pt}_3(\text{RNC})_6]$ (R = Me, Et, or C_6H_{11}). The structural identity of $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$ has been established by analysis of single-crystal *X*-ray data recorded at room temperature on a four-circle diffractometer. The complex is monoclinic, space group $P2_1/n$, $Z = 4$, $a = 18.213(7)$, $b = 11.811(5)$, $c = 21.996(6)$ Å, $\beta = 110.21(3)^\circ$. Using 3 543 reflections, the refinement has converged to R 0.057 (R' 0.070). The molecule contains an essentially equilateral triangle of platinum atoms each of which carries a terminal isocyanide ligand, with the remaining three isocyanide groups bridging the sides of the triangle. The former are effectively linear and the latter bent $[\text{CNC}(\text{mean}) 132.7^\circ]$. The platinum atoms and the six attached carbon atoms are effectively coplanar with maximum deviation 0.08 Å. Hydrogen-1 and ^{13}C n.m.r. studies between room temperature and 120°C reveal that $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$ undergoes dynamic behaviour *via* an intermolecular process involving terminal and bridge isocyanide site exchange catalysed by free ligand.

COMPLEXES of nickel(0) and palladium(0) in which isocyanide groups are the only ligands have been known for many years;¹ however, corresponding platinum isocyanide complexes have not been described. The isolation of binary olefin complexes of platinum, such as bis-(cyclo-octa-1,5-diene)platinum, suggested a route to such complexes by displacement of the olefin ligands with isocyanides.²

RESULTS AND DISCUSSION

t-Butyl isocyanide reacted essentially quantitatively with bis(cyclo-octa-1,5-diene)platinum in light petroleum to give a red-orange air-stable crystalline complex of empirical composition $[\text{Pt}(\text{Bu}^t\text{NC})_2]$. The i.r. spectrum showed the presence of terminal ($2\ 155\ \text{cm}^{-1}$) and bridging ($1\ 714\ \text{cm}^{-1}$) isocyanide ligands, and the ^1H n.m.r. consisted of two sharp singlets corresponding to two environments for the *t*-butyl groups. These properties indicated that the complex was a polynuclear platinum species. Some years ago Malatesta³ and Fischer and Werner⁴ reported several palladium complexes formulated as $[\text{Pd}(\text{RNC})_2]$ but the nature of these species was not clearly understood. Subsequently, $[\text{M}(\text{Bu}^t\text{NC})_2]$ (M = Ni or Pd) were prepared and shown to afford dioxygen complexes,⁵ in contrast to the behaviour of the platinum analogue described herein which is relatively inert to oxygen.

Methyl, ethyl, and cyclohexyl isocyanide also react with $[\text{Pt}(1,5\text{-C}_8\text{H}_{12})_2]$ to give complexes apparently similar to that obtained from Bu^tNC . In order to place this type of complex on a firm structural foundation a single-crystal *X*-ray diffraction study was carried out on the Bu^tNC derivative.²

The overall molecular geometry is shown in Figure 1. The platinum atoms form an approximately equilateral triangle and carry both terminal and bridging isocyanide groups. The former are effectively linear $[\text{CNC}(\text{mean})$

$175^\circ]$, whereas the bridging groups are bent $[\text{CNC}(\text{mean}) 132.7^\circ]$ (Table 1). Concomitant variations in the average Pt-C and C-N distances are observed [$1.90(2)$ and $1.15(3)$ and $2.08(2)$ and $1.21(3)$ Å for terminal and

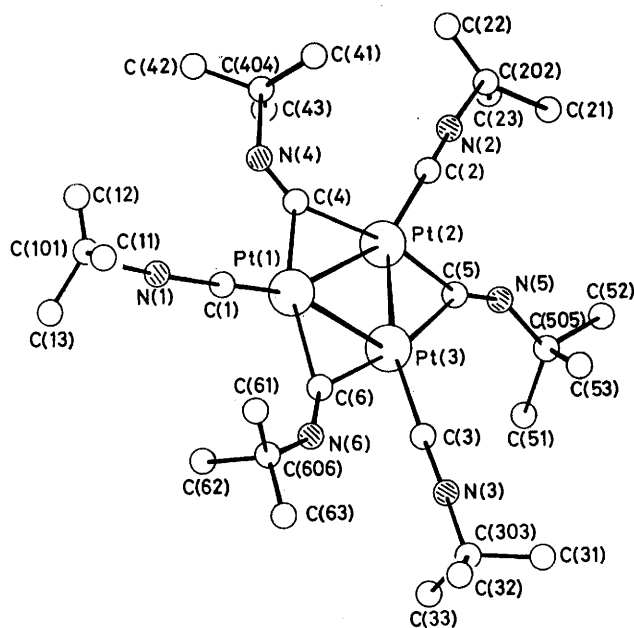


FIGURE 1 Molecular structure of $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$

bridging ligands, respectively]. Similar distances have been recorded for the two square-planar platinum(II) isocyanide complexes *cis*- $[\text{PtCl}_2(\text{EtNC})(\text{PhEt}_2\text{P})]$ and *cis*- $[\text{PtCl}_2(\text{PhNC})_2]$ ⁶ in which the ligands lie *trans* to chloride [Pt-C and C-N $1.83(4)$ and $1.22(5)$, and $1.90(2)$ and $1.16(2)$ Å, respectively]. The $\text{Pt-C}(\text{bridge})$ separations can only be compared with cluster compounds containing $\mu\text{-CO}$ ligands, for example $[\text{RuPt}_2(\text{CO})_5(\text{Ph}_2\text{MeP})_2]$ [$\text{Pt-C}(\text{mean}) 2.08(3)$ Å].⁷ The Pt-Pt

* S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Amer. Chem. Soc.*, **1969**, **91**, 6994.

