Chemistry of Platinum Sulphido-complexes. Part 6.[1] Reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the Rhodium Complexes $[(RhL_2Cl)_2]$ (L = CO or C_2H_4) and $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]PF_6$. Crystal and Molecular Structures of $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2][Rh(CO)_2Cl_2]\cdot C_3H_6O$ and $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$†

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The compound $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ reacts with the chloride-bridged rhodium dimers $[\{Rh(CO)_2Cl\}_2]$ and $[\{Rh(C_2H_4)_2Cl\}_2]$ to give $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2][Rh(CO)_2Cl_2]$ (**1**) and $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]Cl$ (**2a**) respectively. The reactions of compound (**1**) and the PF_6^- derivative of (**2a**) with the chelating diphosphine $Ph_2PCH_2CH_2PPh_2$ have also been studied and the products characterised on the basis of n.m.r. data. The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]PF_6$ results in the formation of $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$ (**3**). The molecular structures of compounds (**1**) and (**3**) have been determined by single-crystal *X*-ray techniques using diffractometer data. Compound (**1**) crystallises in the monoclinic space group $P2_1/c$ with four units of formula $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2][Rh(CO)_2Cl_2]\cdot C_3H_6O$ in a cell of dimensions a = 16.813(3), b = 16.068(4), c = 28.342(5) Å, and β = 99.24(2)°. Least-squares refinement of the structure gave a final R value of 0.033 using 5 406 observed intensities $[I \geqslant 3\sigma(I)]$. Compound (**3**) crystallises in the monoclinic space group $C2/c$ with four units of formula $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$ in a cell of dimensions a = 22.089(8), b = 18.141(7), c = 21.363(11) Å, and β = 105.35(4)°. Least-squares refinement of the structure led to a final R value of 0.036 using 4 867 observed intensities $[I \geqslant 3\sigma(I)]$. The structures of compounds (**1**) and (**3**) both show an approximately equilateral triangular arrangement of the platinum and rhodium atoms capped by two μ_3-sulphido-ligands. The metal–metal distances lie in the range 3.034(1)—3.291(1) Å which is greater than those normally associated with Pt–Pt and Pt–Rh bonding distances. The efficiency of these heterometallic platinum–rhodium compounds as homogeneous hydrogenation catalysts has also been studied.

In previous papers the reactivity of the platinum sulphido-complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards a variety of transition-metal ions has been discussed.[1–3] Derivatives containing Ag^+, Ni^{2+}, Pd^{2+}, and Hg^{2+} have been synthesised and also the platinum–rhodium aggregate $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(cod)]PF_6$ (cod = cyclo-octa-1,5-diene).[1] These complexes have been described as 'aggregates' rather than clusters because the metal–metal separations are 3.0—3.3 Å and therefore longer than those generally associated with single metal–metal bonds. In this paper further reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with the chloride-bridged rhodium dimers $[\{Rh(CO)_2Cl\}_2]$ and $[\{Rh(C_2H_4)_2Cl\}_2]$ and also the complex $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]PF_6$ are described. Some simple substitution reactions of the products with simple donor ligands are also discussed.

The rhodium–platinum aggregates were synthesised in order to establish whether the presence of three adjacent but not bonded metal atoms significantly influenced the catalytic properties of the complex. Rhodium was chosen as one of the metal centres because its role in homogeneous catalysis is well documented.[4]

Table 1. $^{31}P\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ n.m.r. data for complexes (**1**)—(**3**). All spectra were recorded at room temperature as CD_2Cl_2 solutions

	$^{31}P\text{-}\{^1H\}$		$^{195}Pt\text{-}\{^1H\}$	
Complex	δ/p.p.m.	^1J(P–Pt)/Hz	δ/p.p.m.	^2J(Pt–X)/Hz
(**1**)	14.90	3 200	−4 360	^2J(Pt–Rh) 60
(**2a**)	14.85	3 210	−4 465	*a*
(**3**)	14.04	3 170	−4 401	^2J(Pt–Rh) 70 ^2J(Pt–Pt′) 150

$^{13}C\text{-}\{^1H\}$ and ^1H data for complex (**2a**)

$^{13}C\text{-}\{^1H\}$		^1H	
δ/p.p.m.	^1J(C–X)/Hz	δ/p.p.m.	^2J(H–Rh)/Hz
60.2	^1J(C–Rh) 10 ^1J(C–H) 158[b]	2.65	1.5

[a] The value could not be measured from the observed spectrum. [b] Value obtained from a coupled spectrum.

Results and Discussion

The reaction between $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and $[\{Rh(CO)_2Cl\}_2]$ in a 2:1 molar ratio, in acetone, proceeded smoothly but it was apparent that not all the platinum complex was being utilised in the reaction. When the reaction was repeated in a 1:1 molar ratio all the platinum complex was consumed and a clear red-brown solution was obtained. On recrystallisation from acetone–hexane an orange-brown solid was isolated in 83% yield. The analytical data suggested a stoicheiometry for the reaction product of $[Pt_2Rh_2(CO)_4Cl_2(\mu\text{-}S)_2(PPh_3)_4]$. The i.r. spectral data [ν(CO) 2 025s and 1 983s cm^{-1}] suggested that only terminal carbonyl groups were present. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum [δ = 14.9(t) p.p.m., ^1J(P–Pt) = 3 200 Hz] and ^{195}Pt n.m.r. spectrum [δ = −4 360(t) p.p.m., ^2J(Pt–Rh) = 60 Hz] were consistent with the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ unit being intact (see Table 1) and co-ordinated to only one of the rhodium

