Isocyanide Complexes with Pt_2S and Pt_2CS Cores.[†] Crystal Structure of μ-Sulphido-bis[bis(2,4,6-tri-t-butylphenyl isocyanide)platinum][‡]

Yasuhiro Yamamoto * and Hiroshi Yamazaki
Riken (The Institute of Physical and Chemical Research), Wako, Saitama 351-01, Japan

The triplatinum compound $[Pt_3(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_6]$ (**1**) reacts with sulphur or carbon disulphide to give diplatinum complexes $[Pt_2(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_4S]$ (**2**) and $[Pt_2(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_4(CS_2)]$ (**3**). The structure of (**2**) has been established by a single-crystal *X*-ray analysis; it has a triangular Pt_2S core containing terminal isocyanide groups. Crystals are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions $a = 26.988(7)$, $b = 22.704(11)$, $c = 18.211(5)$ Å, and $\beta = 130.01(2)°$.

Metal clusters are of interest as plausible models of surface condition in heterogeneous catalysis.[1] Studies on interactions of cluster complexes with small molecules such as carbon monoxide, sulphur dioxide, and sulphur give information about chemisorption and chemical reactions on the surface of a catalyst.

Many carbonyl clusters are known,[2] but data for isocyanide clusters are relatively limited.[3] Stone and co-workers[4] reported the preparation of the triangular platinum complexes $[Pt_3(RNC)_6]$ (R = Et, Me, or C_6H_{11}) by the reaction of $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) with isocyanides. Recently we reported a convenient preparation of triangular Pt_3 complexes by the chemical or electrochemical reduction of $[PtCl_2(RNC)_2]$ (R = 2,6-$Me_2C_6H_3$ or 2,4-$Bu^t{}_2$-6-MeC_6H_2).[5] The triangular platinum complexes reacted with olefins, acetylenes, or alkyl halides to undergo fragmentation of metal–metal bonds and mainly gave mononuclear complexes.[3,6]

In this paper we report the preparation of complexes having Pt_2S and Pt_2CS cores by the reaction of $[Pt_3(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_6]$ (1) with S or CS_2 and the *X*-ray crystallographic analysis of the complex containing the Pt_2S core.

Results and Discussion

Three-membered Ring Complex.—Treatment of (**1**) with sulphur in CH_2Cl_2 gave the yellow complex, $[Pt_2(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_4S]$ (**2**), which was recrystallized from CH_2Cl_2–hexane. The i.r. spectrum showed the presence of terminal isocyanide groups (2 127 and 2 092 cm^{-1}), and the ^1H n.m.r. spectrum in $CDCl_3$ showed four singlets, assignable to t-butyl groups, comprising a 2:2:1:1 intensity ratio corresponding to two environments for the isocyanide ligands. The overall molecular geometry was established by the *X*-ray structure determination as shown in Figure 1. The complex has a three-membered Pt_2S core, and the aforementioned spectroscopic data were in good agreement with the crystal structure.

Table 1. Interatomic distances (Å) and bond angles (°) for complex (**2**)

(*a*) Distances

Pt(1)–Pt(2)	2.604(2)	Pt(1)–S	2.268(10)
Pt(2)–S	2.268(10)	Pt(1)–C(10)	1.90(3)
Pt(1)–C(20)	1.95(2)	Pt(2)–C(30)	1.92(3)
Pt(2)–C(40)	1.93(2)	C(10)–N(10)	1.16(4)
C(20)–N(20)	1.16(3)	C(30)–N(30)	1.20(4)
C(40)–N(40)	1.14(3)		