⁶ B. Jovanović and Lj. Manojlović-Muir, *J.C.S. Dalton*, **1972**, 1176; B. Jovanović, Lj. Manojlović-Muir, and K. W. Muir, *ibid.*, p. 1178.

⁷ A. Modinos and P. Woodward, *J.C.S. Dalton*, **1975**, 1534.

¹ L. Malatesta and F. Bonati, 'Isocyanide Complexes of Metals,' Wiley-Interscience, New York, 1969.

² M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Chem. Comm.*, **1975**, 3.

³ L. Malatesta, *J. Chem. Soc.*, **1955**, 3924; *Rec. Trav. chim.*, **1956**, **75**, 644.

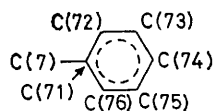
⁴ E. O. Fischer and H. Werner, *Chem. Ber.*, **1962**, **95**, 703.

TABLE 1

Internuclear distances (Å) and angles (°) in tris- μ -(*t*-butyl isocyanide)-tris(*t*-butyl isocyanide)-*triangulo*-tri-platinum

(i) Distances		(ii) Angles	
Pt(1)-Pt(2)	2.629(2)	Pt(1)-Pt(2)-Pt(3)	60.20(4)
Pt(1)-Pt(3)	2.637(2)	Pt(1)-Pt(3)-Pt(2)	59.89(4)
Pt(2)-Pt(3)	2.629(2)	Pt(2)-Pt(1)-Pt(3)	59.90(4)
Pt(1)-C(1)	1.88(2)	Pt(1)-C(4)-Pt(2)	79.6(6)
Pt(1)-C(4)	2.04(2)	Pt(2)-C(5)-Pt(3)	77.8(8)
Pt(2)-C(4)	2.06(2)	Pt(3)-C(6)-Pt(1)	77.5(8)
Pt(2)-C(2)	1.91(3)	Pt(2)-Pt(1)-C(1)	146.7(7)
Pt(2)-C(5)	2.09(2)	Pt(3)-Pt(1)-C(1)	153.3(7)
Pt(3)-C(5)	2.10(2)	Pt(2)-Pt(3)-C(3)	157.1(9)
Pt(3)-C(3)	1.92(2)	Pt(1)-Pt(3)-C(3)	143.0(9)
Pt(3)-C(6)	2.14(2)	Pt(1)-Pt(2)-C(2)	155.6(6)
Pt(1)-C(6)	2.07(2)	Pt(3)-Pt(2)-C(2)	143.7(6)
C(1)-N(1)	1.16(3)	Pt(1)-C(1)-N(1)	176(2)
N(1)-C(101)	1.56(3)	C(1)-N(1)-C(101)	176(2)
C(101)-C(11)	1.49(5)	N(1)-C(101)-C(11)	107(2)
C(101)-C(12)	1.55(4)	N(1)-C(101)-C(12)	103(2)
C(101)-C(13)	1.52(5)	N(1)-C(101)-C(13)	104(2)
C(2)-N(2)	1.14(4)	Pt(2)-C(2)-N(2)	173(2)
N(2)-C(202)	1.55(4)	C(2)-N(2)-C(202)	175(2)
C(202)-C(21)	1.46(6)	N(2)-C(202)-C(21)	104(3)
C(202)-C(22)	1.62(5)	N(2)-C(202)-C(22)	107(2)
C(202)-C(23)	1.44(5)	N(2)-C(202)-C(23)	106(3)
C(3)-N(3)	1.16(3)	Pt(3)-C(3)-N(3)	176(3)
N(3)-C(303)	1.47(3)	C(3)-N(3)-C(303)	174(3)
C(303)-C(31)	1.51(6)	N(3)-C(303)-C(31)	106(3)
C(303)-C(32)	1.51(5)	N(3)-C(303)-C(32)	108(2)
C(303)-C(33)	1.49(6)	N(3)-C(303)-C(33)	105(2)
C(4)-N(4)	1.21(2)	Pt(1)-C(4)-N(4)	135(2)
N(4)-C(404)	1.55(3)	Pt(2)-C(4)-N(4)	145(2)
C(404)-C(41)	1.57(4)	C(4)-N(4)-C(404)	133(2)
C(404)-C(42)	1.61(3)	N(4)-C(404)-C(41)	106(2)
C(404)-C(43)	1.51(4)	N(4)-C(404)-C(42)	105(2)
		N(4)-C(404)-C(43)	106(2)
C(5)-N(5)	1.22(3)	Pt(2)-C(5)-N(5)	135(2)
N(5)-C(505)	1.46(2)	Pt(3)-C(5)-N(5)	147(2)
C(505)-C(51)	1.56(4)	C(5)-N(5)-C(505)	132(2)
C(505)-C(52)	1.56(4)	N(5)-C(505)-C(51)	113(2)
C(505)-C(53)	1.59(3)	N(5)-C(505)-C(52)	106(2)
		N(5)-C(505)-C(53)	110(2)
C(6)-N(6)	1.21(3)	Pt(3)-C(6)-N(6)	131(2)
N(6)-C(606)	1.44(4)	Pt(1)-C(6)-N(6)	151(2)
C(606)-C(61)	1.50(4)	C(6)-N(6)-C(606)	133(2)
C(606)-C(62)	1.64(5)	N(6)-C(606)-C(61)	116(3)
C(606)-C(63)	1.57(4)	N(6)-C(606)-C(62)	107(2)
		N(6)-C(606)-C(63)	108(2)