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† 3,3-Dicarbonyl-di-μ_3-sulphido-1,1,2,2-tetrakis(triphenylphosphine)-diplatinumrhodium dicarbonyldichlororhodate–acetone (1/1) and 3,3-bis(2,6-dimethylphenyl isocyanide)-di-μ_3-sulphido-1,1,2,2-tetrakis(triphenylphosphine)diplatinumrhodium hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 2. Selected molecular dimensions (distances in Å, angles in °) for $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2][Rh(CO)_2Cl_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Pt(1) ··· Pt(2)	3.269(1)	Rh(1)–S(1)	2.357(3)
Rh(1) ··· Pt(1)	3.048(1)	Rh(1)–S(2)	2.354(3)
Rh(1) ··· Pt(2)	3.034(1)	Rh(1)–C(101)	1.833(14)
S(1) ··· S(2)	3.024(3)	Rh(1)–C(102)	1.856(12)
Pt(1)–S(1)	2.362(3)	Rh(2)–Cl(1)	2.328(5)
Pt(1)–S(2)	2.340(3)	Rh(2)–Cl(2)	2.351(6)
Pt(1)–P(1)	2.287(3)	Rh(2)–C(201)	1.833(16)
Pt(1)–P(2)	2.276(3)	Rh(2)–C(202)	1.889(18)
Pt(2)–S(1)	2.339(3)	C(101)–O(101)	1.164(15)
Pt(2)–S(2)	2.368(3)	C(102)–O(102)	1.133(13)
Pt(2)–P(3)	2.287(3)	C(201)–O(201)	1.022(17)
Pt(2)–P(4)	2.273(3)	C(202)–O(202)	0.942(17)
Pt(1)–S(1)–Rh(1)	80.5(1)	P(1)–Pt(1)–P(2)	100.3(1)
Pt(1)–S(2)–Rh(1)	81.0(1)	P(3)–Pt(2)–P(4)	98.9(1)
Pt(2)–S(1)–Rh(1)	80.5(1)	C(101)–Rh(1)–S(1)	172.9(4)
Pt(2)–S(2)–Rh(1)	80.0(1)	C(101)–Rh(1)–S(2)	93.0(4)
Pt(1)–S(1)–Rh(2)	88.1(1)	C(102)–Rh(1)–S(1)	91.8(4)
Pt(1)–S(2)–Rh(2)	88.0(1)	C(102)–Rh(1)–S(2)	171.4(4)
S(1)–Rh(1)–S(2)	79.9(1)	C(101)–Rh(1)–C(102)	95.3(6)
P(1)–Pt(1)–S(1)	87.0(1)	C(201)–Rh(2)–Cl(1)	178.9(7)
P(1)–Pt(1)–S(2)	167.0(1)	C(201)–Rh(2)–Cl(2)	89.3(6)
P(2)–Pt(1)–S(1)	172.5(1)	C(202)–Rh(2)–Cl(1)	90.1(5)
P(2)–Pt(1)–S(2)	92.8(1)	C(202)–Rh(2)–Cl(2)	177.2(5)
P(3)–Pt(2)–S(1)	168.2(1)	C(201)–Rh(2)–C(202)	91.0(8)
P(3)–Pt(2)–S(2)	88.3(1)	Cl(1)–Rh(2)–Cl(2)	89.7(2)
P(4)–Pt(2)–S(1)	92.8(1)		
P(4)–Pt(2)–S(2)	172.2(1)		

atoms. The unusual stoicheiometry of the reaction and the incomplete characterisation from spectroscopic measurements were not sufficient to propose an unambiguous structural assignment.

A subsequent single-crystal *X*-ray diffraction study provided a clear understanding of the unusual reaction stoicheiometry and confirmed the structure of the product to be $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(CO)_2][Rh(CO)_2Cl_2]$ (**1**). Selected intramolecular bond lengths and angles are given in Table 2 and the final fractional atomic co-ordinates of the non-hydrogen atoms in Table 3. The molecular structure is illustrated in Figure 1.

The $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ molecule has effectively cleaved $[\{Rh(CO)_2Cl\}_2]$ in an unsymmetrical fashion leading to co-ordination of the $Rh(CO)_2{}^+$ moiety to the chelating sulphido-ligands and leaving the $[Rh(CO)_2Cl_2]^-$ moiety as a counter anion. This reaction is not without precedent as this ion has been previously observed, on several occasions, as a product in the reactions of $[\{Rh(CO)_2Cl\}_2]$.[5]

All the metal atoms in the structure exhibit approximately square-planar geometries, with the platinum and rhodium atoms of the $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(CO)_2]^+$ unit arranged in an approximately equilateral triangle. No metal–metal distances less than 3.034 Å [*i.e.* Pt(2) ··· Rh(1)] were observed. This suggested that the bonding in the complex can be satisfactorily explained in terms of 16-electron metal centres. No formal metal–metal bonds need be proposed. Deviations from the best PtS_2P_2 least-squares planes are minimal (less than 0.035 Å) as are the deviations from the $Rh(CO)_2Cl_2$ and $Rh(CO)_2S_2$ planes (less than 0.028 Å). The 'hinge angle' between the two best least-squares PtS_2P_2 planes is 132.0°, and that between the $RhS_2(CO)_2$ plane and the two PtS_2P_2 units is 115.74°. The rhodium–carbon distances range from 1.833(14) to 1.889(18) Å and are typical of those found in related species.[5,6] The rhodium-sulphur bond lengths of 2.357(3) and 2.354(3) Å are similar to those reported previously in similar complexes, as are the platinum–sulphur distances, which range from 2.339(3) to 2.368(3) Å.[1]

