Synthesis and Characterisation of Penta- and Hexa-platinum Cluster Compounds†

Jane L. Haggitt[a] **and D. Michael P. Mingos**[*,b]
[a]*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK*
[b]*Department of Chemistry, Imperial College of Science Technology and Medicine, South Kensington, London SW7 2AY, UK*

The reactions of the pentaplatinum cluster compounds $[Pt_5(\mu\text{-}SO_2)_x(\mu\text{-}CNC_8H_9)_{3-x}(CNC_8H_9)_7]$ (x = 0, 2 or 3) with SO_2 and CNC_8H_9 (CNC_8H_9 = 2,6-dimethylphenyl isocyanide) have been studied. The cluster compound $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1** was initially synthesised from the reduction of $[Pt(CNC_8H_9)_2Cl_2]$ with cobaltocene. It reacts with SO_2 to give $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2**. The reaction of CNC_8H_9 with **2** results in the formation of $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3**. The structures of **2** and **3** have been solved using single-crystal X-ray crystallography and both are based on an edge-bridged tetrahedral metal core. They are unusual, both containing only three bridging and seven terminal ligands. In the reaction of **1** with SO_2 a small amount of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ was isolated. This compound was characterised on the basis of IR, ^{1}H NMR spectroscopy and fast atom bombardment mass spectrometry. The metal framework geometry is thought to be related to an edge-bridged trigonal bipyramid.

Many platinum cluster compounds are formed by the reduction of platinum monomers and a wide range of reducing agents have been employed with varying degrees of success. For example, the reduction of *cis*-$[Pt(CNC_8H_9)_2Cl_2]$ with sodium amalgam results in the formation of $[Pt_7(CNC_8H_9)_{12}]$ in low yield,[1] whereas that of *cis*-$[PtCl_2(CO)(PMe_2Ph)]$ with $NaBH_4$ gives $[Pt_4(\mu\text{-}CO)_5(PMe_2Ph)_4]$ in high yield.[2] Cobaltocene has been shown to be a useful and clean one-electron reducing agent which is known to reduce platinum(II) complexes. For example, the addition of 2 equivalents of $[Co(\eta\text{-}C_5H_5)_2]$ to $[Pt(cod)Cl_2]$ in the presence of an excess of cod (cycloocta-1,5-diene) results in the formation of $[Pt(cod)_2]$.[3] The complex $[Pt(CO)_2Cl_2]$ is also reduced by cobaltocene to give $[\{Pt(\mu\text{-}CO)_3(CO)_3\}_3]^{2-}$ and $[\{Pt(\mu\text{-}CO)_3(CO)_3\}_4]^{2-}$.[4] This reducing agent has, however, never been utilised in the synthesis of other platinum cluster compounds. This paper describes the reduction of $[Pt(CNC_8H_9)_2Cl_2]$ with cobaltocene. The complex *cis*-$[Pt(CNC_8H_9)_2Cl_2]$ was of interest as the starting material because only a few examples of platinum isocyanide cluster compounds such as $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$[5] and $[Pt_7(CNC_8H_9)_{12}]$[1] have been previously reported. In addition, the chemistry of these compounds has not been studied previously.

Results and Discussion

When 2 equivalents of cobaltocene were added to a suspension of $[Pt(CNC_8H_9)_2Cl_2]$ in CH_2Cl_2 a deep red solution resulted. The solvent was removed under reduced pressure and the crude product extracted with toluene forming a red solution and a yellow solid which was identified as $[Co(\eta\text{-}C_5H_5)_2]Cl$. The latter was filtered off and the remaining solution reduced to low volume. After standing overnight at −20 °C red crystals of $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3]$[6] formed. These were filtered off and the filtrate was evaporated under reduced pressure to give a red oil. When this oil was redissolved in acetone, red crystals precipitated from the solution on standing which were subsequently filtered off, washed with cold acetone, and dried under reduced pressure. The compound was formulated as $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1** on the basis of elemental analyses, FAB mass spectrometry, IR and ^{1}H and ^{195}Pt-{^{1}H} NMR spectroscopy.

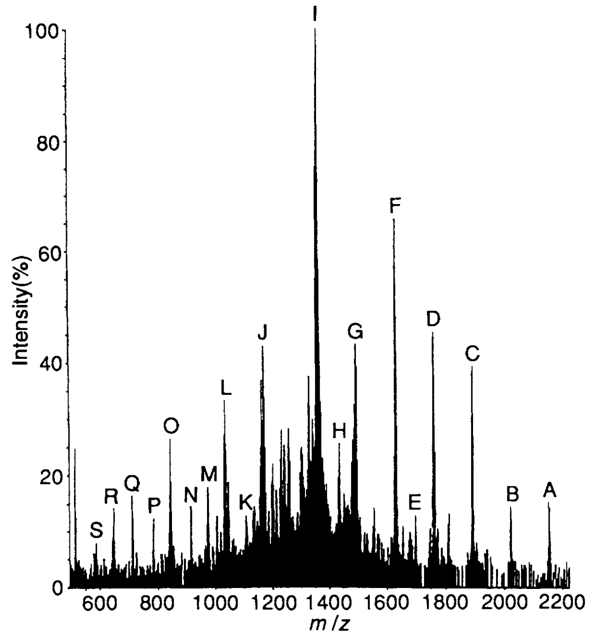


Fig. 1 The FAB mass spectrum of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1**

The IR spectrum of compound **1** exhibited bands due to the presence of terminal isocyanide [ν(CN) at 2119 and 2079 cm^{-1}] and bridging isocyanide ligands [ν(CN) at 1652 and 1585 cm^{-1}]. These values fall within the normal range for terminal and bridging isocyanides. The FAB mass spectrum in the range m/z 500–2300 is shown in Fig. 1 and consists of well resolved peaks. A detailed analysis of this spectrum is presented in Table 1. The highest mass peak observed is at m/z = 2153 corresponding to the ion $[Pt_5(CNC_8H_9)_9]^+$. The most intense peak results from the ion $[Pt_5(CNC_8H_9)_3]^+$ where seven ligands have been lost

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Assignments of the FAB mass spectrum of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1**

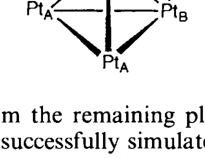
Peak	*m/z*	Relative intensity	Assignment
A	2153	16	$[M - CNC_8H_9]^+$
B	2025	16	$[M - 2CNC_8H_9]^+$
C	1893	40	$[M - 3CNC_8H_9]^+$
D	1761	45	$[M - 4CNC_8H_9]^+$
E	1697	13	$[M - 3CNC_8H_9 - Pt]^+$
F	1630	66	$[M - 5CNC_8H_9]^+$
G	1494	43	$[M - 6CNC_8H_9]^+$
H	1435	25	$[M - 5CNC_8H_9 - Pt]^+$
I	1358	100	$[M - 7CNC_8H_9]^+$
J	1169	43	$[M - 7CNC_8H_9 - Pt]^+$
K	1107	17	$[M - 6CNC_8H_9 - 2Pt]^+$
L	1034	34	$[M - 8CNC_8H_9 - Pt]^+$
M	975	18	$[M - 7CNC_8H_9 - 2Pt]^+$
N	914	15	$[M - 6CNC_8H_9 - 3Pt]^+$
O	843	26	$[M - 5CNC_8H_9 - 4Pt]^+$
P	784	13	$[M - 7CNC_8H_9 - 3Pt]^+$
Q	712	16	$[M - 6CNC_8H_9 - 4Pt]^+$
R	649	15	$[M - 8CNC_8H_9 - 3Pt]^+$
S	589	8	$[M - 7CNC_8H_9 - 4Pt]^+$

$M = [Pt_5(CNC_8H_9)_{10}]$.

from the compound. The fragmentation pattern observed in the spectrum includes the loss of isocyanide ligands and platinum atoms. The parent ion $[Pt_5(CNC_8H_9)_{10}]^+$ is not seen in the FAB mass spectrum, but loss of a ligand from the parent molecule is quite a common feature in FAB mass spectrometry.[7,8]

The ^1H NMR spectrum of the compound showed six singlets in the methyl region at δ 2.35, 2.31, 2.26, 2.15, 1.94 and 1.92 in the intensity ratio 2:2:2:1:1:2 implying that there were ten isocyanide ligands in six chemically distinct environments. The first four singlets from δ 2.35 to 2.15 were due to the presence of seven terminal isocyanide ligands and the two signals upfield at δ 1.94 and 1.92 to three bridging isocyanide ligands. These data are consistent with the ^1H NMR spectrum of the cluster compound $[Hg\{Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3\}_2]$[9] which revealed two signals of equal intensity in the methyl region at δ 2.52 and 2.16 corresponding to the six terminal and the six bridging isocyanide ligands, respectively.

The $^{195}Pt\text{-}\{^1H\}$ NMR spectrum of compound **1** consists of three resonances centred at δ −3441, −4300 and −4260 in the ratio 2:2:1 consistent with the edge-bridged tetrahedral metal framework shown. The first two resonances appear to be essentially broad triplets, with other fine structure, corresponding to Pt_A and Pt_B respectively. The broad signal at δ −4260 arises from the remaining platinum atom Pt_C. The spectrum has been successfully simulated based on the superposition of 18 isotopomers (Fig. 2). Values of ^1J(Pt–Pt) can range between 92 and 9007 Hz and are influenced by the bridging ligands.[10] The observed coupling constants in the $^{195}Pt\text{-}\{^1H\}$ NMR spectrum of compound **1** have the values $^1J(Pt_A\text{–}Pt_B)$ = 687 and $^1J(Pt_B\text{–}Pt_C)$ = 190 Hz. The latter is comparable to those found for other platinum cluster compounds containing bridging isocyanide ligands. For example, $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$[5] and $[Pt_3(\mu\text{-}CO)(\mu\text{-}CNC_8H_9)_2(CNC_8H_9)\{P(C_6H_{11})_3\}_2]$[11] have ^1J(Pt–Pt) 188 and 290 Hz respectively. The similar value of ^1J(Pt–Pt) in $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1** and $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$ could be due to the fact that the geometries of the platinum atoms concerned are very similar in both cluster compounds.