Toluene solvent molecule



C(7)-C(71)	1.48(4)	C(7)-C(71)-C(72)	120(3)
C(71)-C(72)	1.39(4)	C(7)-C(71)-C(76)	120(2)
C(72)-C(73)	1.39(4)	C(71)-C(72)-C(73)	123(3)
C(73)-C(74)	1.53(6)	C(72)-C(73)-C(74)	116(3)
C(74)-C(75)	1.36(5)	C(73)-C(74)-C(75)	115(3)
C(75)-C(76)	1.35(4)	C(74)-C(75)-C(76)	128(3)
C(76)-C(71)	1.42(5)	C(75)-C(76)-C(71)	117(3)
		C(76)-C(71)-C(72)	119(2)

Some nearest contacts in the unit cell

C(7) ... N(6)	3.87(4)	C(11) ... C(6)	3.55(4)
C(72) ... C(61)	3.61(5)	C(11) ... N(6)	3.79(4)
C(73) ... C(61)	3.94(6)	C(1) ... C(61)	3.89(4)
C(7) ... C(6)	3.89(4)	Pt(1) ... C(72)	3.95(3)
C(72) ... C(6)	3.73(4)	Pt(3) ... C(7)	3.99(3)

distances [mean 2.632(2) Å] are approximately equal to the sum (2.62 Å) of the covalent radii, so they could be regarded as normal single platinum-platinum inter-

actions, and compare closely with those found in other diplatinum and cluster platinum complexes.⁸⁻¹⁰

There is some asymmetry [Pt(1)-C(6), 2.07(2); Pt(3)-C(6), 2.14(2) Å] in the isocyanide ligand bridging Pt(1) and Pt(3), and it is also this Pt-Pt separation which

TABLE 2

Final positional (fractional co-ordinates) and isotropic temperature ($\text{Å}^2 \times 10^3$) factors for $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} ^a
Pt(1)	0.336 43(5)	0.074 50(7)	0.179 01(4)	
Pt(2)	0.413 01(5)	-0.055 99(7)	0.124 55(4)	
Pt(3)	0.483 74(6)	0.021 32(8)	0.242 45(4)	
C(1)	0.241 7(13)	0.147 5(19)	0.170 4(11)	5.7(6)
N(1)	0.181 0(12)	0.187 6(16)	0.162 7(9)	6.8(5)
C(101)	0.102 2(15)	0.249 1(23)	0.153 2(13)	7.7(8)
C(11)	0.116 6(19)	0.373 4(31)	0.150 7(14)	12.1(1.2)
C(12)	0.046 9(20)	0.203 8(31)	0.087 0(18)	12.7(1.2)
C(13)	0.082 9(20)	0.217 1(30)	0.212 7(17)	12.3(1.2)
C(2)	0.428 8(13)	-0.137 4(20)	0.055 2(12)	6.1(6)
N(2)	0.446 2(11)	-0.184 5(18)	0.017 1(10)	7.3(6)
C(202)	0.475 0(16)	-0.240 6(25)	-0.034 2(14)	8.4(8)
C(21)	0.559 5(28)	-0.221 8(46)	-0.009 9(24)	20.0(2.1)
C(22)	0.436 5(24)	-0.171 1(37)	-0.101 3(22)	15.9(1.6)
C(23)	0.441 9(22)	-0.352 3(36)	-0.044 7(19)	14.3(1.4)
C(3)	0.567 6(15)	0.042 2(21)	0.323 3(13)	7.1(7)
N(3)	0.616 2(14)	0.050 9(19)	0.373 8(12)	8.8(7)
C(303)	0.672 7(18)	0.072 4(26)	0.439 2(15)	9.2(9)
C(31)	0.751 7(24)	0.035 4(34)	0.438 1(21)	14.7(1.5)
C(32)	0.666 9(23)	0.196 0(36)	0.455 1(20)	15.4(1.6)
C(33)	0.648 6(21)	-0.004 6(33)	0.482 6(19)	13.5(1.3)
C(4)	0.298 9(12)	0.001 1(18)	0.089 3(10)	4.7(5)
N(4)	0.238 6(9)	0.003 4(15)	0.043 0(9)	5.0(4)
C(404)	0.213 1(13)	-0.052 2(18)	-0.025 1(11)	5.4(6)
C(41)	0.265 7(14)	0.001 8(22)	-0.060 8(12)	7.4(7)
C(42)	0.122 6(16)	-0.017 7(25)	-0.059 3(14)	9.1(9)
C(43)	0.225 4(17)	-0.177 9(26)	-0.131 0(15)	9.6(9)
C(5)	0.527 6(13)	-0.084 7(18)	0.186 4(10)	5.1(6)
N(5)	0.583 1(10)	-0.138 6(15)	0.183 3(8)	5.2(5)
C(505)	0.661 6(13)	-0.155 0(20)	0.229 9(11)	5.8(6)
C(51)	0.662 3(15)	-0.210 4(23)	0.294 3(13)	8.1(8)
C(52)	0.704 1(16)	-0.236 0(25)	0.196 7(14)	9.0(9)
C(53)	0.707 0(14)	-0.037 2(21)	0.246 9(12)	7.2(7)
C(6)	0.405 9(11)	0.127 4(18)	0.270 8(10)	4.6(5)
N(6)	0.416 0(11)	0.182 2(16)	0.319 4(10)	6.5(5)
C(606)	0.378 0(16)	0.263 2(24)	0.337 3(14)	8.4(8)
C(61)	0.337 2(17)	0.359 7(26)	0.291 2(15)	9.5(9)
C(62)	0.294 7(18)	0.192 5(27)	0.346 4(16)	10.3(1.0)
C(63)	0.417 1(19)	0.311 5(29)	0.406 1(17)	11.6(1.1)