(*b*) Angles

Pt(2)–Pt(1)–S	55.0(2)	Pt(1)–Pt(2)–S	55.0(3)
Pt(1)–S–Pt(2)	70.1(2)	C(10)–Pt(1)–S	160.4(6)
C(20)–Pt(1)–S	102.8(9)	C(30)–Pt(2)–S	102.0(7)
C(40)–Pt(2)–S	161.0(8)	C(10)–Pt(1)–C(20)	96.2(11)
C(20)–Pt(1)–Pt(2)	105.8(6)	C(30)–Pt(2)–C(40)	96.9(11)
C(30)–Pt(2)–Pt(1)	157.0(7)	C(40)–Pt(2)–Pt(1)	106.1(8)
Pt(1)–C(10)–N(10)	176.3(20)	Pt(1)–C(20)–N(20)	175.5(24)
Pt(2)–C(30)–N(30)	174.0(26)	Pt(2)–C(40)–N(40)	174.0(33)
C(10)–N(10)–C(11)	165.4(29)	C(20)–N(20)–C(21)	179.5(30)
C(30)–N(30)–C(31)	177.8(30)	C(40)–N(40)–C(41)	173.3(26)

(*c*) Non-bonded distances

Intra-molecular system (< 3.75 Å)

C(11)–C(471)	3.46(4)	C(41)–C(172)	3.47(4)
C(172)–C(473)	3.54(7)	N(10)–C(492)	3.59(3)
C(192)–C(271)	3.62(4)	C(42)–C(172)	3.65(6)
N(40)–C(172)	3.68(5)	C(16)–C(491)	3.71(4)

Inter-molecular system (< 3.80 Å)

C(191)–C(471a)	3.58(6)	C(182)–C(273b)	3.70(5)
C(183)–C(183c)	3.74(6)	C(493)–C(22a)	3.76(5)
C(171)–C(472c)	3.78(5)	C(493)–C(23a)	3.79(6)
C(31)–C(393d)	3.79(4)	C(493)–C(24a)	3.80(6)

Symmetry codes: (a) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (b) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (c) $-x, -y + 1, -z$; (d) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$.

The temperature-dependent ^1H n.m.r. spectra in PhCl were examined. The spectrum showed three singlets at δ 1.24, 1.47, and 1.56 in a 1:1:1 intensity ratio at ambient temperature: the first was assigned to two kinds of accidentally degenerate *para* butyl groups and the last two to *ortho* butyl groups. These two singlets were broad and the motion of *ortho* butyl groups is shown to be slow. The ^1H n.m.r. spectral behaviour might be related to the close interactions within the molecule associated with the t-butyl groups: C(11) ⋯ C(471), C(41) ⋯ C(172), and C(172) ⋯ C(473) bond distances are 3.46(4), 3.47(4), and 3.54(7) Å, respectively, shorter than the sum of van der Waals radii.

The motion of the *ortho* butyl groups became active with increase in temperature. At 96 °C each signal became sharp. With further increase in temperature the resonances broaden, suggesting that a slow inter-ligand exchange is occurring. Coalescence of two signals due to the *ortho* butyl groups was not observed even at 137 °C, showing that a rapid exchange between ligands did not occur. In the ^1H n.m.r. spectra of a

---

[†] Taken as 'Studies on Interactions of Isocyanides with Transition Metal Complexes. Part 29.' For Part 28, see Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1843.

[‡] *Supplementary data available* (No. SUP 56435, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