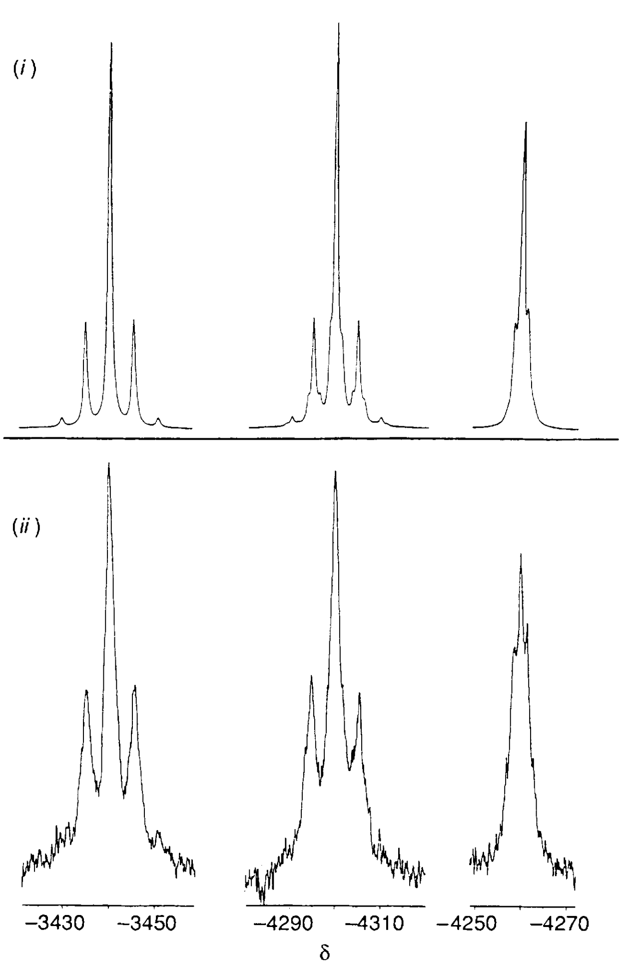
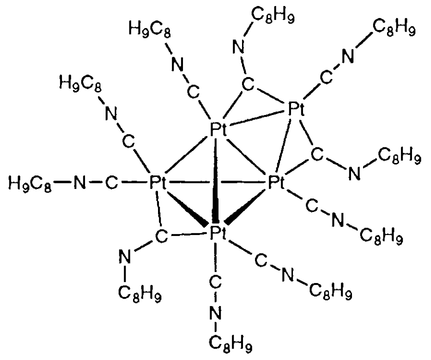


Fig. 2 The $^{195}Pt\text{-}\{^1H\}$ NMR spectrum of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1**: (*i*) simulated and (*ii*) observed



1

The analytical, FAB and NMR data suggest unambiguously the formulation of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$. The proposed structure of this cluster compound consists of an edge-bridged tetrahedron with three bridging isocyanide and seven terminal isocyanide ligands. The presence of only three bridging ligands is unusual since in the structurally related, isoelectronic, pentanuclear platinum clusters $[Pt_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)_2(CO)(PPh_3)_4]$[12] and $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$[13] there are five bridging ligands. Unfortunately no single crystals of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ could be obtained and so an X-ray diffraction study of this compound could not be undertaken to confirm this structure.

It has been shown that the reduction of $[Pt(CNC_8H_9)_2Cl_2]$ with cobaltocene results in the formation of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ which is isolated in approximately 50% yield. Small quantities of the cluster compound $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3]$ were also isolated from the reaction. The use of other solvents such as toluene and tetrahydrofuran were investigated but it was found that CH_2Cl_2 gave the most satisfactory results.

Addition of less than 2 equivalents of cobaltocene to a suspension of $[Pt(CNC_8H_9)_2Cl_2]$ in CH_2Cl_2 yielded a red solution as before. The solvent was removed under reduced pressure and the resultant red oil was recrystallised from CH_2Cl_2–EtOH to give a yellow solid in low yield. This was identified as $[Pt_2(CNC_8H_9)_4Cl_2]$ on the basis of microanalyses, IR and ^1H NMR spectroscopy. Unreacted $[Pt(CNC_8H_9)_2Cl_2]$ and some $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ were also recovered from the reaction mixture. Subsequent addition of 2 equivalents of $[Co(\eta\text{-}C_5H_5)_2]$ to a solution of $[Pt_2(CNC_8H_9)_4Cl_2]$ in CH_2Cl_2 resulted in the formation of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$.

Yamamoto and co-workers[14–16] have studied the electrochemical reactions of dichloro(aryl isocyanide)platinum(II) complexes. They found that $[Pt(CNR)_2Cl_2]$ can undergo either one- or two-electron reductions depending on the reaction conditions. When R = $2,4,6\text{-}Bu^t{}_3C_6H_2$ it undergoes a one-electron reduction to give $[Pt_2(CNR)_4Cl_2]$ or a two-electron reduction to give $[Pt_3(\mu\text{-}CNR)_3(CNR)_3]$. Cobaltocene is known to be a one-electron reducing agent: for example, the reduction of $[Re_2Cl_3(dppm)_2(CO)_2(CNBu^t)]PF_6$ (dppm = $Ph_2PCH_2PPh_2$) involves a one-electron step to give $[Re_2Cl_3(dppm)_2(CO)_2(CNBu^t)]$.[17]

Using this information it is proposed that the chemical reduction of $[Pt(CNC_8H_9)_2Cl_2]$ with cobaltocene proceeded *via* two one-electron-transfer reactions. In the reaction between $[Pt(CNC_8H_9)_2Cl_2]$ and cobaltocene a one-electron reduction initially occurred to give $[Pt_2(CNC_8H_9)_4Cl_2]$. This product proved to be the intermediate in the reaction which then underwent a second one-electron reduction with further quantities of cobaltocene to form $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$. In this reaction the cobaltocene seemed to be acting not only as a reducing agent but also a chloride abstractor since cobaltocenium chloride was always produced in the reactions (Scheme 1).

The reduction of $[Pt(CNBu^t)_2Cl_2]$ with cobaltocene resulted in the formation of $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$ instead of a pentaplatinum cluster compound as observed in the case of CNC_8H_9. The product was characterised on the basis of analyses, IR and ^1H NMR spectroscopy, details of which were consistent with the literature values found for $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$.[5] This compound has been synthesised previously from the addition of $CNBu^t$ to $[Pt(cod)_2]$.

When SO_2 gas was bubbled through a dark red solution of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1** in toluene at 60 °C, the solution lightened and an orange solid started to appear. The solution was reduced to low volume and the resultant orange precipitate was filtered off. Recrystallisation from $CHCl_3$–Et_2O gave orange crystals of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2** in good yield.

The reaction of 3 mol equivalents of CNC_8H_9 with $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2** resulted in the formation of a mixture of $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3]$ and $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1** as demonstrated by IR and ^1H NMR spectroscopy. The reaction of 1 mol equivalent of CNC_8H_9 with **2** gave only one product, $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3**, in quantitative yield.

Compounds **2** and **3** were characterised on the basis of microanalyses, FAB mass spectrometry, IR and ^1H NMR spectroscopy. The FAB mass spectra are shown in Figs. 3 and 4 respectively and the peak assignments are given in Tables 2 and 3 respectively. In the spectrum of **2** the molecular ion peak $[Pt_5(SO_2)_3(CNC_8H_9)_7]^+$ is observed at *m/z* 2086. The most intense peak (*m/z* = 1894) is due to the ion $[Pt_5(CNC_8H_9)_7]^+$ where all the SO_2 ligands have been lost from the molecule. As with the spectrum of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$, there is no evidence for decomposition products containing fragments of the isocyanide ligands. In the spectrum of **3** it is apparent that SO_2 is readily lost under FAB conditions. The $[M]^+$ peak is not observed and the peak with the highest *m/z* ratio is observed at *m/z* = 2026 corresponding to $[M - 2SO_2]^+$. The highest-intensity peak is that due to the $[Pt_5(CNC_8H_9)_5]^+$ ion.

The IR spectrum of compound **2** showed the presence of terminal isocyanides [ν(CN) at 2157 and 2143 cm^{-1}] and the presence of bridging SO_2 ligands [ν(SO_2) at 1216, 1201 and 1064 cm^{-1}]. That of **3** showed the presence of terminal isocyanide ligands [ν(CN) at 2148, 2129 and 2006 cm^{-1}], bridging isocyanides [ν(CN) at 1657 and 1585 cm^{-1}] and bridging SO_2

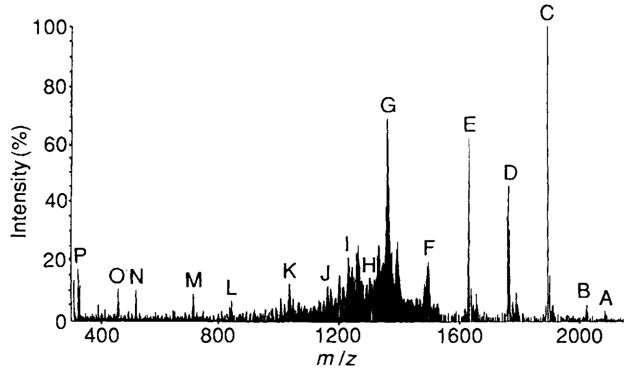


Fig. 3 The FAB mass spectrum of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2**

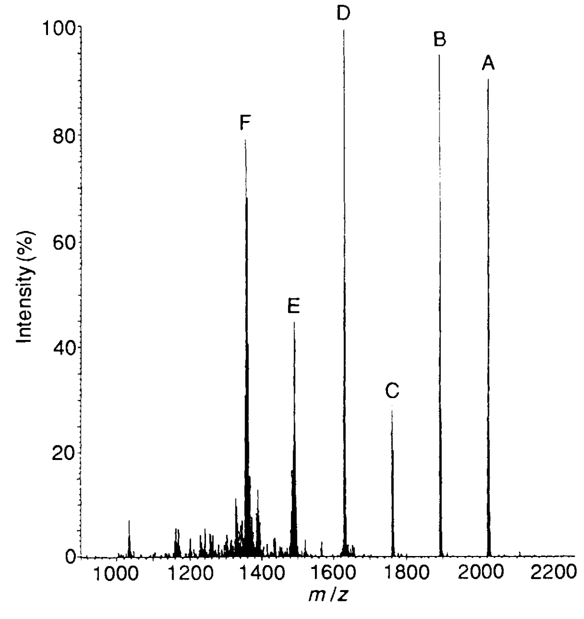
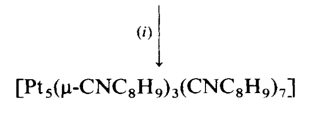


Fig. 4 The FAB mass spectrum of $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3**



Scheme 1 (*i*) $2[Co(\eta\text{-}C_5H_5)_2]$

Table 2 Assignments of the FAB mass spectrum of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2**

Peak	m/z	Relative intensity	Assignment
A	2086	4	$[M]^+$
B	2027	6	$[M - SO_2]^+$
C	1894	100	$[M - 3SO_2]^+$
D	1764	46	$[M - 3SO_2 - CNC_8H_9]^+$
E	1633	63	$[M - 3SO_2 - 2CNC_8H_9]^+$
F	1495	20	$[M - 3SO_2 - 3CNC_8H_9]^+$
G	1360	70	$[M - 3SO_2 - 4CNC_8H_9]^+$
H	1300	15	$[M - 3SO_2 - 3CNC_8H_9 - Pt]^+$
I	1229	21	$[M - 3SO_2 - 5CNC_8H_9]^+$
J	1162	12	$[M - 3SO_2 - 4CNC_8H_9 - Pt]^+$
K	1034	13	$[M - 3SO_2 - 5CNC_8H_9 - Pt]^+$
L	843	7	$[M - 3SO_2 - 5CNC_8H_9 - 2Pt]^+$
M	713	9	$[M - 3SO_2 - 6CNC_8H_9 - 2Pt]^+$
N	518	10	$[M - 3SO_2 - 6CNC_8H_9 - 3Pt]^+$
O	458	11	$[M - 3SO_2 - 5CNC_8H_9 - 4Pt]^+$
P	323	17	$[M - 3SO_2 - 6CNC_8H_9 - 4Pt]^+$

$M = [Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$.

Table 3 Assignments of the FAB mass spectrum of $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3**

Peak	m/z	Relative intensity	Assignment
A	2026	90	$[M - 2SO_2]^+$
B	1894	95	$[M - 2SO_2 - CNC_8H_9]^+$
C	1762	29	$[M - 2SO_2 - 2CNC_8H_9]^+$
D	1632	100	$[M - 2SO_2 - 3CNC_8H_9]^+$
E	1492	45	$[M - 2SO_2 - 4CNC_8H_9]^+$
F	1358	79	$[M - 2SO_2 - 5CNC_8H_9]^+$

$M = [Pt_5(SO_2)_2(CNC_8H_9)_8]$.