Toluene molecule

C(7)	-0.065 1(19)	-0.162 6(29)	0.241 0(17)	11.7(1.1)
C(71)	-0.009 2(17)	-0.088 9(25)	0.289 9(14)	8.5(8)
C(72)	0.064 6(17)	-0.129 3(25)	0.326 2(14)	8.6(8)
C(73)	0.122 9(22)	-0.062 2(33)	0.368 7(19)	13.1(1.3)
C(74)	0.100 8(23)	0.060 7(32)	0.376 0(19)	13.2(1.3)
C(75)	0.025 3(22)	0.088 8(29)	0.341 3(19)	11.5(1.1)
C(76)	-0.030 6(19)	0.022 8(29)	0.300 7(16)	10.5(1)

Anisotropic temperature factors for the platinum atoms

Atom	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Pt(1)	5.67(6)	4.52(6)	5.27(6)	0.14(4)	2.22(5)	-1.02(4)
Pt(2)	6.06(6)	4.54(6)	4.66(6)	0.60(4)	1.98(5)	-0.60(4)
Pt(3)	5.94(6)	5.01(6)	4.78(6)	0.32(5)	1.96(4)	-0.44(4)

^a Defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

is longer than the other two by 4σ (Table 1). It would be unreasonable to suggest that a chemical difference should exist for one side of this otherwise symmetrical

⁸ K. P. Wagner, R. W. Hess, P. M. Treichel, and J. C. Calabrese, *Inorg. Chem.*, 1975, **14**, 1121.

⁹ A. C. Skapski and P. G. H. Troughton, *J. Chem. Soc. (A)*, 1969, 2772.

¹⁰ N. J. Taylor, P. C. Chieh, and A. J. Carty, *J.C.S. Chem. Comm.*, 1975, 448.

molecule, and the source of the variation appears to be crystallographic. From Figure 2 and Table 2, it can be seen that the closest contacts in the unit cell occur between the methyl groups on C(6) and those on C(1) and the toluene solvent molecule. It seems likely, therefore, that packing forces cause the slight asymmetries, since to maintain a more exact three-fold symmetry would bring the t-butyl group on C(6) even closer to C(7)-C(76) and the methyl groups on C(1). It is interesting to note that the C-N bond of each bridging isocyanide lies almost perpendicular to its Pt-Pt bond.

The non-linear nature of the bridging isocyanide

The three platinum atoms and the six attached carbon atoms of the isocyanide ligands are effectively coplanar (maximum deviation 0.08 Å), with the nitrogen and distal carbon atoms showing a small but increasing deviation from this plane. The latter forms an approximate mirror plane for the methyl groups with one lying just off the plane. Thus there is an increasing deviation from planarity outward from the metal so that the remaining two methyl groups of each t-butyl lie above and below the plane, although not exactly symmetrically so.

It is well established that methyl isocyanide ligands can pass rapidly between terminal and bridging sites in

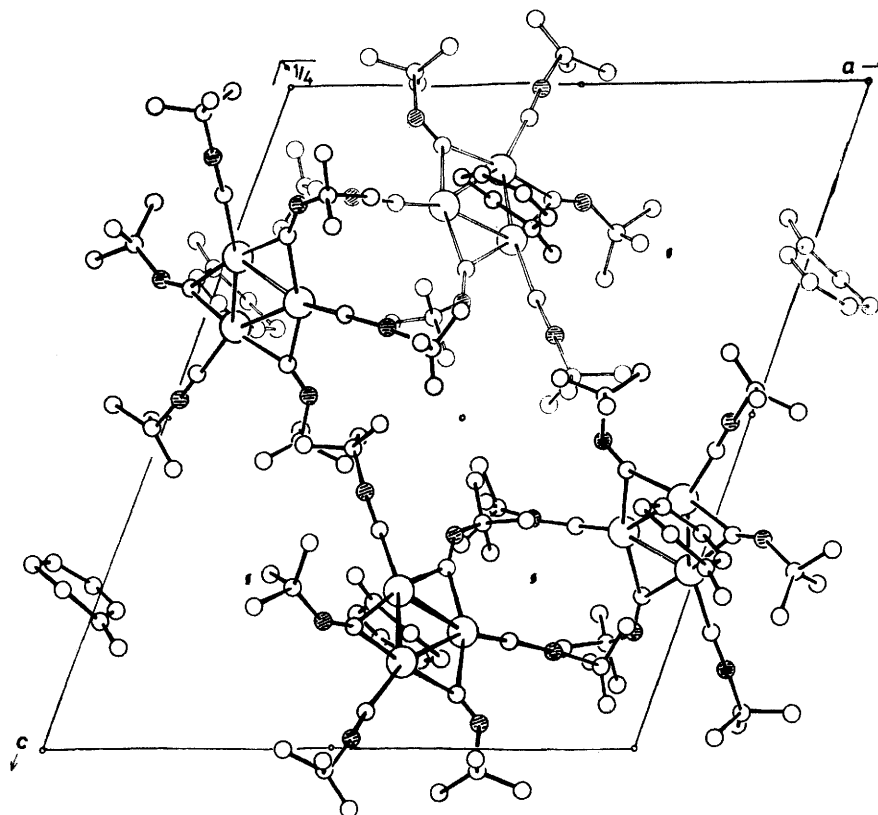


FIGURE 2 Molecular packing diagram viewed down the unique b axis towards the origin. It includes four molecules of toluene solvent per unit cell