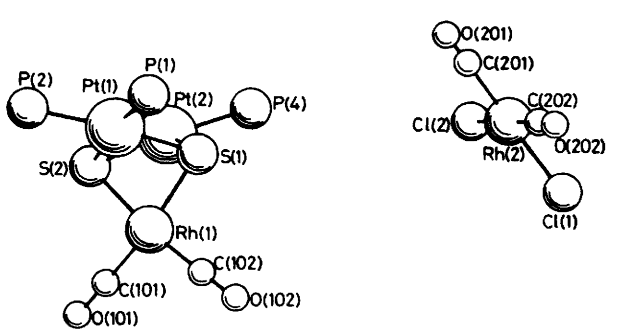

Figure 1. The molecular geometry of $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2]$-$[Rh(CO)_2Cl_2]$

Due to the presence of the $[Rh(CO)_2Cl_2]^-$ anion it proved extremely difficult to isolate pure products from its reactions with alternative ligands. This was clearly illustrated in the reaction with the chelating diphosphine $Ph_2PCH_2CH_2PPh_2$ (dppe). From $^{31}P\text{-}\{^1H\}$ n.m.r. data it appeared that dppe had reacted with both cation and anion to yield the species $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(dppe)][Rh(dppe)Cl_2]$ {cation: δ = 9.8(t) [^1J(P–Pt) = 3 170] and 50.0(d) p.p.m. [^1J(P–Rh) = 186 Hz]; anion: δ = 54.5(d) p.p.m. [^1J(P–Ph) = 133 Hz]}. An i.r. spectrum of the reaction product showed the absence of any bands that could be attributed to co-ordinated CO. Attempted metathesis of the $[Rh(CO)_2Cl_2]^-$ anion with other large anions in an attempt to overcome this problem proved unsuccessful.

The reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $[\{Rh(C_2H_4)_2Cl\}_2]$ in acetone, in a 2:1 molar ratio, occurs at room temperature to yield a brown microcrystalline product formulated as $[(Ph_3P)_4$-$Pt_2(\mu\text{-}S)_2Rh(C_2H_4)_2]Cl$ (**2a**). Metathesis with a methanolic solution of NH_4PF_6 yielded $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(C_2H_4)_2]PF_6$ (**2b**) as a brown microcrystalline solid.

The $^{31}P\text{-}\{^1H\}$, $^{195}Pt\text{-}\{^1H\}$, $^{13}C\text{-}\{^1H\}$, and ^1H n.m.r. spectra suggested that the $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ unit is co-ordinated to one rhodium atom, which in turn is co-ordinated to two ethene molecules [$^{31}P\text{-}\{^1H\}$, δ = 14.85(t), ^1J(P–Pt) = 3 210; $^{195}Pt\text{-}\{^1H\}$, δ = −4 465(t); $^{13}C\text{-}\{^1H\}$, δ = 60.2(d), ^1J(Rh–C) = 10, ^1J(C–H) = 158; ^1H, δ = 2.65(d) p.p.m., ^2J(H–Rh) = 1.5 Hz]. The values of the Rh–C, Rh–H, and C–H coupling constants are all consistent with the ethene molecules being η^2 bonded to the rhodium atom, and are typical of previously reported rhodium–ethene complexes.[7] The proposed structure of the molecule is illustrated in Figure 2.

The co-ordinated ethene ligands are rapidly replaced by carbon monoxide or chelating diphosphines at room temperature and the reaction products were characterised on the basis of spectroscopic data (i.r. and n.m.r.) and elemental analyses. The reaction with CO provided an alternative method for producing the cation $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(CO)_2]^+$ without the presence of the $[Rh(CO)_2]^-$ anion.

The reaction of a 1:1 molar ratio of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]PF_6$ in tetrahydrofuran (thf) occurs swiftly and in high yield at room temperature. The product was isolated as a yellow, highly crystalline compound. From i.r. and the $^{31}P\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ n.m.r. spectra it appeared that the $Pt_2S_2P_4$ unit was still intact and co-ordinated to one rhodium isocyanide moiety [$^{31}P\text{-}\{^1H\}$, δ = 14.04(t), ^1J(P–Pt) = 3 170; $^{195}Pt\text{-}\{^1H\}$, δ = −4 401(t) p.p.m., ^2J(Pt–Pt′) = 150, ^2J(Pt–Rh) = 70 Hz]. The i.r. stretching frequencies of 2 089s, 2 042s, and 2 007m cm^{-1} for ν(NC) suggested that the remaining isocyanide ligands were terminally bound. Together with elemental analysis data, this suggested the formulation $[(Ph_3P)_4$-