Table 4 Comparison of ν(CN) values for platinum isocyanide cluster compounds

Cluster	$\tilde{\nu}(CN)/cm^{-1}$
1 $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$	2119s, 2079s
2 $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$	2157vs, 2143vs
3 $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$	2148vs, 2129vs, 2006w

Table 5 Crystal data for $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2** and $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3**[a]

	2	**3**
Formula	$C_{63}H_{63}N_7O_6Pt_5S_3\cdot CHCl_3$	$C_{72}H_{72}N_8O_4Pt_5S_2\cdot 1.2CHCl_3$
M	2205.2419	2296.2356
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	12.269(4)	14.786(3)
b/Å	13.890(3)	25.376(6)
c/Å	23.690(4)	22.852(7)
α/°	74.59(2)	
β/°	81.81(2)	105.26(2)
γ/°	64.43(2)	
U/Å^3	3509	8272
Z	2	4
D_c/g cm^{-3}	2.0669	1.8392
F(000)	2068	4332
μ/cm^{-1}	101.8942	87.0600
h, k, l range	−12 to 12, −14 to 14, −1 to 25	−15 to 15, −1 to 26, −1 to 24
Horizontal aperture/mm	4.0	2.6
Total data collected	9186	11 353
Total unique data	8551	11 033
Total observed data $[I > 3\sigma(I)]$	4943	4607
Merging R factor	0.0373	0.049
Absorption correction (minimum, maximum)	0.804, 1.269	0.859, 1.199
No. of parameters	393	532
Ratio data : parameters	12.6	9.2
Chebychev weighting scheme parameters	6.70, −5.12, 4.65	21.7, −20.2, 15.4
R[b]	0.0407	0.0466
R'[c]	0.0453	0.0516

[a] Details in common: θ_{min}, θ_{max} 0, 22.0°; ω-scan width 0.90 + 0.35 tanθ; absorption correction by DIFABS.[19] [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R' = [w\Sigma(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

ligands [ν(SO_2) at 1209, 1196 and 1056 cm^{-1}]. Table 4 shows the values of the ν(CN) bands of the terminal isocyanide ligands in the IR spectra of **1**–**3**. As more SO_2 is introduced into the cluster compound the terminal ν(CN) bands occur at higher wavenumbers. The overall shift suggests that the bridging SO_2 ligands are acting as better π acceptors than are the bridging isocyanide ligands. A similar trend has been observed in the cluster compounds $[Pt_3(\mu\text{-}SO_2)_{3-x}(\mu\text{-}CO)_x\{P(C_6H_{11})_3\}_3]$ (x = 1–3).[18]

The ^{1}H NMR spectrum of compound **2** showed four singlets in the methyl region at δ 2.54, 2.46, 2.41 and 2.36 in the ratio 2:2:2:1 confirming the presence of seven terminal isocyanide ligands in four chemically distinct environments. That of **3** showed five singlets in the methyl region at δ 2.47, 2.44, 2.42, 2.29 and 2.01 in the ratio 2:1:2:2:1 indicating the presence of seven terminal and one bridging isocyanide in five different environments.

The spectroscopic evidence relating to $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2** and $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3** suggested that the structures were analogous to that of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1**, *i.e.* an edge-bridged tetrahedron with three bridging and seven terminal ligands. These structures were confirmed by single-crystal crystallographic investigations.

X-Ray Crystallographic Analyses.—Details of the data collection and refinement are summarised in Table 5. Selected bond lengths and angles are shown in Tables 6 and 7 and atomic coordinates in Tables 8 and 9. The structures are illustrated in Figs. 5 and 6.

The molecular structure of compound **2** consists of an edge-bridged tetrahedron of platinum atoms with three bridging SO_2 ligands and seven terminal 2,6-dimethylphenyl isocyanide ligands. The geometry of the metal core is analogous to that of the other 70-electron cluster compounds $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$,[13] $[Pt_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)_2(CO)(PPh_3)_4]$[12] and $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNC_8H_9)_2(CNC_8H_9)_5]$.[20] In **2** the Pt–Pt distances lie in the range 2.6956(9)–3.0089(9) Å. The shortest is Pt(2)–Pt(4), which is the bond bridged by the fifth platinum atom Pt(5). The equivalent bonds in $[Pt_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)_2(CO)(PPh_3)_4]$ and $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNC_8H_9)_2(CNC_8H_9)_5]$ are also the shortest metal–metal bonds. The longest Pt–Pt bond in **2** is Pt(1)–Pt(3) [3.0089(9) Å] which is that furthest away from the metal bridge. This bond is relatively long compared to the equivalent bond in the other pentaplatinum cluster compounds. Similar values, however, have been observed in the structure of $[Pt_7(CNC_8H_9)_{12}]$[1] and attributed to the steric hindrance caused by the bulky isocyanide groups.

As anticipated from the spectroscopic evidence, there are only three bridging ligands in the molecule which is unusual for these cluster compounds; $[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNC_8H_9)_2(CNC_8H_9)_5]$, $[Pt_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)_2(CO)(PPh_3)_4]$ and $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$ all have five terminal and five bridging ligands. The longest bond, Pt(1)–Pt(3), is bridged by an SO_2 ligand as are both the bonds to the bridging Pt(5) atom, Pt(2)–Pt(5) and Pt(4)–Pt(5). In **2**, $[Pt_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)_2(CO)(PPh_3)_4]$ and

Table 6 Selected bond lengths (Å) and angles (°) for $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2**

Pt(1)–Pt(2)	2.818(1)	S(1)–O(11)	1.41(1)	Pt(3)–Pt(4)	2.8186(9)	C(6)–N(6)	1.15(2)
Pt(1)–Pt(3)	3.0089(9)	S(1)–O(12)	1.46(1)	Pt(3)–S(1)	2.256(5)	C(7)–N(7)	1.18(2)
Pt(1)–Pt(4)	2.7732(9)	S(2)–O(21)	1.47(2)	Pt(3)–C(3)	1.93(2)	C(11)–N(1)	1.43(2)
Pt(1)–S(1)	2.230(4)	S(2)–O(22)	1.45(1)	Pt(3)–C(7)	1.95(2)	C(21)–N(2)	1.41(2)
Pt(1)–C(1)	1.98(2)	S(3)–O(31)	1.43(1)	Pt(4)–Pt(5)	2.7373(9)	C(31)–N(3)	1.41(2)
Pt(1)–C(6)	1.92(2)	S(3)–O(32)	1.46(1)	Pt(4)–S(3)	2.231(5)	C(41)–N(4)	1.41(3)
Pt(2)–Pt(3)	2.8300(9)	C(1)–N(1)	1.16(2)	Pt(4)–C(4)	1.87(2)	C(51)–N(5)	1.39(2)
Pt(2)–Pt(4)	2.6956(9)	C(2)–N(2)	1.17(2)	Pt(5)–S(2)	2.288(5)	C(61)–N(6)	1.41(2)
Pt(2)–Pt(5)	2.7522(9)	C(3)–N(3)	1.18(2)	Pt(5)–S(3)	2.285(5)	C(71)–N(7)	1.43(2)
Pt(2)–S(2)	2.235(5)	C(4)–N(4)	1.21(2)	Pt(5)–C(5)	1.92(2)		
Pt(2)–C(2)	1.90(2)	C(5)–N(5)	1.16(2)				
Pt(3)–Pt(1)–Pt(2)	58.00(2)	S(1)–Pt(3)–Pt(2)	95.0(1)	C(2)–Pt(2)–S(2)	96.1(6)	S(3)–Pt(5)–Pt(2)	110.6(1)
Pt(4)–Pt(1)–Pt(2)	57.64(2)	S(1)–Pt(3)–Pt(4)	100.8(1)	Pt(2)–Pt(3)–Pt(1)	57.62(2)	S(3)–Pt(5)–Pt(4)	51.8(1)
Pt(4)–Pt(1)–Pt(3)	58.18(2)	C(3)–Pt(3)–Pt(1)	135.4(6)	Pt(4)–Pt(3)–Pt(1)	56.72(2)	S(3)–Pt(5)–S(2)	162.1(2)
S(1)–Pt(1)–Pt(2)	95.9(1)	C(3)–Pt(3)–Pt(2)	145.7(6)	Pt(4)–Pt(3)–Pt(2)	57.01(2)	C(5)–Pt(5)–Pt(2)	149.0(6)
S(1)–Pt(1)–Pt(3)	48.2(1)	C(3)–Pt(3)–Pt(4)	155.4(6)	S(1)–Pt(3)–Pt(1)	47.5(1)	C(5)–Pt(5)–Pt(4)	152.0(6)
S(1)–Pt(1)–Pt(4)	102.8(1)	C(3)–Pt(3)–S(1)	88.0(6)	C(5)–Pt(5)–S(2)	97.6(6)	N(5)–C(5)–Pt(5)	178.0(17)
C(1)–Pt(1)–Pt(2)	78.9(6)	C(7)–Pt(3)–Pt(1)	126.2(5)	C(5)–Pt(5)–S(3)	100.3(6)	N(6)–C(6)–Pt(1)	177.9(16)
C(1)–Pt(1)–Pt(3)	125.6(6)	C(7)–Pt(3)–Pt(2)	80.9(5)	Pt(3)–S(1)–Pt(1)	84.2(1)	N(7)–C(7)–Pt(3)	171.3(15)
C(1)–Pt(1)–Pt(4)	71.7(6)	C(7)–Pt(3)–Pt(4)	72.8(5)	O(11)–S(1)–Pt(1)	115.5(6)	N(1)–C(11)–C(12)	116.3(19)
C(1)–Pt(1)–S(1)	173.8(6)	C(7)–Pt(3)–S(1)	173.5(5)	O(11)–S(1)–Pt(3)	112.8(6)	N(1)–C(11)–C(16)	115.8(18)
C(6)–Pt(1)–Pt(2)	150.9(5)	C(7)–Pt(3)–C(3)	98.3(8)	O(12)–S(1)–Pt(1)	113.8(6)	N(2)–C(21)–C(22)	118.5(17)
C(6)–Pt(1)–Pt(3)	141.1(5)	Pt(2)–Pt(4)–Pt(1)	62.02(2)	O(12)–S(1)–Pt(3)	114.2(6)	N(2)–C(21)–C(26)	116.0(17)
C(6)–Pt(1)–Pt(4)	145.4(5)	Pt(3)–Pt(4)–Pt(1)	65.10(2)	O(12)–S(1)–O(11)	113.2(8)	N(3)–C(31)–C(32)	118.7(17)
C(6)–Pt(1)–S(1)	93.7(5)	Pt(3)–Pt(4)–Pt(2)	61.71(2)	Pt(5)–S(2)–Pt(2)	74.9(1)	N(3)–C(31)–C(36)	118.6(17)
C(6)–Pt(1)–C(1)	92.5(8)	Pt(5)–Pt(4)–Pt(1)	100.16(3)	O(21)–S(2)–Pt(2)	113.9(6)	N(4)–C(41)–C(42)	115.4(20)
Pt(3)–Pt(2)–Pt(1)	64.38(2)	Pt(5)–Pt(4)–Pt(2)	60.87(2)	O(21)–S(2)–Pt(5)	115.4(6)	N(4)–C(41)–C(46)	117.3(20)
Pt(4)–Pt(2)–Pt(1)	60.34(2)	Pt(5)–Pt(4)–Pt(3)	114.39(3)	O(22)–S(2)–Pt(2)	116.6(6)	N(5)–C(51)–C(52)	116.0(18)
Pt(4)–Pt(2)–Pt(3)	61.28(2)	S(3)–Pt(4)–Pt(1)	141.3(1)	O(22)–S(2)–Pt(5)	116.3(6)	N(5)–C(51)–C(56)	118.5(18)
Pt(5)–Pt(2)–Pt(1)	108.41(3)	S(3)–Pt(4)–Pt(2)	114.5(1)	O(22)–S(2)–O(21)	114.2(9)	N(6)–C(61)–C(62)	115.4(17)
Pt(5)–Pt(2)–Pt(3)	113.56(3)	S(3)–Pt(4)–Pt(3)	151.2(1)	Pt(5)–S(3)–Pt(4)	74.6(1)	N(6)–C(61)–C(66)	117.7(17)
Pt(5)–Pt(2)–Pt(4)	60.32(2)	S(3)–Pt(4)–Pt(5)	53.6(1)	O(31)–S(3)–Pt(4)	115.8(6)	N(7)–C(71)–C(72)	122.8(17)
S(2)–Pt(2)–Pt(1)	145.3(1)	C(4)–Pt(4)–Pt(1)	88.7(5)	O(31)–S(3)–Pt(5)	115.7(6)	N(7)–C(71)–C(76)	115.0(16)
S(2)–Pt(2)–Pt(3)	146.7(1)	C(4)–Pt(4)–Pt(2)	148.2(5)	O(32)–S(3)–Pt(4)	115.4(6)	C(11)–N(1)–C(1)	174.4(19)
S(2)–Pt(2)–Pt(4)	113.6(1)	C(4)–Pt(4)–Pt(3)	96.0(5)	O(32)–S(3)–Pt(5)	116.6(6)	C(21)–N(2)–C(2)	168.4(18)
S(2)–Pt(2)–Pt(5)	53.4(1)	C(4)–Pt(4)–Pt(5)	148.7(5)	O(32)–S(3)–O(31)	113.4(8)	C(31)–N(3)–C(3)	173.6(18)
C(2)–Pt(2)–Pt(1)	95.4(6)	C(4)–Pt(4)–S(3)	96.0(5)	N(1)–C(1)–Pt(1)	168.6(18)	C(41)–N(4)–C(4)	177.6(19)
C(2)–Pt(2)–Pt(3)	94.0(6)	Pt(4)–Pt(5)–Pt(2)	58.82(2)	N(2)–C(2)–Pt(2)	175.6(16)	C(51)–N(5)–C(5)	175.6(19)
C(2)–Pt(2)–Pt(4)	150.3(6)	S(2)–Pt(5)–Pt(2)	51.7(1)	N(3)–C(3)–Pt(3)	174.0(17)	C(61)–N(6)–C(6)	171.7(19)
C(2)–Pt(2)–Pt(5)	149.3(6)	S(2)–Pt(5)–Pt(4)	110.4(1)	N(4)–C(4)–Pt(4)	169.8(16)	C(71)–N(7)–C(7)	174.3(17)