ligands, with accompanying lengthening of their C-N bond, has been observed previously in the dimeric molecules $[\text{Fe}_2(\mu\text{-CO})(\mu\text{-PhNC})(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$,¹¹ $[\text{Fe}_2(\mu\text{-MeNC})_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)_2]$,¹² and $[\text{Ni}_2(\mu\text{-MeNC})_2(\eta^5\text{-C}_5\text{H}_5)_2]$ ¹³ where the CNC angles are reported as 131, 125, and 136°, respectively. In the case of the two structures having methyl isocyanide ligands there is a significant asymmetry in the carbon-metal bridging distances, thought to be steric in origin, with those *syn* to the methyl groups being longer than those *anti*. Since these structures contain two $\mu\text{-MeNC}$ groups for each metal-metal interaction the same steric considerations are unlikely to apply to $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$.

¹¹ K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Comm.*, 1965, 181.

¹² F. A. Cotton and B. A. Frenz, *Inorg. Chem.*, 1974, **13**, 253.

binuclear carbonyl(cyclopentadienyl)(methylisocyanide)-iron or -molybdenum complexes.¹⁴ The n.m.r. spectra (¹H and ¹³C) of $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$ are in agreement with the molecular structure established by the X-ray crystallographic studies, but variable-temperature experiments reveal dynamic behaviour of the Bu^tNC ligands.

In the ¹H n.m.r. spectrum (ambient temperature, $[\text{C}_6\text{H}_6]$ toluene) there are two sharp signals (τ 8.25 and 8.63) which show no splitting or satellites due to ¹⁹⁵Pt. On warming a sample in *o*-dichlorobenzene ($\text{C}_6\text{H}_4\text{Cl}_2$ -1,2) these two signals broaden and coalesce in the typical

¹³ R. D. Adams, F. A. Cotton, and G. A. Rusholme, *J. Coordination Chem.*, 1971, **1**, 275.

¹⁴ R. D. Adams and F. A. Cotton, 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, ch. 12.

manner of signals of exchanging chemical environments, with a coalescence temperature of 100 °C. This indicates that exchange is occurring between the terminal and bridging t-butyl isocyanide ligands in the molecule, but gives no information on the mechanism of the exchange.

hauser Effect which would be expected to be associated with these carbons.

To overcome these sensitivity problems a labelled sample of the complex was synthesised containing *ca.* 10% ^{13}C in the NC isocyanide groups. The enrichment