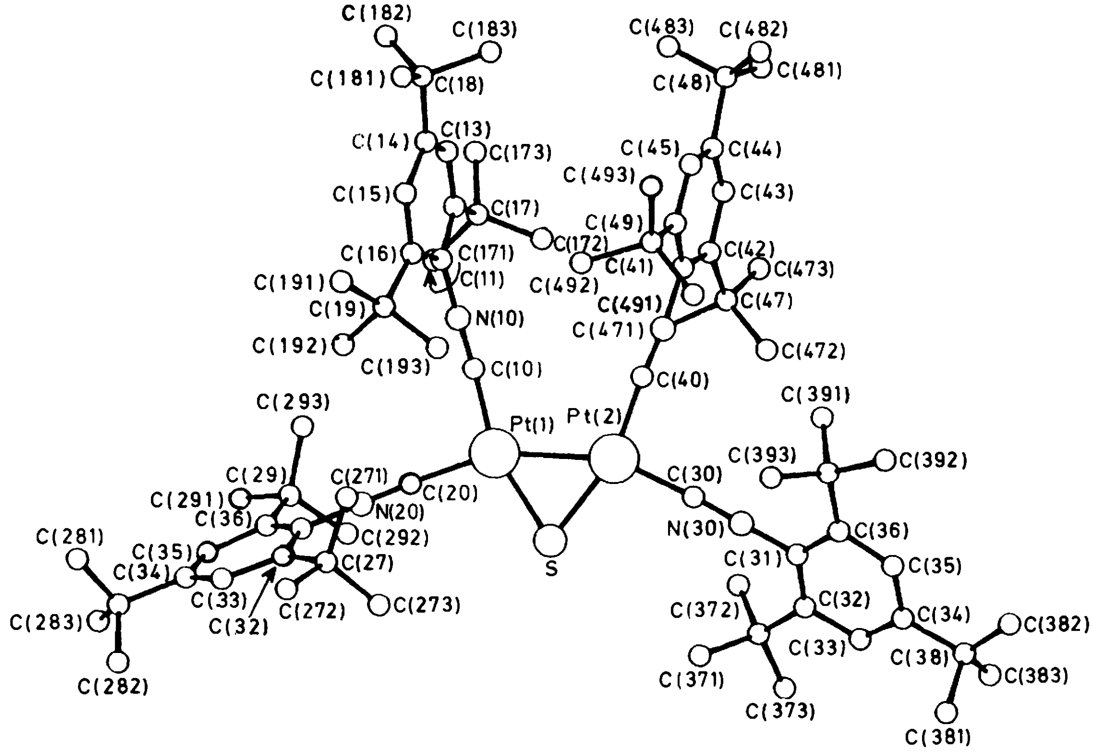


Figure 1. Molecular structure of $[Pt_2(2,4,6-Bu^t_3C_6H_2NC)_4S]$ (**2**)

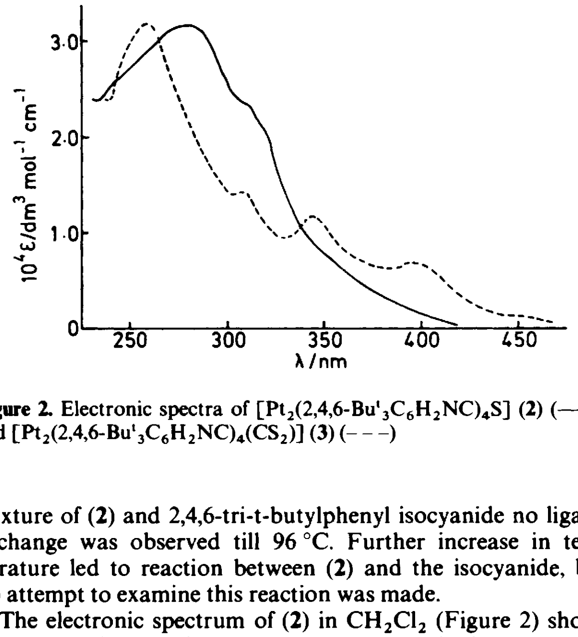


Figure 2. Electronic spectra of $[Pt_2(2,4,6-Bu^t_3C_6H_2NC)_4S]$ (**2**) (——) and $[Pt_2(2,4,6-Bu^t_3C_6H_2NC)_4(CS_2)]$ (**3**) (– – –)

mixture of (**2**) and 2,4,6-tri-t-butylphenyl isocyanide no ligand exchange was observed till 96 °C. Further increase in temperature led to reaction between (**2**) and the isocyanide, but no attempt to examine this reaction was made.

The electronic spectrum of (**2**) in CH_2Cl_2 (Figure 2) shows two absorption bands at 282 and 311 nm. The latter band is attributable to a σ–σ^* transition, comparable with those (*ca.* 320 nm) of the dimeric complex $[\{Pt(RNC)_2Cl\}_2]$,[5] having no bridging ligand.