Table 3. Final fractional atomic co-ordinates (× 10^4) for $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2][Rh(CO)_2Cl_2]$ with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt(1)	1 745.0(2)	2 326.2(2)	1 826.0(1)	C(225)	656(7)	2 410(8)	3 623(4)
Pt(2)	2 850.8(2)	2 196.7(2)	980.4(1)	C(226)	1 121(6)	2 816(6)	3 315(4)
Rh(1)	2 384.3(5)	677.3(5)	1 509.9(3)	C(231)	2 016(6)	3 962(6)	2 636(3)
Rh(2)	7 352.2(7)	2 382.8(8)	4 008.7(4)	C(232)	1 790(7)	4 442(7)	2 236(4)
S(1)	1 576(2)	1 694(2)	1 065.1(9)	C(233)	1 836(8)	5 313(7)	2 263(4)
S(2)	3 068(2)	1 893(2)	1 808.8(9)	C(234)	2 091(7)	5 678(7)	2 696(4)
Cl(1)	7 010(3)	2 381(3)	3 179(2)	C(235)	2 320(8)	5 212(7)	3 100(4)
Cl(2)	8 207(4)	1 238(4)	3 961(2)	C(236)	2 291(7)	4 350(7)	3 070(4)
P(1)	401(2)	2 637(2)	1 671.0(9)	C(311)	4 773(6)	1 833(6)	1 424(4)
P(2)	2 063(2)	2 840(2)	2 581.0(9)	C(312)	4 658(7)	1 014(7)	1 292(4)
P(3)	4 167(2)	2 612(2)	1 059(1)	C(313)	5 086(8)	380(7)	1 563(4)
P(4)	2 499(2)	2 364(2)	177.5(9)	C(314)	5 610(8)	590(8)	1 955(5)
C(101)	3 094(9)	−6(8)	1 886(5)	C(315)	5 721(8)	1 385(8)	2 106(5)
O(101)	3 555(7)	−416(7)	2 135(4)	C(316)	5 297(7)	2 027(7)	1 839(4)
C(102)	1 770(8)	−180(7)	1 199(4)	C(321)	4 345(6)	3 606(6)	1 363(4)
O(102)	1 368(7)	−683(6)	1 009(4)	C(322)	3 719(6)	4 025(7)	1 526(4)
C(201)	7 626(9)	2 362(13)	4 661(6)	C(323)	3 850(8)	4 818(8)	1 729(5)
O(201)	7 758(8)	2 323(11)	5 025(5)	C(324)	4 606(9)	5 160(9)	1 782(5)
C(202)	6 707(10)	3 337(11)	4 042(6)	C(325)	5 235(8)	4 747(9)	1 637(6)
O(202)	6 373(8)	3 802(7)	4 061(4)	C(326)	5 107(7)	3 974(8)	1 410(5)
C(111)	189(6)	3 489(6)	1 248(4)	C(331)	4 672(6)	2 748(7)	535(4)
C(112)	796(6)	3 829(6)	1 035(4)	C(332)	4 684(7)	3 504(7)	319(4)
C(113)	613(7)	4 493(7)	713(4)	C(333)	5 058(8)	3 609(8)	−89(5)
C(114)	−149(8)	4 801(8)	616(5)	C(334)	5 421(9)	2 963(9)	−259(5)
C(115)	−738(8)	4 469(8)	807(5)	C(335)	5 411(9)	2 191(9)	−54(5)
C(116)	−584(7)	3 813(7)	1 137(4)	C(336)	5 030(8)	2 078(7)	350(5)
C(121)	−169(6)	1 746(6)	1 397(3)	C(411)	2 647(6)	3 396(6)	−42(3)
C(122)	−8(7)	973(7)	1 606(4)	C(412)	2 567(7)	3 601(7)	−526(4)
C(123)	−444(8)	272(8)	1 412(5)	C(413)	2 710(8)	4 410(8)	−666(4)
C(124)	−1 012(7)	346(7)	1 019(4)	C(414)	2 898(8)	5 010(7)	−327(5)
C(125)	−1 161(8)	1 091(8)	802(4)	C(415)	2 907(8)	4 855(7)	142(4)
C(126)	−742(7)	1 800(7)	991(4)	C(416)	2 773(7)	4 040(7)	281(4)
C(131)	−156(6)	2 948(6)	2 145(4)	C(421)	1 429(5)	2 176(6)	−40(3)
C(132)	−525(7)	2 348(6)	2 401(4)	C(422)	892(6)	2 829(6)	−67(4)
C(133)	−938(8)	2 593(7)	2 766(4)	C(423)	72(6)	2 699(7)	−181(4)
C(134)	−1 001(8)	3 416(8)	2 870(5)	C(424)	−219(7)	1 909(7)	−282(4)
C(135)	−636(8)	3 997(7)	2 635(5)	C(425)	303(7)	1 252(7)	−252(5)
C(136)	−200(7)	3 776(7)	2 270(4)	C(426)	1 130(6)	1 376(6)	−133(4)
C(211)	3 093(5)	2 644(6)	2 877(3)	C(431)	3 017(6)	1 588(6)	−137(3)
C(212)	3 713(6)	3 104(7)	2 737(4)	C(432)	3 079(7)	806(7)	61(4)
C(213)	4 513(7)	2 987(7)	2 954(4)	C(433)	3 448(9)	159(8)	−156(5)
C(214)	4 688(7)	2 404(8)	3 308(5)	C(434)	3 759(9)	317(9)	−573(5)
C(215)	4 089(8)	1 955(8)	3 462(5)	C(435)	3 730(9)	1 093(8)	−756(5)
C(216)	3 283(6)	2 067(7)	3 242(4)	C(436)	3 369(7)	1 745(7)	−536(4)
C(221)	1 450(6)	2 371(6)	2 984(3)	C(51)	7 266(17)	3 398(17)	2 014(11)
C(222)	1 335(7)	1 522(7)	2 951(4)	C(52)	7 295(17)	3 186(21)	1 536(11)
C(223)	899(8)	1 113(7)	3 266(5)	C(53)	7 138(16)	2 465(18)	1 231(10)
C(224)	565(8)	1 569(8)	3 587(5)	O(51)	7 252(14)	3 860(15)	1 295(8)

The carbon atoms C(111)—C(116), C(121)—C(126), and C(131)—C(136) belong to phenyl rings attached to P(1) with the numbering going in a sequential fashion around the ring from the attached carbon atom. Similarly, C(2*m*1)—C(2*m*6) are attached to P(2), C(3*m*1)—C(3*m*6) to P(3), and C(4*m*1)—C(4*m*6) to P(4), where *m* = 1—3.