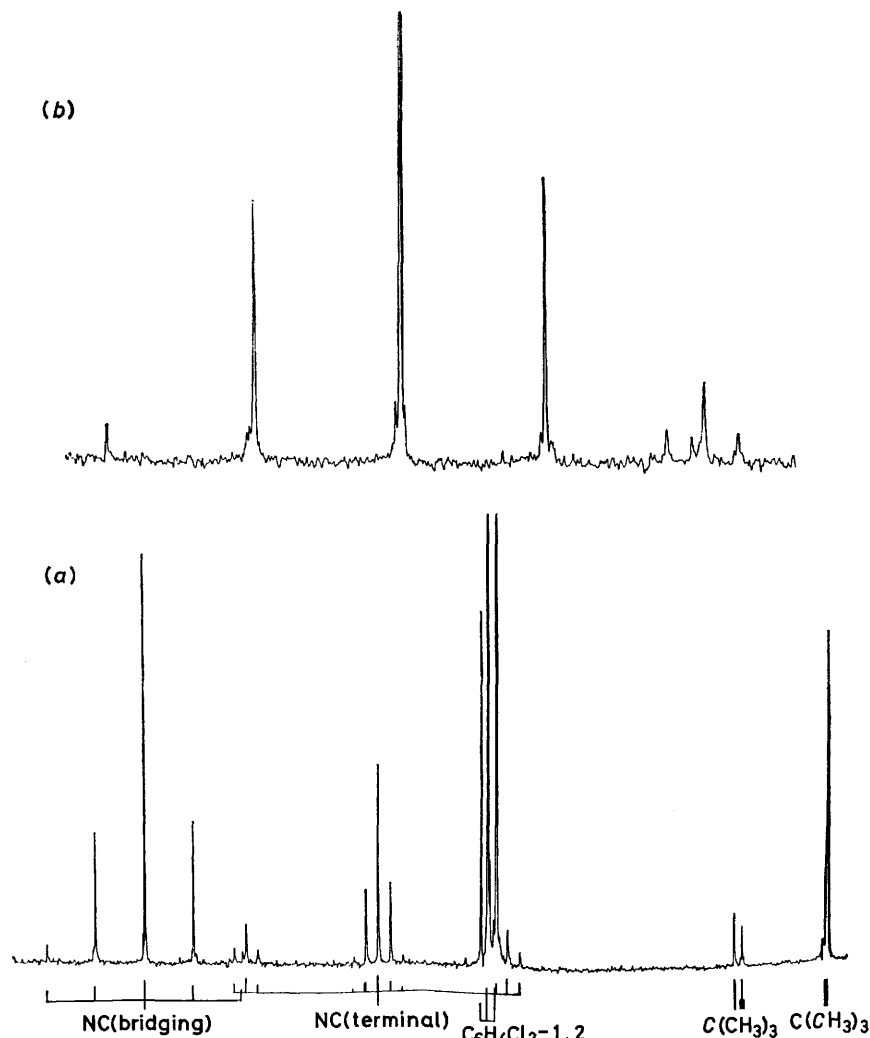


FIGURE 3 Carbon-13 n.m.r. spectrum of $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$ in $\text{C}_6\text{H}_4\text{Cl}_2-1,2$ at 30 °C: (a) total spectrum, spectral width = 66 250 Hz; (b) expansion ($\times 3$) of high-frequency region. The small satellite peaks observed are due to ^{13}C - ^{13}C coupling, and were not further analysed

The ^{13}C n.m.r. spectrum should theoretically be capable of giving more information on the exchange mechanism, since coupling to ^{195}Pt should be observable. However, the natural-abundance ^{13}C spectrum of a saturated solution in benzene shows only signals ascribable to the methyl groups of the t-butyl groups (δ 31.0 and 30.3 p.p.m. *) and two very weak signals (δ 57.8 and 55.4 p.p.m.) assigned to the quaternary carbons of the t-butyl groups. None of these signals show observable ^{195}Pt satellites. No signals due to the carbons of the isocyanide groups were observed, which is consistent with the long relaxation time (T_1) and low Nuclear Over-

was intentionally kept low to avoid complications due to ^{13}C - ^{13}C coupling, which would be expected in more enriched samples. A saturated solution of this 10% enriched material in $\text{C}_6\text{H}_4\text{Cl}_2-1,2$ gave an excellent ^{13}C spectrum (Figure 3) in which sharp signals due to both terminal and bridging isocyanide groups were observed at room temperature. It is interesting that no appreciable coupling or broadening due to the ^{14}N nuclei was observed. The data obtained from the spectrum were as follows:

Terminal NC: δ 163.3 p.p.m., $^1J(\text{Cpt})$ 1 936,
 $^2J(\text{Cpt})$ 180 Hz

Bridging NC: δ 231.3 p.p.m., $^1J(\text{Cpt})$ 357, $^2J(\text{Cpt})$
0 Hz

* δ is relative to internal tetramethylsilane, positive values indicating signals to high frequency of the reference.

It is interesting that a single value of $^1J(\text{Cpt})$ is observed for the bridging isocyanide ligands although the two C-Pt bonds are crystallographically distinct (Figure 1). This suggests that the bent C-N-C framework of this ligand is 'flipping' rapidly on the n.m.r. time scale. Also, because of the increased solubility in $\text{C}_6\text{H}_4\text{Cl}_2$ -1,2 satellite peaks were observed on the low-frequency quaternary carbon signal [δ 55.9 p.p.m., $^3J(\text{Cpt})$ 23 Hz]. The intensity of these satellites (about a quarter of the central peak) suggests that this signal is due to the terminal ligands. Further information was obtained from the signals due to molecules containing two ^{195}Pt nuclei. The terminal carbons in these molecules form an AA'X spin system with the two ^{195}Pt nuclei, and the X part of the spectrum of this spin system should consist of five signals: two lines, separated by $^1J(\text{Cpt}) + ^2J(\text{Cpt})$ and centred at ν_{C} ; a line at ν_{C} (this will be obscured by the much stronger line due to non-active platinum species); and a pair of lines, centred at ν_{C} , whose positions depend on $^1J(\text{PtPt})$ as well as the ^{13}C - ^{195}Pt coupling constants. The first pair of lines were observed at $\nu_{\text{C}} \pm 1058$ Hz, indicating that $^1J(\text{Cpt}) + ^2J(\text{Cpt}) = 2116$ Hz, and therefore these two coupling constants have the same sign. Only one of the other pair of lines was observed, since the other line was obscured by the solvent signals. The position of the observed line ($\nu_{\text{C}} + 885$ Hz) allowed a value of $^1J(\text{PtPt})$ of 110 Hz to be determined, but the accuracy of this value is limited by the insensitivity of the position of the observed line to $^1J(\text{PtPt})$; a repeat measurement with a different solution gave a value of 134 Hz.

In order to observe both of the lines sensitive to $^1J(\text{PtPt})$, a spectrum was run of the enriched material in CD_2Cl_2 . This gave the following parameters for the isocyanide carbons:

Terminal NC: δ 161.4 p.p.m., $^1J(\text{Cpt})$ 1 935, $^2J(\text{Cpt})$ 180 Hz

Bridging NC: δ 228.7 p.p.m., $^1J(\text{Cpt})$ 354, $^2J(\text{Cpt})$ 0 Hz

$^1J(\text{PtPt})$ 188 Hz

Despite the inaccuracy involved in the determination of $^1J(\text{PtPt})$, the difference between the values for $\text{C}_6\text{H}_4\text{Cl}_2$ -1,2 and CD_2Cl_2 solutions is quite significant, and probably reflects the effect of solvation on the platinum triangle. In both solvents, the low value of $^1J(\text{PtPt})$ is of some interest, although there are not many values of $^1J(\text{PtPt})$ available for comparison. Since the few values known do extend as high as 8 196 Hz,¹⁵ it seems that the value observed here is remarkably low, which presumably reflects a very low contribution of platinum s orbitals to the metal-metal bonds.