$[Pd_5(\mu\text{-}SO_2)_3(\mu\text{-}CNC_8H_9)_2(CNC_8H_9)_5]$ the SO_2 ligands occupy analogous positions.

The structure of compound **3** is closely related to that of **2** with the metal core geometry based on an edge-bridged tetrahedron. Again there are only three bridging ligands and seven terminal ligands. The Pt–Pt distances range between 2.689(1) and 2.843(1) Å. As with $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$, the shortest bond is Pt(2)–Pt(4) which is the bond bridged by the fifth Pt atom Pt(5). The longest Pt–Pt bond is that between Pt(3) and Pt(4) which is also the longest Pt–Pt bond found in the cluster compounds $[Pt_5(\mu\text{-}SO_2)_3(\mu\text{-}CO)_2(CO)(PPh_3)_4]$ and $[Pt_5(\mu\text{-}CO)_5(CO)(PPh_3)_4]$.

Both of the bonds to the bridging Pt atom are themselves bridged by SO_2 ligands. The bond furthest away from the metal bridge, Pt(1)–Pt(3), is bridged by an isocyanide ligand. This bond at 2.788(1) Å is approximately 0.22 Å shorter than the equivalent bond in $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2**. This is probably due to the greater steric requirements of the sulfur atom since the length of a Pt–Pt bond depends, in part, on the size of the bridging atom.

The Pt–C bond lengths for the terminal isocyanide ligands lie in the range 1.88(3)–1.98(3) Å which is average for these types of cluster compounds. The C–N–C angles for these terminal isocyanides lie in the range 170(2)–179(2)° which deviate only slightly from linearity. The Pt–C bond lengths for the bridging isocyanide ligand are 1.99(2) and 2.00(3) Å. The C–N–C angle is 129(2)° which is comparable to those found in $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$,[5] $[Pt_3(\mu\text{-}CO)(\mu\text{-}CNC_8H_9)_2(CNC_8H_9)\{P(C_6H_{11})_3\}_2]$[11] and $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_2\{P(C_6H_{11})_3\}]$[11] where the angles are 132.7, 128.5 and 132.0° respectively.

The orientations of the terminal 2,6-dimethylphenyl groups in compound **3** differ from those in **2**. In **3** the phenyl group attached to N(6) is parallel to the phenyl group on the bridging isocyanide. In **2** this group is rotated by approximately 90°. The groups attached to N(2) and N(4) in **3** are approximately perpendicular to the bridging isocyanide. Again, in **2** these groups are rotated by 90°. All of these observations confirm that **3** is more sterically crowded compared with **2** because of the presence of the additional bridging isocyanide ligand. The orientation of the isocyanide ligands have to be altered to accommodate it.

The molecular structures of both $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ and $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ are related to that proposed for the parent isocyanide cluster $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ and provide further confirmation of the proposed structure of the latter. The solution of the structures has highlighted the effects on the Pt–Pt bond distances of replacing SO_2 by isocyanide ligands.

The compound $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ can also be synthesised in high yield from the reaction of $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3]$ with SO_2 gas at 60 °C and from the reaction of $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3** with SO_2.

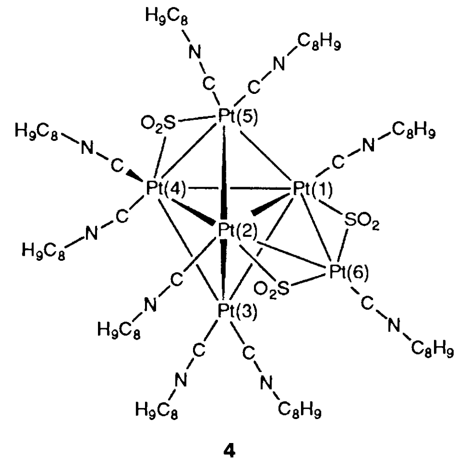
Synthesis of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$.—In the reaction of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ **1** with SO_2 some dark red crystals were also isolated in low yield. These crystals were formulated as $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ **4** using microanalyses,

Table 7 Selected bond lengths (Å) and angles (°) for $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3**

Pt(1)–Pt(2)	2.796(1)	S(25)–O(251)	1.49(2)	Pt(3)–Pt(4)	2.843(1)	N(4)–C(41)	1.37(3)
Pt(1)–Pt(3)	2.788(1)	S(25)–O(252)	1.46(2)	Pt(3)–C(3)	1.94(3)	N(5)–C(5)	1.16(2)
Pt(1)–Pt(4)	2.842(1)	S(45)–O(451)	1.46(2)	Pt(3)–C(7)	1.92(3)	N(5)–C(51)	1.38(2)
Pt(1)–C(1)	1.98(3)	S(45)–O(452)	1.42(2)	Pt(3)–C(8)	2.00(3)	N(6)–C(6)	1.15(3)
Pt(1)–C(6)	1.89(3)	N(1)–C(1)	1.19(3)	Pt(4)–Pt(5)	2.731(1)	N(6)–C(61)	1.42(3)
Pt(1)–C(8)	1.99(2)	N(1)–C(11)	1.36(3)	Pt(4)–S(45)	2.206(6)	N(7)–C(7)	1.21(3)
Pt(2)–Pt(3)	2.802(1)	N(2)–C(2)	1.19(3)	Pt(4)–C(4)	1.88(3)	N(7)–C(71)	1.39(3)
Pt(2)–Pt(4)	2.689(1)	N(2)–C(21)	1.42(3)	Pt(5)–S(25)	2.269(6)	N(8)–C(8)	1.28(3)
Pt(2)–Pt(5)	2.743(1)	N(3)–C(3)	1.13(3)	Pt(5)–S(45)	2.267(7)	N(8)–C(81)	1.42(3)
Pt(2)–S(25)	2.191(6)	N(3)–C(31)	1.40(2)	Pt(5)–C(5)	1.95(2)		
Pt(2)–C(2)	1.89(3)	N(4)–C(4)	1.19(3)				
Pt(3)–Pt(1)–Pt(2)	60.24(3)	C(3)–Pt(3)–Pt(2)	150.0(9)	C(2)–Pt(2)–Pt(1)	87.9(7)	C(4)–Pt(4)–S(45)	103.3(6)
Pt(4)–Pt(1)–Pt(2)	56.96(3)	C(3)–Pt(3)–Pt(4)	147.6(10)	C(2)–Pt(2)–Pt(3)	89.5(6)	Pt(4)–Pt(5)–Pt(2)	58.84(3)
Pt(4)–Pt(1)–Pt(3)	60.65(3)	C(7)–Pt(3)–Pt(1)	127.5(9)	C(2)–Pt(2)–Pt(4)	146.1(6)	S(25)–Pt(5)–Pt(2)	50.8(2)
C(1)–Pt(1)–Pt(2)	69.2(7)	C(7)–Pt(3)–Pt(2)	69.8(9)	C(2)–Pt(2)–Pt(5)	153.5(6)	S(25)–Pt(5)–Pt(4)	109.5(2)
C(1)–Pt(1)–Pt(3)	126.3(7)	C(7)–Pt(3)–Pt(4)	80.1(9)	C(2)–Pt(2)–S(25)	100.2(6)	S(45)–Pt(5)–Pt(2)	110.2(2)
C(1)–Pt(1)–Pt(4)	78.0(7)	C(7)–Pt(3)–C(3)	94.2(13)	Pt(2)–Pt(3)–Pt(1)	60.03(3)	S(45)–Pt(5)–Pt(4)	51.3(2)
C(6)–Pt(1)–Pt(2)	151.7(7)	C(8)–Pt(3)–Pt(1)	45.4(7)	Pt(4)–Pt(3)–Pt(1)	60.61(3)	S(45)–Pt(5)–S(25)	160.7(2)
C(6)–Pt(1)–Pt(3)	143.6(6)	C(8)–Pt(3)–Pt(2)	102.0(7)	Pt(4)–Pt(3)–Pt(2)	56.89(3)	C(5)–Pt(5)–Pt(2)	152.7(6)
C(6)–Pt(1)–Pt(4)	139.2(8)	C(8)–Pt(3)–Pt(4)	97.0(6)	C(3)–Pt(3)–Pt(1)	137.6(9)	C(5)–Pt(5)–Pt(4)	148.4(6)
C(6)–Pt(1)–C(1)	90.0(9)	C(8)–Pt(3)–C(3)	92.4(11)	C(5)–Pt(5)–S(25)	102.2(6)	C(31)–N(3)–C(3)	176.4(24)
C(8)–Pt(1)–Pt(2)	102.5(8)	C(8)–Pt(3)–C(7)	171.6(11)	C(5)–Pt(5)–S(45)	97.0(6)	C(41)–N(4)–C(4)	173.4(23)
C(8)–Pt(1)–Pt(3)	45.8(7)	Pt(2)–Pt(4)–Pt(1)	60.67(3)	Pt(5)–S(25)–Pt(2)	75.9(2)	C(51)–N(5)–C(5)	175.9(24)
C(8)–Pt(1)–Pt(4)	97.4(7)	Pt(3)–Pt(4)–Pt(1)	58.74(3)	O(251)–S(25)–Pt(2)	113.8(9)	C(61)–N(6)–C(6)	176.7(25)
C(8)–Pt(1)–C(1)	171.7(10)	Pt(3)–Pt(4)–Pt(2)	60.79(3)	O(251)–S(25)–Pt(5)	114.0(9)	C(71)–N(7)–C(7)	172.1(24)
C(8)–Pt(1)–C(6)	97.9(10)	Pt(5)–Pt(4)–Pt(1)	114.48(4)	O(252)–S(25)–Pt(2)	119.0(9)	C(81)–N(8)–C(8)	129.0(19)
Pt(3)–Pt(2)–Pt(1)	59.73(3)	Pt(5)–Pt(4)–Pt(2)	60.79(3)	O(252)–S(25)–Pt(5)	117.1(8)	N(1)–C(1)–Pt(1)	164.4(22)
Pt(4)–Pt(2)–Pt(1)	62.37(3)	Pt(5)–Pt(4)–Pt(3)	111.44(4)	O(252)–S(25)–O(251)	112.5(12)	N(2)–C(2)–Pt(2)	174.1(21)
Pt(4)–Pt(2)–Pt(3)	62.32(3)	S(45)–Pt(4)–Pt(1)	151.3(2)	Pt(5)–S(45)–Pt(4)	75.3(2)	N(3)–C(3)–Pt(3)	178.6(27)
Pt(5)–Pt(2)–Pt(1)	115.61(4)	S(45)–Pt(4)–Pt(2)	114.2(2)	O(451)–S(45)–Pt(4)	116.3(9)	N(4)–C(4)–Pt(4)	176.2(23)
Pt(5)–Pt(2)–Pt(3)	112.35(4)	S(45)–Pt(4)–Pt(3)	147.0(2)	O(451)–S(45)–Pt(5)	113.7(10)	N(5)–C(5)–Pt(5)	171.9(18)
Pt(5)–Pt(2)–Pt(4)	60.37(3)	S(45)–Pt(4)–Pt(5)	53.4(2)	O(452)–S(45)–Pt(4)	115.5(9)	N(6)–C(6)–Pt(1)	175.8(23)
S(25)–Pt(2)–Pt(1)	155.6(2)	C(4)–Pt(4)–Pt(1)	84.1(6)	O(452)–S(45)–Pt(5)	117.9(9)	N(7)–C(7)–Pt(3)	170.2(25)
S(25)–Pt(2)–Pt(3)	142.3(2)	C(4)–Pt(4)–Pt(2)	142.2(6)	O(452)–S(45)–O(451)	113.2(13)	Pt(3)–C(8)–Pt(1)	88.8(11)
S(25)–Pt(2)–Pt(4)	113.6(2)	C(4)–Pt(4)–Pt(3)	90.3(6)	C(11)–N(1)–C(1)	178.5(24)	N(8)–C(8)–Pt(1)	137.2(19)
S(25)–Pt(2)–Pt(5)	53.3(2)	C(4)–Pt(4)–Pt(5)	156.4(6)	C(21)–N(2)–C(2)	170.2(26)	N(8)–C(8)–Pt(3)	132.6(18)