Description of the Structure of (**2**).—Crystals suitable for *X*-ray analysis were obtained by recrystallization from CH_2Cl_2–ethanol. The molecule consists of a PtPtS triangle, and contains ethanol of solvation. Similar complexes containing the PtPtS ring are $[Pt_2(\mu\text{-}S)(PPh_3)_3(CO)]$ (**4**)[7] and $[Pt_2(\mu\text{-}S)(PPh_3)_2(MeNC)_2]$ (**5**).[8]

The Pt–Pt distance of 2.604(2) Å is considered as a single covalent Pt–Pt bond, in agreement with the sum of the covalent radii (2.62 Å) and is shorter than that found in the metal (2.78 Å). This distance is somewhat shorter than that [2.647(2) Å] found in (**4**), but the average Pt–S distance (2.268 Å) is longer than that (2.223 Å) in (**4**). The difference of these distances within the PtPtS ring causes the Pt–S–Pt angle [70.1(2)°] of (**2**) to be narrower than that [73.1(4)°] of (**4**). The mean Pt–C distance (1.93 Å) and mean Pt–C–N angle (175°) in (**2**) are

Table 2. Some least-squares planes and interplanar angles for complex (**2**): distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Pt(1), Pt(2), S
$-0.6369x + 0.6694y + 0.7024z = 2.8681$

Plane (2): C(11), C(12), C(13), C(14), C(15), C(16)
$-0.5053x - 0.6769y - 0.0852z = -7.9829$
[C(11), 0.059; C(12), −0.039; C(13), −0.028; C(14), 0.063; C(15), −0.017; C(16), −0.040]

Plane (3): C(21), C(22), C(23), C(24), C(25), C(26)
$-0.6096x - 0.4525y + 0.8905z = -3.6666$
[C(21), −0.014; C(22), 0.025; C(23), −0.022; C(24), 0.005; C(25), 0.014; C(26), −0.006]

Plane (4): C(31), C(32), C(33), C(34), C(35), C(36)
$0.6863x - 0.6304y - 0.1633z = -2.4345$
[C(31), 0.011; C(32), −0.002; C(33), −0.008; C(34), 0.007; C(35), 0.003; C(36), −0.010]

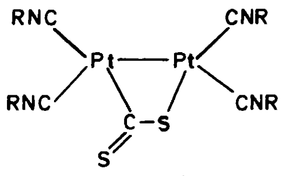
Plane (5): C(41), C(42), C(43), C(44), C(45), C(46)
$-0.5521x - 0.7189y + 0.0314z = -4.0293$
[C(41), −0.030; C(42), 0.032; C(43), 0.000; C(44), −0.026; C(45), 0.012; C(46), 0.015]

Angles (°) between least-squares planes: (1)—(2), 109.6(7); (1)—(3), 70.5(8); (1)—(4), 136.1(8); (1)—(5), 106.9(7); (2)—(3), 74.6(10); (2)—(4), 96.6(11); (2)—(5), 7.4(10); (3)—(4), 84.1(10); (3)—(5), 67.2(10); (4)—(5), 94.5(11)