Since both terminal and bridging carbons show easily observable coupling to ^{195}Pt , it should be possible to

* Throughout this paper: 1 mmHg \approx 13.6 \times 9.8 Pa.

¹⁵ M. Murray, unpublished work.

¹⁶ H. L. Jackson and B. C. McKusick, 'Organic Syntheses,' Coll. vol. IV, p. 438.

distinguish between an inter- and an intra-molecular exchange process of the ligand molecules. On warming the samples, the first effect that was noticed was a broadening of the signals of the terminal carbons (at 40–70 °C), indicating a preferential intermolecular exchange of these ligands. On further heating (to ca. 100 °C) these signals became so broad that they were no longer observable, and slight broadening of the signals of the bridging carbons was also observed. The high-temperature limit, where an average signal should be observed, could not be attained due to decomposition of the sample. Moreover, even samples which had only been heated to 70 °C exhibited on cooling much broader signals for the terminal carbons than were observed in fresh samples. That this broadening was caused by trace amounts of free t-butyl isocyanide produced by decomposition was confirmed by adding a small amount of the free ligand to an unheated solution of the complex. This caused immediate disappearance of the ^{195}Pt satellites of the terminal carbon signals, indicating rapid intermolecular exchange catalysed by free Bu^tNC .

The experimental results thus show that the exchange observed is an intermolecular process, catalysed by free ligand produced by decomposition of the complex on warming. While the possibility of an intramolecular exchange process cannot be ruled out, it must have a higher activation energy than the ligand-promoted intermolecular exchange. Also, not surprisingly, the intermolecular exchange is faster for the terminal than for the bridging ligands.

EXPERIMENTAL

Carbon-13-enriched t-butyl isocyanide (25% yield) was prepared from Ag^{13}CN and Me_3CI by a method similar to that described¹⁶ for the synthesis of ethyl isocyanide. Carbon-13 n.m.r. studies were carried out with a JEOL JNM-PFT-100 spectrometer operating in the Fourier-transform mode at 25.15 MHz.

Synthesis of Tris- μ -(t-butyl isocyanide)-tris(t-butyl isocyanide)-triangulo-triplatinum.—t-Butyl isocyanide (0.75 cm^3 , ca. 7 mmol) in light petroleum (20 cm^3) was treated with bis(cyclo-octa-1,5-diene)platinum¹⁷ (1.23 g, 3 mmol), the latter being added as a finely powdered solid in portions (ca. 0.1 g) with stirring. An orange microcrystalline precipitate formed immediately, which was allowed to settle. The supernatant liquid was decanted and the residue (1.0 g, 92%) was washed with light petroleum (5 \times 3 cm^3) and dried (20 °C, 0.1 mmHg) * to give on recrystallisation from toluene well formed orange crystals as the toluene solvate (Found: C, 37.2; H, 5.6; N, 7.0. $\text{C}_{32}\text{H}_{62}\text{N}_6\text{Pt}$ requires C, 37.8; H, 5.3, N, 7.1%). ν_{max} (Nujol) at 2 155vs, 2 190 (sh), 1 730 (sh), 1 714vs, 1 367s, 1 238s, 1 210s, 1 039w, 873m, 740m, 602m, 520w, 465m, and 444w cm^{-1} . For ^1H n.m.r. spectrum see text.

Reactions of Bis(cyclo-octa-1,5-diene)platinum with Methyl, Ethyl, and Cyclohexyl Isocyanides.—These reactions were carried out in an identical manner to that described above for the preparation of $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$.

(i) $[\text{Pt}_3(\text{MeNC})_6]$, orange microcrystals (95% yield) (Found: C, 17.5; H, 2.3; N, 10.1. $\text{C}_{12}\text{H}_{18}\text{N}_6\text{Pt}_3$ requires

¹⁷ M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J.C.S. Dalton*, 1977, 271.

C, 17.3; H, 2.2; N, 10.1%). $\nu_{\max}(\text{NC})$ at 2 195 vs and 1 725 vs cm^{-1} .

(ii) $[\text{Pt}_3(\text{EtNC})_6]$, orange crystals (90% yield) (Found: C, 24.6; H, 3.6; N, 9.7. $\text{C}_{18}\text{H}_{30}\text{N}_6\text{Pt}_3$ requires C, 23.6; H, 3.3; N, 9.2%). $\nu_{\max}(\text{NC})$ at 2 170 vs, 1 730 vs, and 1 700 (sh) cm^{-1} . Hydrogen-1 n.m.r. spectrum in $\text{C}_6\text{H}_5\text{Cl}$ (25 °C); τ 6.17 (br, 2 H, CH_3CH_2), 7.09 (br, 2 H, CH_3CH_2), 8.67 (t, 3 H, CH_3CH_2), and 9.07 (m, 3 H, CH_3CH_2).

(iii) $[\text{Pt}_3(\text{C}_6\text{H}_{11}\text{NC})_6]$, orange crystals (95% yield) (Found: C, 41.5; H, 5.8; N, 6.8. $\text{C}_{42}\text{H}_{66}\text{N}_6\text{Pt}_3$ requires C, 40.7; H, 5.4; N, 6.8%). $\nu_{\max}(\text{NC})$ at 2 140 vs and 1 705 vs cm^{-1} .