FAB mass spectrometry, IR and ^1H NMR spectroscopy. The FAB mass spectrum is shown in Fig. 7 and the peak assignments are given in Table 10. In the spectrum the $[M]^+$ peak is not observed and the highest peak occurs at $m/z = 2350$ corresponding to the ion $[Pt_6(CNC_8H_9)_9]^+$ where all the three SO_2 ligands are lost from the compound. The loss of all the SO_2 ligands before any other ligands is a common feature in these cluster compounds as has been shown before. The IR spectrum showed evidence of terminal isocyanides [ν(CN) 2124 cm^{-1}] and bridging SO_2 ligands [ν(SO_2) 1190 and 1045 cm^{-1}]. The ^1H NMR spectrum showed seven singlets in the methyl region at δ 2.58, 2.55, 2.49, 2.37, 2.35, 2.25 and 2.17 in the ratio 2:1:1:1:1:1:2 indicating the presence of nine terminal isocyanides in seven distinct environments.

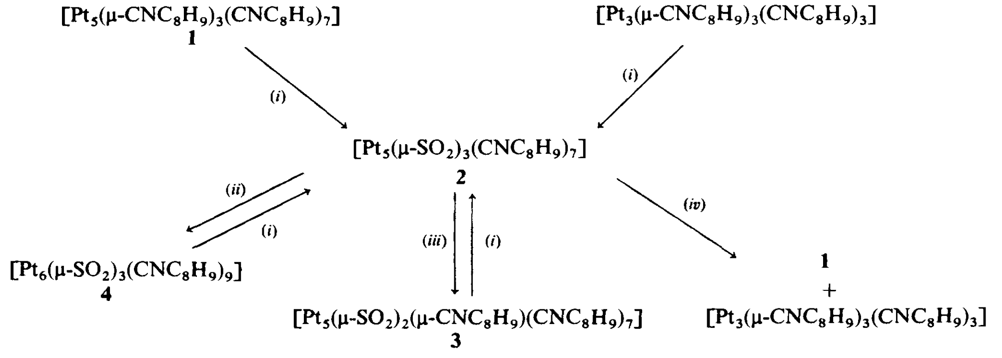
An X-ray crystallographic study of the compound was undertaken [space group $P2_1/c$, $a = 22.055(4)$, $b = 16.634(9)$, $c = 25.01(1)$ Å, $\beta = 106.05(2)°$], however the accuracy of the analysis was severely limited due to extensive absorption problems. Attempts to obtain a more suitable crystal are now being undertaken. The metal framework of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ consists of an edge-bridged trigonal bipyramid with the sixth platinum atom bridging two equatorial platinum atoms. There are three bridging SO_2 ligands, two of which bridge the bonds to the bridging platinum atom. The other SO_2 ligand bridges the bond furthest away from the metal bridge. The X-ray and spectroscopic evidence is consistent with the structure shown. All of the isocyanide ligands are terminal. Atoms Pt(6), Pt(1) and Pt(2) have one isocyanide ligand each co-ordinating to them, Pt(4), Pt(5) and Pt(3) each have two. The same geometry has been observed in the cluster compound $[Os_6(NCO)(CO)_{17}]^-$,[21] but this is the first time it has been observed in a platinum cluster compound. The only known hexanuclear platinum cluster reported to date is $[Pt_6(CO)_{12}]^{2-}$ which has a distorted trigonal-prismatic structure.[22] There are two other platinum cluster compounds that have been structurally characterised which are based on the trigonal-bipyramid geometry, $[Pt_5(\mu\text{-}H)_6H_2(PBu^t_3)_5]$[23] and $[Pt_7(CNC_8H_9)_{12}]$.[1] In $[Pt_7(CNC_8H_9)_{12}]$ the two extra platinum atoms bridge between equatorial and apical platinum atoms instead of between two equatorial platinum atoms as in $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$. This proposed structure can also be viewed in terms of a $Pt(CNC_8H_9)_2$ fragment capping the $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2** cluster compound described previously. The cluster valence-electron count of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ is 84. This disagrees with the theory which predicts a count of 82,[24] two electrons short of that found in $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$. This disagreement could possibly be due to the



4

Table 8 Fractional atomic coordinates for $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2**

Atom	*X/a*	*Y/b*	*Z/c*
Pt(1)	0.354 01(6)	0.388 98(6)	0.235 27(3)
Pt(2)	0.318 59(6)	0.216 07(6)	0.211 87(3)
Pt(3)	0.140 65(6)	0.429 17(6)	0.169 22(3)
Pt(4)	0.169 93(6)	0.328 62(6)	0.289 52(3)
Pt(5)	0.250 01(6)	0.105 33(6)	0.314 97(3)
S(1)	0.268 5(4)	0.511 9(4)	0.154 4(2)
S(2)	0.364 2(4)	0.036 4(4)	0.238 1(2)
S(3)	0.127 6(4)	0.224 5(4)	0.371 1(2)
O(11)	0.210(1)	0.622(1)	0.159 6(6)
O(12)	0.345(1)	0.498(1)	0.101 8(6)
O(21)	0.305(1)	0.000(1)	0.203 3(6)
O(22)	0.490(1)	−0.036(1)	0.249 2(6)
O(31)	0.005(1)	0.237(1)	0.379 1(6)
O(32)	0.179(1)	0.219(1)	0.424 3(6)
C(1)	0.418(2)	0.273(2)	0.306 8(9)
C(2)	0.411(2)	0.213(2)	0.140 5(8)
C(3)	0.056(2)	0.534(2)	0.101 5(9)
C(4)	0.100(1)	0.459(1)	0.315 7(7)
C(5)	0.264(2)	−0.032(2)	0.366 7(8)
C(6)	0.458(2)	0.457(1)	0.241 3(8)
C(7)	0.037(2)	0.350(1)	0.191 0(8)
C(11)	0.519(2)	0.149(2)	0.403 9(9)
C(12)	0.483(2)	0.198(2)	0.448(1)
C(13)	0.542(2)	0.130(2)	0.503(1)
C(14)	0.616(2)	0.031(2)	0.507(1)
C(15)	0.652(2)	−0.017(2)	0.461(1)
C(16)	0.602(2)	0.043(2)	0.404(1)
C(21)	0.544(2)	0.169(2)	0.048 7(8)
C(22)	0.562(2)	0.249(2)	0.002 9(8)
C(23)	0.633(2)	0.211(2)	−0.044 4(9)
C(24)	0.680(2)	0.103(2)	−0.047(1)
C(25)	0.659(3)	0.027(2)	−0.001(1)
C(26)	0.586(2)	0.060(2)	0.049(1)
C(31)	−0.024(2)	0.679(1)	0.005 6(8)
C(32)	0.047(2)	0.733(2)	−0.021 5(9)
C(33)	0.003(2)	0.814(2)	−0.072 1(9)
C(34)	−0.103(2)	0.838(2)	−0.094(1)
C(35)	−0.173(2)	0.788(2)	−0.067(1)
C(36)	−0.134(2)	0.705(2)	−0.014 1(9)
C(41)	0.033(2)	0.621(2)	0.367 7(9)
C(42)	−0.053(2)	0.622(2)	0.413(1)
C(43)	−0.083(3)	0.710(2)	0.442(1)
C(44)	−0.034(3)	0.779(3)	0.426(1)
C(45)	0.044(2)	0.778(2)	0.378(1)
C(46)	0.085(2)	0.696(2)	0.348(1)
C(51)	0.291(2)	−0.217(2)	0.433 4(9)
C(52)	0.378(2)	−0.308(2)	0.414 4(9)
C(53)	0.388(3)	−0.411(2)	0.449(1)
C(54)	0.313(3)	−0.415(2)	0.501(1)
C(55)	0.232(2)	−0.324(2)	0.516(1)
C(56)	0.214(2)	−0.222(2)	0.483 2(9)
C(62)	0.698(2)	0.456(2)	0.292 4(9)
C(63)	0.788(2)	0.493(2)	0.296(1)
C(64)	0.780(2)	0.592(2)	0.268(1)
C(65)	0.680(2)	0.669(2)	0.234(1)
C(66)	0.590(2)	0.635(2)	0.228 5(9)
C(71)	−0.122(2)	0.268(1)	0.200 1(8)
C(72)	−0.108(2)	0.167(2)	0.229 8(9)
C(73)	−0.195(2)	0.132(2)	0.229 1(9)
C(74)	−0.295(2)	0.196(2)	0.198(1)
C(75)	−0.308(2)	0.299(2)	0.164 5(9)
C(76)	−0.221(2)	0.337(2)	0.163(1)
C(121)	0.391(3)	0.313(2)	0.443(1)
C(161)	0.633(3)	−0.013(2)	0.356(1)
C(221)	0.513(2)	0.363(2)	0.006(1)
C(261)	0.561(3)	−0.021(2)	0.097(1)
C(321)	0.167(2)	0.704(2)	0.001(1)
C(361)	−0.218(3)	0.647(3)	0.018(1)
C(421)	−0.102(3)	0.539(3)	0.432(1)
C(461)	0.180(3)	0.680(2)	0.302(1)
C(521)	0.455(3)	−0.299(2)	0.360(1)
C(561)	0.130(2)	−0.124(2)	0.503(1)
C(621)	0.706(2)	0.348(2)	0.326(1)
C(661)	0.481(3)	0.717(2)	0.191(1)
C(721)	0.002(2)	0.098(2)	0.267(1)
C(761)	−0.234(2)	0.445(2)	0.127(1)
N(1)	0.466(1)	0.214(1)	0.348 9(7)
N(2)	0.470(1)	0.203(1)	0.097 2(6)
N(3)	0.014(1)	0.600(1)	0.058 3(7)
N(4)	0.069(2)	0.535(1)	0.338 6(7)
N(5)	0.272(1)	−0.116(1)	0.396 5(7)
N(6)	0.519(1)	0.497(1)	0.246 7(7)
N(7)	−0.032(1)	0.309(1)	0.197 0(7)
C(800)	−0.014(1)	0.834(1)	0.157 8(6)
Cl(1)	0.061 9(9)	0.907 5(9)	0.170 4(5)
Cl(2)	−0.088(1)	0.904(1)	0.091 8(5)
Cl(3)	−0.122(1)	0.835(1)	0.214 9(5)