Table 3. Positional parameters for complex (**2**)*

Atom	x	y	z	Atom	x	y	z
Pt(1)	1 788	2 758(1)	1 368(1)	C(47)	−1 286(12)	3 490(12)	−1 525(18)
Pt(2)	695	2 215(1)	544(1)	C(48)	−2 030(15)	4 252(15)	−4 748(22)
S	1 631(3)	2 018(4)	2 037(5)	C(49)	−343(11)	2 608(11)	−3 020(17)
N(10)	1 585(9)	3 609(8)	−107(14)	C(171)	132(2)	484(2)	7(2)
C(10)	1 640(10)	3 283(12)	434(16)	C(172)	29(2)	430(2)	−117(3)
C(11)	1 545(11)	3 870(12)	−839(14)	C(173)	49(2)	527(2)	−160(3)
C(12)	1 121(11)	4 364(11)	−1 373(18)	C(181)	149(2)	408(2)	−369(3)
C(13)	1 022(11)	4 525(10)	−2 168(18)	C(182)	123(2)	506(2)	−348(2)
C(14)	1 311(12)	4 242(11)	−2 494(19)	C(183)	39(2)	432(2)	−425(3)
C(15)	1 792(11)	3 808(10)	−1 900(17)	C(191)	289(1)	313(1)	−73(2)
C(16)	1 924(11)	3 620(11)	−1 048(16)	C(192)	293(1)	345(1)	64(2)
C(17)	796(10)	4 673(9)	−1 043(16)	C(193)	220(1)	257(1)	−44(2)
C(18)	1 146(10)	4 415(10)	−3 472(15)	C(271)	367(1)	215(1)	215(2)
C(19)	2 489(9)	3 192(9)	−399(14)	C(272)	468(2)	166(1)	354(2)
N(20)	3 260(8)	2 996(9)	2 950(13)	C(273)	372(1)	169(1)	352(2)
C(20)	2 707(11)	2 932(12)	2 355(17)	C(281)	626(2)	355(2)	547(3)
C(21)	3 927(10)	3 076(11)	3 663(17)	C(282)	632(2)	277(2)	643(3)
C(22)	4 341(10)	2 608(10)	3 810(16)	C(283)	611(2)	375(2)	668(3)
C(23)	5 019(11)	2 716(12)	4 538(16)	C(291)	404(2)	462(2)	475(3)
C(24)	5 235(11)	3 241(12)	5 107(17)	C(292)	322(2)	383(2)	426(2)
C(25)	4 807(12)	3 663(12)	4 944(19)	C(293)	328(1)	435(1)	303(2)
C(26)	4 141(10)	3 596(11)	4 215(17)	C(371)	63(1)	98(1)	258(2)
C(27)	4 072(9)	2 036(9)	3 260(14)	C(372)	−20(1)	178(1)	190(2)
C(28)	5 987(10)	3 327(10)	5 907(14)	C(373)	−19(2)	93(1)	280(2)
C(29)	3 663(10)	4 096(10)	4 043(16)	C(381)	−122(2)	−107(2)	87(3)
N(30)	−217(8)	1 273(9)	374(14)	C(382)	−216(3)	−86(3)	−73(4)
C(30)	109(11)	1 661(13)	425(18)	C(383)	−198(2)	−39(2)	65(4)
C(31)	−608(10)	842(10)	315(17)	C(391)	−133(1)	125(1)	−181(2)
C(32)	−541(12)	763(13)	1 155(18)	C(392)	−156(1)	19(1)	−222(2)
C(33)	−915(11)	296(11)	1 090(19)	C(393)	−41(1)	54(1)	−119(2)
C(34)	−1 305(13)	−49(11)	269(18)	C(471)	−140(1)	288(1)	−134(2)
C(35)	−1 355(11)	55(11)	−528(18)	C(472)	−185(1)	391(1)	−181(2)
C(36)	−1 008(10)	513(11)	−526(17)	C(473)	−65(1)	376(1)	−58(2)
C(37)	−87(9)	1 108(10)	2 091(14)	C(481)	−253(2)	456(2)	−477(3)
C(38)	−1 700(10)	−564(10)	207(15)	C(482)	−232(3)	390(3)	−559(4)
C(39)	−1 062(12)	626(12)	−1 398(17)	C(483)	−162(2)	473(2)	−466(4)
N(40)	−329(8)	2 800(10)	−1 404(13)	C(491)	−46(1)	197(1)	−283(2)
C(40)	75(11)	2 587(10)	−690(17)	C(492)	40(1)	279(1)	−225(2)
C(41)	−770(10)	3 111(9)	−2 249(15)	C(493)	−48(1)	262(1)	−398(2)
C(42)	−1 209(11)	3 472(11)	−2 306(18)	C(1)	113(2)	290(2)	287(2)
C(43)	−1 625(11)	3 843(13)	−3 094(17)	C(2)	83(2)	351(2)	229(3)
C(44)	−1 590(12)	3 801(13)	−3 847(19)	O	119(1)	398(1)	220(2)
C(45)	−1 188(11)	3 412(11)	−3 816(16)				
C(46)	−782(10)	3 067(10)	−3 030(16)				

* Positional parameters from Pt(1) to C(49) were refined anisotropically and are multiplied by 10^4; others from C(171) to O, by 10^3.



(**3**); R = $C_6H_2Bu^t_3$-2,4,6

comparable with those found in the other isocyanide complexes. The bond angle C(10)–N(10)–C(11) is 165.4(29)° and the other three corresponding bond angles are linear. The C–Pt–S angles are 102.0(7) and 102.8(9)°, being smaller than the P–Pt–S angles [106.8(4) and 104.5(4)°] in (**4**). The closest interatomic distance in the crystal is 3.58(6) Å for C(191) ··· C(471) ($x + \frac{1}{2}$, $-y + \frac{1}{2}$, z). This is less than the sum of the van der Waals radii of the corresponding atoms.