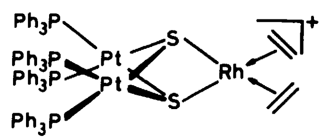

Figure 2. Proposed molecular structure of the $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]^+$ cation

$Pt_2(\mu\text{-}S)_2Rh(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$ (**3**). The ^{195}Pt n.m.r. spectrum was of particular interest as the resolution was such that the $^2J(Pt\text{-}Pt')$ coupling constant could be estimated (see Figure 3). It is approximately 150 Hz, which lies in the range for previously reported coupling constants for Pt–Pt non-metal–metal bonded species.[8] It was decided to perform an *X*-ray crystallographic analysis of this reaction product to investigate whether any features were present which might account for the improved coupling pathways and hence the greater resolution of the ^{195}Pt n.m.r. spectrum.

The *X*-ray crystallographic analysis confirmed the structure of the complex to be $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$ which is illustrated in Figure 4. Selected intramolecular bond lengths and angles are given in Table 4, final fractional atomic co-ordinates of the non-hydrogen atoms in Table 5. The three metal atoms define an approximately equilateral triangle and are all essentially square-planar moieties. All deviations from square planarity are small. The PtP_2S_2 and the RhS_2C_2 planes make a 'hinge angle' of 112.1°. The Pt $\cdots$ Pt distance of 3.291(1) Å is comparable to that found in the structures of $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(cod)]PF_6$[1] and $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(CO)_2][Rh(CO)_2Cl_2]$ as is the Rh $\cdots$ Pt

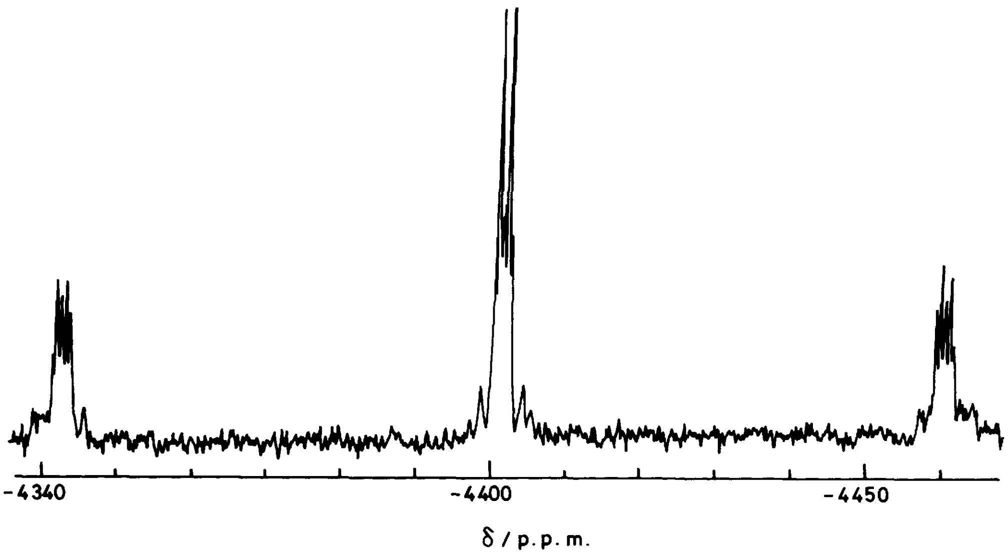

Figure 3. Observed ^{195}Pt n.m.r. spectrum for the complex $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$

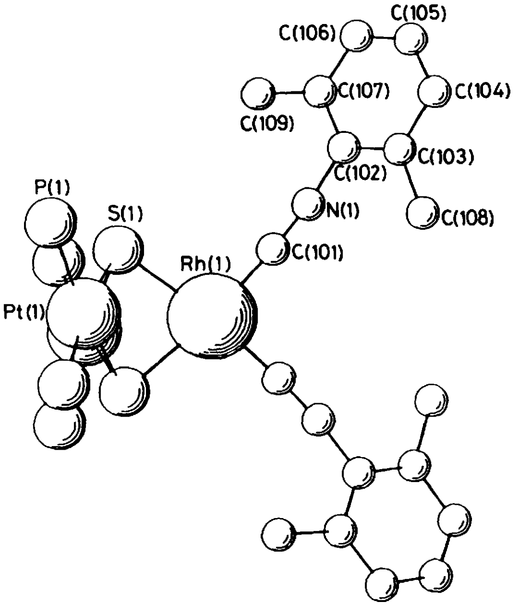

Figure 4. The molecular geometry of the $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]^+$ cation

distance of 3.054(1) Å. These distances are significantly greater than the sum of the covalent radii, and thus the bonding can be satisfactorily explained in terms of 16-electron, square-planar metal centres. No distortions were apparent that would help rationalise the greatly clarified coupling observed in the ^{195}Pt n.m.r. spectrum. The Rh–C distance of 1.90(1) Å is comparable to those previously reported for rhodium isocyanide complexes.[9,10]

Complex (**3**) proved to be extremely unreactive. The reaction with the chelating diphosphine dppe occurred only very slowly at room temperature. After 3 d there was very little evidence of formation of the complex $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(dppe)]^+$. No reaction occurred when carbon monoxide was bubbled through a solution of (**3**). When sulphur dioxide was bubbled through a

Table 4. Selected molecular dimensions (distances in Å, angles in °) for $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$ with e.s.d.s in parentheses