Scheme 2 (*i*) SO_2; (*ii*) $\frac{1}{5}[Pt_5(CNC_8H_9)_{10}]$; (*iii*) CNC_8H_9; (*iv*) $3CNC_8H_9$

fact that platinum cluster compounds can accommodate different electron counts. For example, the trinuclear *triangulo*-platinum clusters have been synthesised with 42, 43, 44 and 46 valence electrons.[25]

The isolation and subsequent characterisation of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ led to attempts to design a more rational and higher-yield synthesis of this cluster. Since the structure could be viewed as $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ capped by a $Pt(CNC_8H_9)_2$ fragment, it was thought that $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ could be acting as a source of $Pt(CNC_8H_9)_2$. The reaction of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ with 5 equivalents of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ was carried out to verify this proposal. The cluster $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ was formed in high yield from this reaction.

It was found that the reaction of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ with SO_2 resulted in the formation of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$.

To summarise, a series of platinum cluster compounds containing isocyanide and SO_2 ligands have been synthesised.

Table 9 Fractional atomic coordinates for $[Pt_5(\mu-SO_2)_2(\mu-CNC_8H_9)(CNC_8H_9)_7]$ **3**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt(1)	−0.171 80(6)	0.475 44(4)	0.199 50(4)
Pt(2)	−0.128 64(6)	0.578 35(4)	0.240 75(4)
Pt(3)	−0.150 56(6)	0.553 46(4)	0.118 41(4)
Pt(4)	0.007 30(6)	0.521 65(4)	0.212 32(4)
Pt(5)	0.054 97(6)	0.596 12(4)	0.301 27(4)
S(25)	−0.075 5(5)	0.639 7(3)	0.308 4(3)
S(45)	0.149 9(4)	0.540 9(3)	0.266 9(3)
O(251)	−0.084(1)	0.693 8(8)	0.283(1)
O(252)	−0.099(1)	0.637 2(8)	0.366 7(8)
O(451)	0.211(1)	0.567 6(9)	0.235(1)
O(452)	0.196(1)	0.500 4(8)	0.306 5(8)
N(1)	−0.103(2)	0.467 8(9)	0.342(1)
N(2)	−0.342(2)	0.595(1)	0.210(1)
N(3)	−0.231(1)	0.578 4(8)	−0.016 3(8)
N(4)	0.037(1)	0.426 0(8)	0.137(1)
N(5)	0.208(1)	0.646 6(8)	0.405 4(9)
N(6)	−0.258(2)	0.369 1(8)	0.211 7(9)
N(7)	−0.047(1)	0.661 3(8)	0.140 3(7)
N(8)	−0.283(1)	0.464 5(9)	0.067 3(9)
C(1)	−0.120(2)	0.476 8(9)	0.289(1)
C(2)	−0.259(2)	0.591(1)	0.223 9(9)
C(3)	−0.201(3)	0.570(1)	0.033(1)
C(4)	0.027(1)	0.464(1)	0.165(1)
C(5)	0.153(1)	0.630 5(7)	0.364(1)
C(6)	−0.225(2)	0.409(1)	0.205 0(9)
C(7)	−0.088(2)	0.620(1)	0.137(1)
C(8)	−0.220(2)	0.485(1)	0.111(1)
C(11)	−0.084 9(9)	0.456 1(4)	0.401 8(7)
C(12)	−0.160(1)	0.452 7(4)	0.428 2(7)
C(13)	−0.136(1)	0.437 6(4)	0.491 9(7)
C(14)	−0.046(1)	0.427 6(4)	0.521 6(6)
C(15)	0.025(1)	0.431 0(4)	0.495 5(7)
C(16)	0.008(1)	0.445 9(4)	0.432 3(7)
C(121)	−0.259 1(9)	0.464 2(4)	0.393 2(9)
C(161)	0.086(1)	0.450 3(4)	0.401 3(9)
C(21)	−0.439(1)	0.605 7(5)	0.185 5(7)
C(22)	−0.497(1)	0.586 6(5)	0.219 6(7)
C(23)	−0.596(1)	0.596 7(5)	0.194 7(9)
C(24)	−0.616(1)	0.622 3(5)	0.142 7(8)
C(25)	−0.566(1)	0.641 5(5)	0.107 4(8)
C(26)	−0.466(1)	0.632 8(5)	0.130 6(7)
C(221)	−0.461(2)	0.557 8(5)	0.278 3(7)
C(261)	−0.398(2)	0.651 6(5)	0.096 8(9)
C(31)	−0.262 3(7)	0.590 0(5)	−0.078 0(7)
C(32)	−0.289 1(7)	0.643 0(6)	−0.093 7(7)
C(33)	−0.318 2(7)	0.651 7(7)	−0.158 4(7)
C(34)	−0.318 1(7)	0.612 2(7)	−0.196 5(7)
C(35)	−0.293 4(7)	0.562 6(7)	−0.181 8(7)
C(36)	−0.262 0(7)	0.547 5(6)	−0.118 3(7)
C(321)	−0.286 9(8)	0.684 1(6)	−0.048 5(8)
C(361)	−0.233 3(7)	0.494 1(5)	−0.098 2(9)
C(41)	0.042 3(7)	0.379 0(6)	0.108 9(6)
C(42)	0.069 3(7)	0.333 6(6)	0.145 8(6)
C(43)	0.072 6(7)	0.286 8(6)	0.111 9(7)
C(44)	0.051 3(7)	0.286 6(6)	0.050 4(7)
C(45)	0.026 1(7)	0.331 0(6)	0.017 3(7)
C(46)	0.019 5(7)	0.381 1(6)	0.044 9(6)
C(421)	0.091 2(7)	0.335 0(8)	0.210 6(6)
C(461)	−0.007 5(7)	0.427 9(6)	0.010 2(8)
C(51)	0.279(1)	0.665 3(5)	0.452 6(7)
C(52)	0.371(1)	0.649 8(5)	0.454 1(7)
C(53)	0.442(1)	0.669 1(5)	0.506 6(7)
C(54)	0.415(1)	0.699 8(5)	0.548 7(7)
C(55)	0.324(1)	0.714 2(5)	0.545 9(7)
C(56)	0.249(1)	0.696 1(5)	0.494 5(7)
C(521)	0.395(2)	0.616 7(5)	0.407 3(8)
C(561)	0.150(1)	0.710 5(6)	0.489(1)
C(61)	−0.294(1)	0.319 1(7)	0.221 9(5)
C(62)	−0.249(1)	0.275 4(8)	0.207 4(5)
C(63)	−0.289(1)	0.224 4(7)	0.214 7(5)
C(64)	−0.370(1)	0.227 7(7)	0.236 1(5)
C(65)	−0.416(1)	0.271 6(8)	0.251 0(5)
C(66)	−0.372(1)	0.321 4(8)	0.242 6(5)
C(621)	−0.166(1)	0.274(1)	0.185 7(5)
C(661)	−0.418(1)	0.376 7(8)	0.257 4(5)
C(71)	−0.012(1)	0.712 3(7)	0.141 9(4)
C(72)	0.083(1)	0.719 5(7)	0.146 7(4)
C(73)	0.117(1)	0.772 1(7)	0.145 8(4)
C(74)	0.055(1)	0.811 2(7)	0.140 7(4)
C(75)	−0.037(1)	0.806 7(7)	0.136 3(4)
C(76)	−0.074(1)	0.754 7(7)	0.136 9(4)
C(721)	0.147(1)	0.672 7(8)	0.152 0(4)
C(761)	−0.176(1)	0.745(1)	0.132 3(4)
C(81)	−0.339 4(9)	0.419 5(6)	0.068 3(4)
C(82)	−0.422(1)	0.429 1(6)	0.084 5(4)
C(83)	−0.476(1)	0.384 3(7)	0.088 2(5)
C(84)	−0.446(1)	0.333 6(6)	0.075 9(5)
C(85)	−0.361(1)	0.327 7(6)	0.059 6(5)
C(86)	−0.305 2(9)	0.371 5(7)	0.055 1(4)
C(821)	−0.452(1)	0.483 5(6)	0.097 6(4)
C(861)	−0.214 1(9)	0.365 5(9)	0.037 7(4)
C(900)	0.643(1)	0.942 7(6)	0.110 1(7)
C(950)	0.262(2)	0.151(1)	0.092(1)
Cl(1)	0.674 2(9)	0.877 8(5)	0.121 1(6)
Cl(2)	0.539(1)	0.952 7(6)	0.127 7(6)
Cl(3)	0.631(1)	0.959 0(6)	0.035 6(6)
Cl(4)	0.235(2)	0.175(1)	0.025(1)
Cl(5)	0.353(3)	0.182(2)	0.128(2)
Cl(6)	0.297(3)	0.093(1)	0.085(2)

These compounds undergo interconversion reactions with SO_2 and CNC_8H_9. All the reactions carried out are summarised in Scheme 2.