*Crystal-structure Determination of Tris- μ -(*t*-butyl isocyanide)-tris(*t*-butyl isocyanide)-triangulo-triplatinum.* — Crystals of the title complex grow as dark red trigonal prisms from toluene, and that used for data collection, of dimensions ca. $0.18 \times 0.18 \times 0.15$ mm, was enclosed with a very small amount of the solvent in a Lindemann glass capillary, since loss of solvent occurs on long exposure to air. Intensity data were collected at room temperature on a Syntex P2₁ four-circle diffractometer in the range $2.9 \leq 2\theta \leq 50^\circ$ based on methods described earlier.¹⁸ Of a total of 6 970 reflections, 3 543 were deemed independently observable according to the criterion $I \geq 2.5\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measured intensity based on counting statistics. Only the observed data, corrected for Lorentz and polarisation effects and for X-ray absorption, were used in solution and refinement of the structure.

Crystal data. $\text{C}_{37}\text{H}_{62}\text{N}_6\text{Pt}_3$, $M = 1 176.2$, Monoclinic, space group $P2_1/n$, $F(000) = 2 040$, $Z = 4$, $a = 18.213$ (7), $b = 11.811$ (5), $c = 21.996$ (6) Å, $\beta = 110.21$ (3)°, $U = 4 440.3$ Å³, $D_m = 1.75$, $D_c = 1.76$ g cm^{-3} , Mo- K_α X-radiation ($\lambda = 0.710 69$ Å), $\mu(\text{Mo-}K_\alpha) = 99.02$ cm^{-1} .

Structure solution and refinement. The molecular structure was solved from electron-density difference syntheses, following successful location of the triangle of platinum atoms from a Patterson synthesis. Inclusion of the solvent toluene in the lattice, suspected from density measurements, showed clearly in the first electron-density maps. In the final stages of refinement only the platinum atoms were refined with anisotropic thermal parameters. Inclusion of anisotropic temperature factors for all the atoms required the matrix to be blocked. This was deemed unjustified since the refinement then became unstable, producing physically rather meaningless values for the U_{ii} of the *t*-butyl carbon atoms, which already showed considerable thermal activity (Table 2). The same instability in the blocked refinement was produced if hydrogen-atom contributions were considered. Location of every hydrogen atom for the *t*-butyl carbon atoms from the electron-density maps had been unsuccessful and to generate the remaining atomic co-ordinates for the other hydrogens bound to the

already thermally active methyl groups seemed unwarranted.

Weights were applied according to the scheme $1/w = [c/\sigma(F)] + eF^2$ where $c = 1$, $e = 0.000 8$, and $\sigma(F)$ are the estimated errors of the observed structure factors based on counting statistics only. This gave a satisfactory weight analysis for the variation of $W\Delta^2$ with F_o and $\sin\theta$ for intervals of approximately equal numbers of reflections ($\Delta = F_o - F_c$). Refinement converged to $R = 0.057$ ($R' = 0.070$) for the 3 543 independent intensities, with a mean shift: error ratio for the last three cycles of 0.04:1 and a maximum of 0.30:1. The highest peaks remaining in a final electron-density difference synthesis were ca. $1.5 \text{ e}\text{\AA}^{-3}$ near one metal atom and $0.9 \text{ e}\text{\AA}^{-3}$ elsewhere. Hydrogen atoms, where located, showed diffuse peaks at ca. $0.6 - 1.0 \text{ e}\text{\AA}^{-3}$. The atomic scattering factors used were those of ref. 19 for platinum and ref. 20 for carbon and nitrogen. Corrections for the effects of anomalous dispersion were applied for the platinum atom ($\Delta f' = -2.352$, $\Delta f'' = 8.388$). Computational work was carried out using the 'X-Ray' system of programs at the University of London Computing Centre. The atomic co-ordinates are given in Table 2, and equations of some least-squares planes in Table 3. The molecular packing diagram is shown in

TABLE 3

Equations of least-squares planes for $[\text{Pt}_3(\text{Bu}^t\text{NC})_6]$ in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates

Plane 1: Pt(1), Pt(2), Pt(3), C(1), C(2), C(3), C(4), C(5), C(6)
 $-8.258x - 9.596y + 11.009z = -1.535$

Deviations (Å) of the atoms forming the pseudo-mirror from this plane:

C(1)	-0.00	N(1)	0.03	C(101)	-0.01	C(13)	0.15
C(2)	-0.08	N(2)	-0.19	C(202)	-0.45	C(23)	0.77
C(3)	0.00	N(3)	0.07	C(303)	0.12	C(31)	-0.19
C(4)	0.04	N(4)	0.00	C(404)	0.00	C(42)	0.04
C(5)	0.04	N(5)	0.07	C(505)	0.09	C(52)	0.15
C(6)	-0.06	N(6)	-0.13	C(606)	-0.31	C(63)	-0.43

Plane 2: (toluene) C(7), C(71), C(72), C(73), C(74), C(75), C(76)
 $-11.113x - 3.637y + 19.704z = 6.126$

Deviations of given atoms from this plane:

C(7)	-0.06	C(71)	0.01	C(72)	0.05	C(73)	-0.00
C(74)	-0.06	C(75)	-0.00	C(76)	0.06		

Figure 2. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 22036 (14 pp.).*

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

¹⁸ A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

¹⁹ 'International Tables for X-ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. IV.

²⁰ D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **424**, 321.