The dihedral angle between the PtPtS ring and the phenyl plane C(31)—C(36) is 44°. The dihedral angles with the other four phenyl rings fall in the range 70—110°, and these are tilted in the same direction. The phenyl rings C(11)—C(16) and C(41)—C(46) lie in a nearly parallel plane (dihedral angle 7°), in order to minimize steric repulsion. Least-squares planes are given in Table 2.

Four-membered Ring Complex.—The reaction of (**1**) with CS_2 in CH_2Cl_2 at room temperature gave stable yellow crystals of (**3**), formulated as $[Pt_2(2,4,6\text{-}Bu^t_3C_6H_2NC)_4(CS_2)]$. The i.r. spectrum showed three peaks at 2 181, 2 152, and 2 125 cm^{-1} due to the terminal isocyanide groups and a peak[9] at 1 153 cm^{-1} due to the C=S vibration.

The ^1H n.m.r. spectrum showed the presence of four kinds of terminal isocyanide groups. The electronic spectrum in the short-wavelength range is closely similar to that of (**2**). The band at 309 nm is assigned to a σ–σ* transition.

We propose a four-membered ring structure containing two platinum atoms, on the basis of the aforementioned spectroscopic data. There is a precedent for such a compound having a four-membered ring, $[(cod)Pt\{(CF_3)_2CO\}Pt(cod)]$.[10]

Experimental

Infrared spectra were recorded on a Shimazu IR-27G spectrometer. Hydrogen-1 n.m.r. spectra were obtained on JEOL C-60HL and internal Varian HA-100B spectrometers, with $SiMe_4$ as reference. Electronic spectra were recorded on a Shimazu UV-180 spectrometer. All operations were performed under nitrogen. 2,4,6-Tri-t-butylphenyl isocyanide[11] and $[Pt_3(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_6]$ (**1**)[5] were prepared by procedures described in the literature.

Preparation of (**2**).—A mixture of (**1**) (0.2 g, 0.10 mmol) and sulphur (0.2 g) in CH_2Cl_2 (15 cm^3) was stirred for 5 h at room temperature. The mixture was chromatographed on alumina. Elution with benzene gave a yellow solution. Removal and crystallization of the residue from CH_2Cl_2–hexane gave yellow crystals of (**2**), yield 0.05 g, m.p. 246—250 °C (decomp.). I.r. (Nujol): 2 127 and 2 092 cm^{-1}. N.m.r. ($CDCl_3$): δ 1.26 (s, 2,6-Bu^t), 1.28 (s, 4-Bu^t), 1.34 (s, 2,6-Bu^t), 1.48 (s, 2,6-Bu^t), 7.19 (s, 3,5-H), and 7.28 (s, 3,5-H). Electronic spectrum(CH_2Cl_2): λ 282 (ε 31 760) and 311 nm (23 750 $dm^3\ mol^{-1}\ cm^{-1}$) (Found: C, 60.55, H, 7.75; N, 3.70; S, 2.05. Calc. for $C_{76}H_{116}N_4Pt_2S$: C, 60.55; H, 7.75; N, 3.70; S, 2.15%).

Preparation of (**3**).—Excess carbon disulphide was added to (**1**) (0.1 g, 0.05 mmol) in CH_2Cl_2 (15 cm^3) at room temperature. After stirring for 4 h, the volatile materials were removed under reduced pressure. The residue was chromatographed on alumina. Elution with CH_2Cl_2 (containing *ca.* 5% ethyl acetate) gave a yellow solution. Removal of the solvent and crystallization of the residue from CH_2Cl_2–hexane gave yellow crystals of (**3**) (0.02 g). Molecular weight (C_6H_6): 1 485 (calc. 1 508). I.r. (Nujol): 2 181, 2 152, and 2 125 cm^{-1}. N.m.r. ($CDCl_3$): δ 1.30 (s, Bu^t), 1.32 (s, Bu^t), 1.38 (s, Bu^t), 1.40 (s, Bu^t), 1.46 (s, Bu^t), 1.60 (s, Bu^t), 1.64 (s, Bu^t), 5.30 (s, CH_2Cl_2), 7.30, 7.33, and 7.35 (s, 3,5-H). Electronic spectrum (CH_2Cl_2): λ 397 (ε 13 610), 344 (23 530), 309 (28 330), and 260 nm (63 960 $dm^3\ mol^{-1}\ cm^{-1}$) (Found: C, 58.05; H, 7.25; N, 3.20. Calc. for $C_{77}H_{116}N_4Pt_2S_2$: C, 58.4; H, 7.40; N, 3.50%).