Experimental

Reactions were routinely carried out using standard Schlenk-line techniques under an atmosphere of pure dry nitrogen, with dry, dioxygen-free solvents. Microanalyses (C, H, N) were carried out by Mr. M. Gascoyne and his staff at this laboratory. Infrared spectra were recorded on a Perkin Elmer FT-1710 or a Mattson Polaris spectrometer. Solid samples were mulled with Nujol and recorded between KBr discs. Proton and $^{195}Pt-\{^1H\}$ NMR spectra were recorded on a Bruker AM-300 spectrometer operating at frequencies of 299.96 and 64.50 MHz respectively. Samples for ^1H were referenced to $SiMe_4$ and $^{195}Pt-\{^1H\}$ samples were referenced to $Na_2[PtCl_6]$ in D_2O. The NMR computer simulations were carried out using the Oxford University VAX computer system and a program developed by Professor R. K. Harris, then of the University of East Anglia, and adapted for use by the late Dr. A. E. Derome in Oxford. The FAB mass spectra were recorded by Dr. J. Ballantine and his staff at the SERC Mass Spectrometry Service Centre at the University of Swansea. X-Ray data were collected on an Enraf-Nonius CAD-4 diffractometer at ambient temperature in the Chemical Crystallography Laboratory in Oxford. The data were processed on the Chemical Crystallography VAX computer. The programs used and sources of scattering factor data are given in refs. 19, 26–28.

The compounds $[Pt(CNC_8H_9)_2Cl_2]$[29] and $[Pt_3(\mu-CNC_8H_9)_3(CNC_8H_9)_3]$[6] were synthesised using standard literature methods.

Syntheses.—$[Pt_5(\mu-CNC_8H_9)_3(CNC_8H_9)_7]$ **1**. A solution of $[Co(\eta-C_5H_5)_2]$ (0.63 g, 3.4 mmol) in CH_2Cl_2 (10 cm^3) was added to a suspension of $[Pt(CNC_8H_9)_2Cl_2]$ (0.884 g, 1.7 mmol) in CH_2Cl_2 (10 cm^3). After stirring for 2 h a deep red solution formed. The solvent was removed under reduced pressure and the crude product dissolved in toluene and filtered to remove the $[Co(\eta-C_5H_5)_2]Cl$. The red solution was reduced

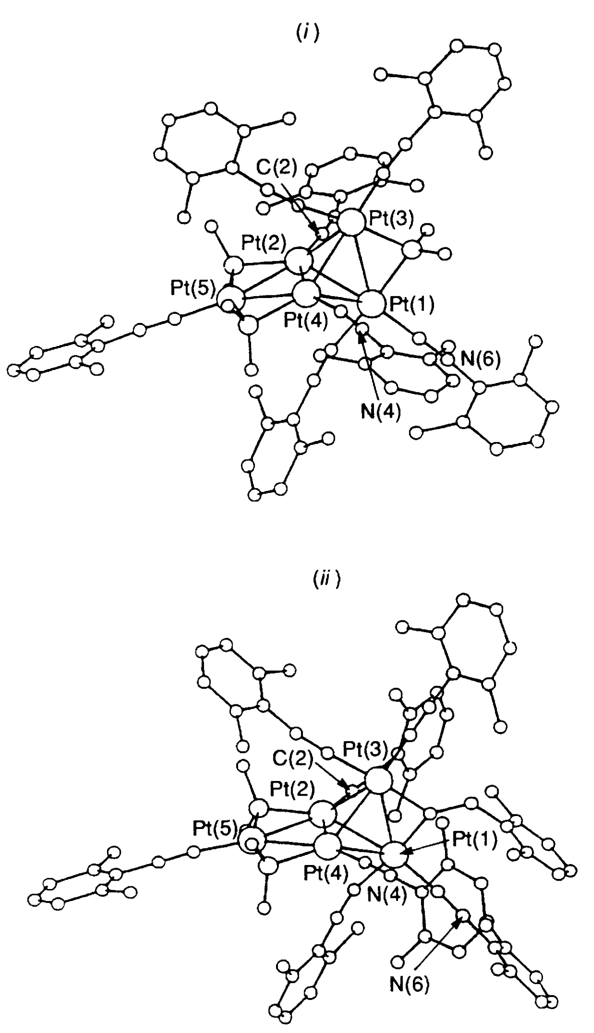


Fig. 5 Molecular structures of (*i*) $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2** and (*ii*) $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3** with the hydrogen atoms omitted for clarity

in volume until red crystals of $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3]$ appeared. The mixture was left in a freezer overnight after which time the red crystals were filtered off. The solvent was removed under reduced pressure and the resultant red oil crystallised from acetone to give red crystals of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$. Yield 0.41 g (53%) (Found: C, 47.2; H, 4.0; N, 5.9. $C_{90}H_{90}N_{10}Pt_5$ requires C, 47.3; H, 3.9; N, 6.1%).

$[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3]$ (Found: C, 47.2; H, 4.0; N, 5.9. $C_{54}H_{54}N_6Pt_3$ requires C, 47.3; H, 3.9; N, 6.1%). IR(Nujol): ν(CN) 2125vs and 1718s (br) cm^{-1} [lit.,[6] 2130vs (br) and 1717m (br) cm^{-1}]; ^1H NMR ($CDCl_3$): δ 2.43 (s, 18 H, CH_3) and 2.26 (s, 18 H, CH_3).

$[Pt_2(CNC_8H_9)_4Cl_2]$. A solution of $[Co(\eta\text{-}C_5H_5)_2]$ (0.07 g, 0.38 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of $[Pt_2(CNC_8H_9)_2Cl_2]$ (0.20 g, 0.38 mmol) in CH_2Cl_2 (20 cm^3). After stirring for 2 h a brown solution formed. The solvent was removed under reduced pressure and the crude product washed with toluene and EtOH. The resultant yellow solid was recrystallised from CH_2Cl_2–EtOH to give yellow microcrystals of $[Pt_2(CNC_8H_9)_4Cl_2]$ in low yield (Found: C, 43.6; H, 3.5; N, 5.4. $C_{36}H_{36}Cl_2N_4Pt_2$ requires C, 43.9; H, 3.7; N, 5.7%). IR(Nujol): ν(CN) 2153vs (br) cm^{-1} (lit.,[16] 2142 cm^{-1}). ^1H NMR ($CDCl_3$): δ 2.51 (lit.,[16] δ 2.55).

Reaction of $[Pt_2(CNC_8H_9)_4Cl_2]$ *with* $[Co(\eta\text{-}C_5H_5)_2]$. A solution of $[Co(\eta\text{-}C_5H_5)_2]$ (0.1 g, 0.54 mmol) in CH_2Cl_2 (10 cm^3) was added to a solution of $[Pt_2(CNC_8H_9)_4Cl_2]$ (0.27 g, 0.27 mmol) in CH_2Cl_2 (30 cm^3). After stirring for 1.75 h a deep red solution formed. The solvent was removed under reduced pressure and the crude product dissolved in toluene and filtered to remove the $[Co(\eta\text{-}C_5H_5)_2]Cl$. The red solution was reduced in volume until red crystals of $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3]$ (0.03 g) appeared. The mixture was left in a freezer overnight after which time the red crystals were filtered off. The solvent was removed under reduced pressure and the product recrystallised from acetone to give red crystals of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$. Yield 0.11 g (44%).

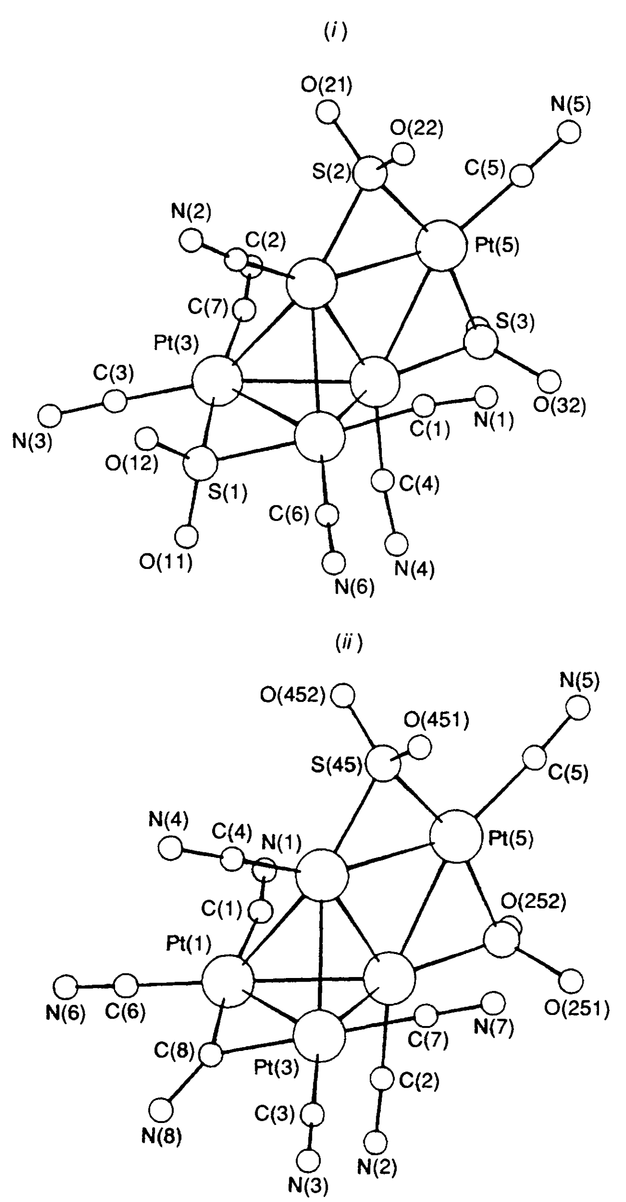


Fig. 6 Molecular structures of (*i*) $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2** and (*ii*) $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3** with the 2,6-dimethylphenyl groups omitted for clarity

Reaction of $[Pt(CNBu^t)_2Cl_2]$ *with* $[Co(\eta\text{-}C_5H_5)_2]$. A solution of $[Co(\eta\text{-}C_5H_5)_2]$ (0.40 g, 2.1 mmol) in CH_2Cl_2 (15 cm^3) was added to a solution of $[Pt(CNBu^t)_2Cl_2]$ (0.45 g, 1.04 mmol) in CH_2Cl_2 (10 cm^3). After stirring for 90 min the solution turned red and the solvent was removed under reduced pressure. Recrystallisation from toluene–hexane gave red crystals of $[Pt_3(\mu\text{-}CNBu^t)_3(CNBu^t)_3]$. IR(Nujol): ν(CN) 2136vs, 2067 (sh), 1740 (sh) and 1713vs cm^{-1} [lit.,[5] 2155vs, 2090 (sh), 1730 (sh) and 1714vs cm^{-1}]. ^1H NMR (C_6D_6): δ 1.65 (s, 27 H, CH_3) and 1.20 (s, 27 H, CH_3) (lit.,[5] δ 1.75 and 1.37).