Rh ··· Pt(1)	3.054 3(10)	Pt(1)–S(1)–Pt(2)	88.8(1)
Pt(1) ··· Pt(2)	3.290 7(6)	Pt(1)–S(1)–Rh	81.1(1)
S(1) ··· S(2)	3.008(4)	Pt(2)–S(1)–Rh	80.4(1)
Pt(1)–S(1)	2.334(2)	S(1)–Pt(1)–S(2)	79.5(1)
Pt(1)–S(2)	2.369(2)	S(1)–Rh–S(2)	79.0(1)
Rh–S(1)	2.365(2)	S(1)–Pt(1)–P(1)	93.3(1)
Pt(1)–P(1)	2.268(2)	S(1)–Pt(1)–P(2)	168.1(1)
Pt(1)–P(2)	2.288(2)	S(2)–Pt(2)–P(1)	171.4(1)
Rh–C(101)	1.90(1)	S(2)–Pt(2)–P(2)	88.6(1)
C(101)–N(1)	1.16(1)	P(1)–Pt(1)–P(1)	98.5(1)
N(1)–C(102)	1.38(1)	S(1)–Rh–C(101)	172.3(3)
		S(1)–Rh–C(101)	93.4(3)
		C(101)–Rh–C(101)	94.2(6)
		C(101)–N(1)–C(102)	168.8(10)

solution of complex (**3**) a colour change from yellow to orange was noted. However, removal of the solvent *in vacuo* caused a reversal of the colour change and it appeared that the orange complex was stable only under an atmosphere of SO_2. The lack of reactivity noted could be explained by the bulky nature and steric shielding of the isocyanide and phosphine ligands.

The effectiveness of $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(C_2H_4)_2]PF_6$ to act as a hydrogenation catalyst toward cyclohexene was investigated and compared with that shown by $[Rh(PPh_3)_3Cl]$ to obtain a qualitative measure of the potential of the heterometallic aggregate as a catalyst. The experimental conditions used are described in the Experimental section. At 25 °C and 1 atm (101 325 Pa) pressure of H_2 the complex $[(Ph_3P)_4Pt_2(\mu\text{-}S)_2Rh(C_2H_4)_2]PF_6$ catalysed the hydrogenation of cyclohexene only extremely slowly and the relative rate compared to that shown by $[Rh(PPh_3)_3Cl]$ was approximately 1:500. However, this reactivity, although extremely small, is significantly greater than that shown by the other platinum–rhodium aggregate complexes discussed in this paper. Therefore, in this series of complexes we have found no evidence for co-operative effects resulting from the presence of several metal atoms.

Table 5. Final fractional atomic co-ordinates (× 10^4) for $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$ with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Rh	0	3 165.7(5)	2 500	C(122)	−1 703(4)	2 852(5)	3 231(3)
Pt(1)	−731.9(1)	1 747.2(2)	3 382.5(9)	C(123)	−2 181(4)	3 367(6)	3 205(4)
S(1)	214.5(9)	2 159(1)	3 229.5(9)	C(124)	−2 745(4)	3 144(5)	3 287(4)
P(1)	−1 151.8(9)	1 493(1)	3 382.5(9)	C(125)	−2 862(5)	2 421(5)	3 387(4)
P(2)	−1 572.4(9)	1 425(1)	1 707.8(9)	C(126)	−2 391(4)	1 905(5)	3 415(3)
P(3)	0	7 701(2)	2 500	C(131)	−651(3)	1 625(4)	4 208(3)
N(1)	363(4)	4 288(5)	3 609(4)	C(132)	−737(4)	2 178(4)	4 619(4)
F(1)	577(5)	7 711(7)	3 076(6)	C(133)	−342(4)	2 215(5)	5 252(4)
F(2)	0	8 558(13)	2 500	C(134)	126(4)	1 713(5)	5 458(4)
F(3)	0	6 890(16)	2 500	C(135)	226(4)	1 169(5)	5 026(4)
F(4)	402(9)	7 717(11)	2 035(9)	C(136)	−163(4)	1 123(5)	4 430(4)
F(5)	258(12)	7 074(14)	2 162(12)	C(211)	−1 667(3)	2 119(4)	1 072(3)
F(6)	288(12)	8 292(15)	2 137(12)	C(212)	−1 648(3)	1 939(4)	446(4)
C(101)	218(5)	3 879(6)	3 174(5)	C(213)	−1 690(3)	2 483(5)	−16(5)
C(102)	651(3)	4 714(4)	4 142(4)	C(214)	−1 758(3)	3 195(5)	174(4)
C(103)	970(4)	5 351(5)	4 040(5)	C(215)	−1 770(3)	3 397(5)	753(4)
C(104)	1 296(4)	5 767(6)	4 578(5)	C(216)	−1 717(3)	2 855(4)	1 237(4)
C(105)	1 282(4)	5 530(6)	5 186(5)	C(221)	−1 467(3)	556(4)	1 317(3)
C(106)	965(4)	4 906(5)	5 297(5)	C(222)	−883(4)	220(4)	1 479(3)
C(107)	635(4)	4 480(5)	4 768(4)	C(223)	−793(4)	−439(5)	1 185(4)
C(108)	972(8)	5 580(9)	3 355(8)	C(224)	−1 287(4)	−769(5)	741(4)
C(109)	280(7)	3 784(8)	4 841(7)	C(225)	−1 869(4)	−440(5)	575(4)
C(111)	−1 397(3)	544(4)	3 452(3)	C(226)	−1 961(4)	223(4)	866(3)
C(112)	−1 222(3)	10(4)	3 068(4)	C(231)	−2 366(3)	1 323(4)	1 818(3)
C(113)	−1 384(4)	−731(5)	3 127(4)	C(232)	−2 788(3)	1 909(4)	1 706(3)
C(114)	−1 713(4)	−918(6)	3 561(4)	C(233)	−3 387(4)	1 816(5)	1 785(3)
C(115)	−1 879(4)	−396(5)	3 955(4)	C(234)	−3 567(4)	1 145(5)	1 969(3)
C(116)	−1 715(3)	339(5)	3 903(4)	C(235)	−3 158(4)	562(5)	2 087(3)
C(121)	−1 815(3)	2 115(4)	3 340(3)	C(236)	−2 554(4)	656(4)	2 010(3)

The carbon atoms C(111)—C(116), C(121)—C(126), and C(131)—C(136) belong to phenyl rings attached to P(1) with the numbering going in a sequential fashion from the attached carbon atom. Similarly, C(211)—C(216), C(221)—C(226), and C(231)—C(236) are attached to P(2).