Collection of X-*Ray Data and Solution of the Structure of* (**2**).—The yellow crystals of $[Pt_2(2,4,6\text{-}Bu^t{}_3C_6H_2NC)_4S]\cdot C_2H_5OH$ were obtained by recrystallization from CH_2Cl_2–C_2H_5OH.

Crystal data. $C_{78}H_{122}N_4OPt_2S$, M = 1 553.0, monoclinic, space group $P2_1/a$, a = 26.988(7), b = 22.704(11), c = 18.211(5) Å, β = 130.01(2)°, U = 8 546.8 $Å^3$, Z = 4, D_c = 1.207 g cm^{-3}, $F(000)$ = 3 192, $\mu(Mo\text{-}K_\alpha)$ = 37.84 cm^{-1}.

Data collection[12] was carried out using the ω–2θ scan technique and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) with $2 < 2\theta < 45°$. Intensities were corrected for Lorentz and polarisation effects. Of the total 5 719 reflections, 5 160 were considered observed $[I \geqslant 3\sigma(I)]$.

The positions of two Pt atoms were determined from a Patterson map. Subsequent difference Fourier maps and cycles of least-squares refinement revealed the positions of the remaining non-hydrogen atoms. The atomic scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref. 13. Two platinum, sulphur, four nitrogen, and 40 carbon atoms (except 36 methyl carbons) were refined anisotropically and the remaining non-hydrogen atoms were refined isotropically. Several block-diagram least-squares cycles led to convergence of R $(=\Sigma|\Delta F|/\Sigma|F_o|)$ and R' $\{=[\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ to 0.070 and 0.081 respectively. The final difference synthesis showed no peak higher than 0.4 e $Å^{-3}$. No attempt was made to locate the hydrogen atoms; no correction was made for absorption. The final atomic co-ordinates are listed in Table 3.

References

1 R. Ugo, *Catal. Rev.*, 1975, **11**, 225; E. L. Muetterties, *Bull. Chem. Soc. Chim. Belg.*, 1975, **84**, 959.

2 B. F. G. Johnson, 'Transition Metal Clusters,' Wiley, London, 1980.

3 Y. Yamamoto, *Coord. Chem. Rev.*, 1980, **32**, 193.

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

5 Y. Yamamoto, K. Takahashi, and H. Yamazaki, *Chem. Lett.*, 1985, 201; Y. Yamamoto and H. Yamazaki, unpublished work.

6 J. B. B. Heyns and F. G. A. Stone, *J. Organomet. Chem.*, 1978, **160**, 337; J. L. Spencer, F. G. A. Stone, and J. Vincente, *J. Chem. Soc., Dalton Trans.*, 1979, 536; J. Fornies, M. Green, A. Laguna, M. Murray, J. L. Spencer, and F. G. A. Stone, *ibid.*, 1977, 1515.

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

8 C. T. Hunt, G. B. Matson, and A. L. Balch, *Inorg. Chem.*, 1981, **20**, 2270.

9 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1958, p. 350.

10 M. Green, J. A. K. Howard, A. Laguna, L. E. Smart, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1977, 278.

11 Y. Yamamoto, K. Aoki, and H. Yamazaki, *Inorg. Chem.*, 1979, **18**, 1681.

12 T. Sakurai and K. Kobayashi, UNICS III program, Riken, 1978.

13 D. T. Cromer, *Acta Crystallogr.*, 1965, **18**, 17.

Received 3rd *June* 1985; *Paper* 5/928