$[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2**. (*i*) Sulfur dioxide was bubbled

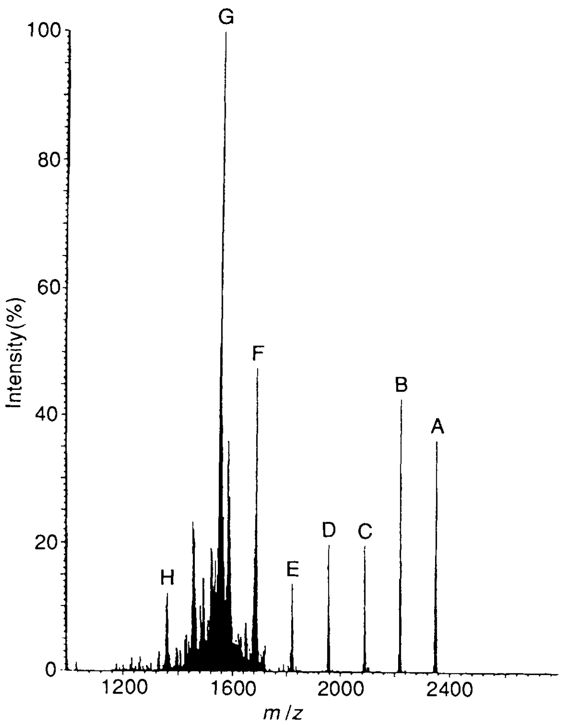


Fig. 7 The FAB mass spectrum of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ **4**

Table 10 Assignments of the FAB mass spectrum of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ **4**

Peak	*m/z*	Relative intensity	Assignment
A	2350	36	$[M - 3SO_2]^+$
B	2219	43	$[M - 3SO_2 - CNC_8H_9]^+$
C	2088	20	$[M - 3SO_2 - 2CNC_8H_9]^+$
D	1956	20	$[M - 3SO_2 - 3CNC_8H_9]^+$
E	1821	14	$[M - 3SO_2 - 4CNC_8H_9]^+$
F	1687	48	$[M - 3SO_2 - 5CNC_8H_9]^+$
G	1554	100	$[M - 3SO_2 - 6CNC_8H_9]^+$
H	1360	12	$[M - 3SO_2 - 6CNC_8H_9 - Pt]^+$

$M = [Pt_6(SO_2)_3(CNC_8H_9)_9]$.

through a solution of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ (0.12 g, 0.05 mmol) in toluene (20 cm^3) for 10 min at 70 °C causing a colour change from dark red to dark orange. After stirring under SO_2 for 1 h the solution was reduced to low volume and filtered. The orange solid was recrystallised from $CHCl_3$–Et_2O to give orange crystals. Yield 0.09 g (86%).

(*ii*) Sulfur dioxide was bubbled through a solution of $[Pt_3(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_3]$ (0.12 g, 0.09 mmol) in toluene (20 cm^3) for 1 h at 70 °C causing a colour change from dark red to dark orange. After stirring under SO_2 for 30 min the solution was reduced to low volume and filtered. The orange solid was recrystallised from CH_2Cl_2–Et_2O to give orange crystals. Yield 0.08 g (71%) (Found: C, 34.7; H, 2.9; N, 4.2. $C_{63}H_{63}N_7O_6Pt_5S_3\cdot CHCl_3$ requires C, 34.8; H, 2.9; N, 4.5%).

$[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3**. A solution of CNC_8H_9 (0.006 g, 0.05 mmol) in CH_2Cl_2 (15 cm^3) was added to a solution of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ (0.1 g, 0.05 mmol) in CH_2Cl_2 (15 cm^3). After 20 min of stirring the yellow solution had darkened to orange. It was concentrated to low volume and MeOH added to give orange crystals of $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$. Yield 0.08 g (75%) (Found: C, 39.4; H, 3.2; N, 4.9. $C_{72}H_{72}N_8O_4Pt_5S_2\cdot 1.2CH_2Cl_2$ requires C, 39.2; H, 3.3; N, 5.0%).

$[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ **4**. A solution of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ (0.11 g, 0.05 mmol) in CH_2Cl_2–toluene (10:20 cm^3) was heated to 70 °C. A solution of $[Pt_5(\mu\text{-}CNC_8H_9)_3(CNC_8H_9)_7]$ (0.03 g, 0.01 mmol) in toluene was added. The dark red solution was stirred for 1 h after which time the solvent was removed under reduced pressure to give a dark oil. Recrystallisation from toluene–MeOH gave dark red crystals of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ (Found: C, 38.2; H, 3.1; N, 4.9. $C_{81}H_{81}N_9O_6Pt_6S_3$ requires C, 38.2; H, 3.2; N, 5.0%).

Reaction of compound **3** *with* SO_2. Sulfur dioxide was bubbled through a solution of $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3** (0.1 g, 0.05 mmol) in toluene–CH_2Cl_2 (1 : 1, 40 cm^3) at 70 °C for 30 min. The solution was stirred for 2 h under SO_2 at room temperature by which time the solution had lightened and an orange solid had started to precipitate. It was reduced to low volume and the solid filtered off. Recrystallisation of the solid from CH_2Cl_2–Et_2O gave light orange crystals of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$. Yield 0.09 g (88%).

Reaction of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ *with* SO_2. Sulfur dioxide was bubbled through a solution of $[Pt_6(\mu\text{-}SO_2)_3(CNC_8H_9)_9]$ in toluene (50 cm^3) at 70 °C for 20 min. The solution was stirred for 30 min under SO_2 at room temperature by which time a colour change from red to orange was observed. It was reduced to low volume and an orange solid precipitated. The solid was filtered off and crystallised from $CHCl_3$–Et_2O to give orange crystals of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$.

Crystal Structure Determinations.—$[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2**. Orange crystals of $[Pt_5(\mu\text{-}SO_2)_3(CNC_8H_9)_7]$ **2** were grown from a $CHCl_3$–Et_2O solution of the compound. A crystal of dimensions 0.7 × 0.3 × 0.3 mm suitable for a single-crystal X-ray analysis was sealed in a Lindemann capillary and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. The data were measured using graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å) and a ω–2θ scan mode. Details of the data collection and refinement are given in Table 5. The structure was solved by standard SHELXS[26] and Fourier methods. Refinement was by full-matrix least-squares methods with the platinum and sulfur atoms refined anisotropically and the other non-hydrogen atoms isotropically. The hydrogen atoms were placed in idealised positions (C–H 1.0 Å) and were not included in the final cycles of refinement. An occluded chloroform molecule was located and assigned isotropic thermal parameters. The C–Cl bond lengths in the chloroform molecule were restrained to have a mean value.

Atomic coordinates are given in Table 8, selected bond lengths and angles in Table 6. Estimated standard deviations are given in parentheses.

$[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3**. Red crystals of $[Pt_5(\mu\text{-}SO_2)_2(\mu\text{-}CNC_8H_9)(CNC_8H_9)_7]$ **3** were grown from a $CHCl_3$–MeOH solution of the compound. A crystal of dimensions 0.5 × 0.5 × 0.4 mm suitable for a single-crystal X-ray analysis was sealed in a Lindemann capillary and transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. The data were measured as above. The platinum atoms were located by direct methods (SHELXS[26]) and the other non-hydrogen atoms were found from subsequent Fourier difference syntheses. Refinement was by full-matrix least-squares methods. The platinum, sulfur, C(*n*) and N(*n*) (*n* = 1–8) atoms were assigned anisotropic thermal parameters and the carbon atoms in the 2,6-dimethylphenyl groups were assigned isotropic thermal parameters. The hydrogen atoms were treated as before. The 2,6-dimethylphenyl groups were refined as rigid groups. Two chloroform molecules with partial occupancy were located and were assigned isotropic thermal parameters. The C–Cl bond lengths in the chloroform molecules were restrained to have a mean value.

Atomic coordinates are given in Table 9, selected bond lengths and angles in Table 7.

Additional material for both structures available from the

Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

References

1 Y. Yamamoto, K. Aoki and H. Yamazaki, *Organometallics*, 1983, **2**, 1377.

2 D. G. Evans, M. F. Hallam, D. M. P. Mingos and R. W. M. Wardle, *J. Chem. Soc., Dalton Trans.*, 1987, 1889.

3 G. E. Heberich and B. Hessner, *Z. Naturforsch., Teil B*, 1979, **34**, 638.

4 G. Longoni and P. Chini, *J. Am. Chem. Soc.*, 1976, **98**, 7225.

5 M. Green, J. A. K. Howard, M. Murray, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 1509.

6 A. Christofides, J. A. K. Howard, J. A. Rattue, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 2095.

7 S. Naylor and M. D. Vargas, *J. Organomet. Chem.*, 1990, **386**, 275.

8 M. I. Bruce and M. J. Liddell, *Appl. Organomet. Chem.*, 1987, **1**, 191.

9 Y. Yamamoto, H. Yamazaki and T. Sakurai, *J. Am. Chem. Soc.*, 1982, **104**, 2329.

10 N. M. Boag, J. Browning, C. Crocker, P. L. Goggin, R. J. Goodfellow, M. Murray and J. L. Spencer, *J. Chem. Res.*, 1978, (*S*) 228, (*M*) 2962.

11 C. E. Briant, D. I. Gilmour, D. M. P. Mingos and R. W. M. Wardle, *J. Chem. Soc., Dalton Trans.*, 1985, 1693.

12 C. E. Briant, D. G. Evans and D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1982, 1144.

13 J. P. Barbier, R. Bender, P. Braunstein, J. Fischer and L. Ricard, *J. Chem. Res.*, 1978, (*S*) 230, (*M*) 2913.

14 K. Takahashi, Y. Yamamoto, K. Matsuda and H. Yamazaki, *Electrochim. Acta*, 1988, **11**, 1489.

15 Y. Yamamoto, K. Takahashi and H. Yamazaki, *Chem. Lett.*, 1985, 201.

16 Y. Yamamoto, K. Takahashi, K. Matsuda and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1987, 1833.

17 F. A. Cotton, K. R. Dunbar, L. R. Falvello and R. A. Walton, *Inorg. Chem.*, 1985, **24**, 4180.

18 S. G. Bott, A. D. Burrows, O. J. Ezomo, M. F. Hallam, J. G. Jeffrey and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1990, 3335.

19 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

20 A. D. Burrows, H. Fleischer and D. M. P. Mingos, *J. Organomet. Chem.*, 1992, **433**, 311.

21 D. R. Mantell and W. L. Gladfelter, *New J. Chem.*, 1988, **12**, 487.

22 J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni and S. Martinengo, *J. Am. Chem. Soc.*, 1974, **96**, 2614.

23 D. Gregson, J. A. K. Howard, M. Murray and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 1981, 716.

24 D. M. P. Mingos and D. G. Evans, *J. Organomet. Chem.*, 1983, **251**, C13.

25 D. M. P. Mingos and T. Slee, *J. Organomet. Chem.*, 1990, **394**, 679.

26 G. M. Sheldrick, SHELXS 86 program for crystal structure determination, University of Göttingen, 1986.

27 D. J. Watkin, J. R. Carruthers and R. W. Betteridge, *CRYSTALS User Manual*, Chemical Crystallography Laboratory, University of Oxford, 1985.

28 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974.

29 Y. Yamamoto and H. Yamazaki, *J. Chem. Soc., Dalton Trans.*, 1989, 2161.

Received 28*th October* 1993; *Paper* 3/06470K