Experimental

Reactions were routinely carried out, using standard Schlenk-line procedures, under an atmosphere of pure dry N_2, and using dry O_2-free solvents. Microanalyses (C, H, N, and Cl) were carried out by Mr. M. Gascoyne and his staff of this laboratory. Grating i.r. spectra were recorded as Nujol mulls using a Pye-Unicam SP-2000 spectrometer and Fourier-transform i.r. spectra were recorded as Nujol mulls using a Perkin-Elmer 1710 spectrometer.

Proton-decoupled ^{31}P, ^{195}Pt, and ^{13}C n.m.r. spectra were recorded using a Bruker AM-250 spectrometer. Samples were referenced as follows: $^{31}P\text{-}\{^1H\}$, trimethyl phosphate in D_2O; $^{195}Pt\text{-}\{^1H\}$, $Na_2[PtCl_6]$ in D_2O; $^{13}C\text{-}\{^1H\}$ and ^{13}C, internally to the solvent used. The machine operating frequencies were 101.26 MHz for ^{31}P, 53.55 MHz for ^{195}Pt, and 62.90 MHz for ^{13}C. Proton spectra were recorded on a Bruker WM-300 spectrometer and referenced to $SiMe_4$ (external). All samples were run in deuteriated solvents.

X-Ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer at ambient temperature in the Chemical Crystallography Laboratory at Oxford. The data were processed on the VAX computer.

Gas chromatograms were recorded using a Shimadzu G.C. Mini-3 gas chromatograph fitted with a Chromosorb (80—100 mesh) column treated with 2,5-dimethylthiophene 1,1-dioxide.

The following compounds were prepared by standard literature methods: $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$;[11] $[\{Rh(CO)_2Cl\}_2]$;[12] $[\{Rh(C_2H_4)_2Cl\}_2]$;[12] and $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]PF_6$.[13]

Syntheses.—$[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2][Rh(CO)_2Cl_2]$ (**1**). The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (0.2 g, 0.13 mmol) was suspended in acetone (40 cm^3), and to this was added a solution of $[\{Rh(CO)_2Cl\}_2]$ (0.05 g, 0.13 mmol) in acetone (20 cm^3). The mixture was stirred at room temperature for 1 h to yield a red-brown solution. The solution was filtered and the solvent removed *in vacuo* to yield a red-brown solid. Recrystallisation from acetone–hexane yielded $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2][Rh(CO)_2Cl_2]$ (**1**) (0.21 g, 83%) as brown crystals (Found: C, 48.4; H, 3.3. $C_{76}H_{60}Cl_2O_4P_4Pt_2Rh_2S_2$ requires C, 48.5; H, 3.4%); ν(CO) 2 025s and 1 983s cm^{-1}.

$[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(dppe)_2][Rh(dppe)Cl_2]$. The complex $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2][Rh(CO)_2Cl_2]$ (0.1 g, 0.05 mmol) was dissolved in acetone (30 cm^3) and to this was added a solution of dppe (0.08 g, 0.1 mmol) in acetone (20 cm^3). After stirring at room temperature for 30 min the initially red-brown solution lightened to pale brown. The solution was filtered and the solvent removed *in vacuo* to yield a buff solid. This was washed with diethyl ether (2 × 50 cm^3) and dried *in vacuo*. Subsequent recrystallisation from acetone–hexane yielded $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(dppe)][Rh(dppe)Cl_2]$ (0.14 g, 70%) as a pale buff solid (Found: C, 58.1; H, 3.2. $C_{124}H_{84}Cl_2P_8Pt_2Rh_2S_2$ requires C, 58.3; H, 3.3%).

$[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]Cl$ (**2a**). The complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (0.2 g, 0.13 mmol) and $[\{Rh(C_2H_4)_2Cl\}_2]$ (0.025 g, 0.065 mmol) were suspended in acetone (40 cm^3) and stirred at room temperature for 4 h to yield a brown solution. This was filtered and the solvent removed *in vacuo* to yield a brown solid. Subsequent recrystallisation of the solid from acetone–hexane yielded $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]Cl$ (**2a**) (0.13 g, 57%) as a brown microcrystalline solid (Found: C, 57.0; H, 3.9. $C_{76}H_{64}ClP_4Pt_2RhS_2$ requires C, 57.0; H, 4.0%).

$[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]PF_6$ (**2b**). The metathesis of an acetone–methanol solution of $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]Cl$ with methanolic NH_4PF_6, and subsequent recrystallisation from CH_2Cl_2–hexane, yielded $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]PF_6$ (**2b**) (> 80%) as a brown crystalline solid (Found: C, 50.4; H, 3.5. $C_{76}H_{64}F_6P_5Pt_2RhS_2$ requires C, 50.6; H, 3.6%).

$[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2]PF_6$. A solution of $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]PF_6$ (0.2 g, 0.11 mmol) in CH_2Cl_2 (40 cm^3) was saturated with carbon monoxide at room temperature and stirred under an atmosphere of carbon monoxide for 1 h. During this time the colour changed from brown to red-brown. Removal of the solvent *in vacuo* and subsequent recrystallisation from CH_2Cl_2–hexane yielded $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(CO)_2]PF_6$ (0.14 g, 69%) as a red-brown solid (Found: C, 49.7; H, 3.3. $C_{76}H_{60}F_6O_2P_5RhS_2$ requires C, 49.8; H, 3.2%); ν(CO) 2 023s and 1 982s cm^{-1}.

$[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$ (**3**). The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ (0.27 g, 0.18 mmol) was suspended in thf (30 cm^3) and a solution of $[Rh(2,6\text{-}Me_2C_6H_3NC)_4]PF_6$ (0.14 g, 0.18 mmol) in thf (30 cm^3) added with stirring. The suspended orange solid dissolved on stirring at room temperature for 30 min to yield a yellow solution. This was filtered and the solvent removed *in vacuo* to yield a yellow solid. The solid was washed with diethyl ether (3 × 30 cm^3) and dried *in vacuo*. Recrystallisation from CH_2Cl_2–cyclohexane yielded $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(2,6\text{-}Me_2C_6H_3NC)_2]PF_6$ (**3**) (0.33 g, 90%) as yellow crystals (Found: C, 53.5; H, 3.6; N, 1.3. $C_{90}H_{78}F_6N_2P_5Pt_2RhS_2$ requires C, 53.7; H, 3.9; N, 1.4%); ν(C=N) 2 089s, 2 042s, and 2 007m cm^{-1}.

In a typical hydrogenation reaction, a 10^{-3} mol dm^{-3} solution of $[Pt_2Rh(\mu\text{-}S)_2(PPh_3)_4(C_2H_4)_2]PF_6$ (0.018 g) was made up in methanol (10 cm^3) in a reaction vessel fitted with a sidearm with a rubber septum. Cyclohexene (1 cm^3) was added and this mixture was stirred for 5 min to allow equilibration. It was then placed under an atmosphere of H_2 (1 atm) and stirred at room temperature. The solution was sampled at regular intervals using a 1-μl G.C. syringe *via* the rubber septum and the samples analysed using a gas chromatograph. The rate of production of cyclohexane against time was monitored and the results plotted graphically. An analogous method was used with $[Rh(PPh_3)_3Cl]$ in order to obtain a comparative rate for the hydrogenation process.

Crystal Data for Compound (**1**).—$C_{76}H_{60}Cl_2O_4P_4Pt_2Rh_2S_2\cdot C_3H_6O$, M = 1 950.2, monoclinic, a = 16.813(3), b = 16.068(4), c = 28.342(5) Å, β = 99.24(2)°, U = 7 557.6 $Å^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $P2_1/c$, Z = 4, D_c = 1.71 g cm^{-3}, $F(000)$ = 3 808. Red-brown crystals grown by slow diffusion of cyclohexane into an acetone solution of (**1**), and sealed in a 0.7-mm Lindemann capillary tube. Crystal dimensions 0.45 × 0.4 × 0.25 mm, $\mu(Mo\text{-}K_\alpha)$ = 45.6 cm^{-1}.

Geometric diffraction data were collected on an Enraf-Nonius CAD4 diffractometer in the ω–2θ scan mode with an ω scan width of 0.9°, using graphite-monochromated Mo-K_α (λ = 0.710 69 Å) radiation. Of 10 110 reflections measured in the range θ 1—20°, 5 406 unique, absorption-corrected reflections with $I \geqslant 3\sigma(I)$ (merging R = 0.021) were used to solve the structure by normal heavy-atom (Patterson and Fourier) methods.

The refinement was performed using blocked-matrix, least-squares methods with the Pt, Rh, S, P, Cl, and carbonyl atoms assigned anisotropic thermal parameters. All the other atoms were refined isotropically. A Chebyshev weighting scheme with coefficients of 257.3, 341.0, and 123.0 gave satisfactory agreement analyses. The refinement converged to give final R and R' values of 0.033 and 0.038 respectively.

Crystal Data for Compound (**3**).—$C_{90}H_{78}F_6N_2P_5Pt_2RhS_2$, M = 2 013.5, monoclinic, a = 22.089(8), b = 18.141(7), c = 21.363(11) Å, β = 105.35(4)°, U = 8 255 $Å^3$ (by least-squares refinement of diffractometer angles for 25 automatically centred reflections, λ = 0.710 69 Å), space group $C2/c$, Z = 4, D_c = 1.62 g cm^{-3}, $F(000)$ = 3 976. Yellow crystals grown by slow diffusion of cyclohexane into a dichloromethane solution of (**3**) and mounted in a 0.5-mm Lindemann capillary tube. Crystal dimensions 0.3 × 0.2 × 0.3 mm, $\mu(Mo\text{-}K_\alpha)$ = 39.6 cm^{-1}.

Geometric diffraction data were collected in the same scanning mode as described above. Of 12 682 reflections measured in the range θ 1—25°, 4 867 unique, absorption-corrected reflections with $I \geqslant 3\sigma(I)$ (merging R = 0.0168) were used to solve the structure by normal heavy-atom (Patterson and Fourier) methods.

The refinement was carried out using blocked-matrix, least-squares methods with the Pt, P, S, and N atoms, and terminal C atoms of the isocyanide anisotropic. All other atoms were refined isotropically. The rhodium atom is on a crystallographic special position (0, y, 0.25).

All hydrogen atoms of the phenyl and xylyl rings were placed in calculated positions (C–H 0.99 Å, with U_{iso} = 0.05 $Å^2$). A Chebyshev weighting scheme with coefficients of 43.1, 57.0, and 20.7 gave satisfactory agreement analyses. Final R and R' values were 0.036 and 0.039 respectively.

Programs and sources of scattering factor data are given in refs. 14—16.

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