Oxidative Addition of Thiols to a Binuclear Platinum Complex; The Crystal Structure of $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$ †

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Reactions of the diplatinum(0) complex $[Pt_2(\mu\text{-dppm})_3]$ (**1**) with H_2S and RSH, R = alkyl or aryl, have been studied. With H_2S the products were $[Pt_2H_2(\mu\text{-}S)(\mu\text{-dppm})_2]$ (**2**) and the cation $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$, probably as the HS^- salt. With RSH the products using an excess of thiol were usually $[Pt(SR)_2(dppm)]$ (**4**; R = Me, Et, Bu^t, CH_2CO_2Et, Ph, $4\text{-}MeC_6H_4$, or $PhCH_2$). With $HSCH_2CH_2SH$ the chelate complex $[Pt(SCH_2CH_2S)(dppm)]$ (**5**) was formed. Intermediate binuclear complexes were identified as $[Pt_2H(SR)(\mu\text{-dppm})_2]$ (**7**) when R = Et, and $[Pt_2(SR)_2(\mu\text{-dppm})_2]$ (**6**) when R = Ph or $4\text{-}MeC_6H_4$. With $PhCH_2SH$, a major product was the 'A-frame' complex $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-dppm})_2]$ (**8**) whose structure has been determined by *X*-ray diffraction.

The chemistry of diphosphine-bridged binuclear platinum compounds has, for the most part, been focused on those with platinum(I) or -(II) centres.[1,2] In comparison, relatively little work has been reported on the reactivity of platinum(0) dimeric species. Although many mononuclear complexes of formulae $[PtL_2]$, $[PtL_3]$, and $[PtL_4]$ (L = tertiary phosphine) are known and their chemistry is well developed,[3] it was only recently that binuclear systems such as $[Pt_2(\mu\text{-}R_2PCH_2PR_2)_3(PPh_3)_n]$ (R = Me, Et, Ph, OMe, or OEt; n = 0—2) were prepared and fully characterized.[4—7] The reactivity of these complexes towards alkyl halides, protic acids, and halogens has been studied, and there are preliminary reports of several other reactions.[4—11] Catalysis by $[Pt_2(\mu\text{-dppm})_3]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$) of the oxidation of CO by O_2 or NO has been established.[12] This paper reports a study of the reactions of $[Pt_2(\mu\text{-dppm})_3]$[4—6] with thiol derivatives RSH, with emphasis on the sequence of reactions leading to the various products. The diplatinum(0) complexes are capable of undergoing multi-electron oxidation processes (potentially involving up to eight electrons though four electron oxidation is the maximum yet observed),[8—10] and the nature of such oxidations in binuclear complexes is of current interest.[1,2] The reactivity of the palladium analogue $[Pd_2(\mu\text{-dppm})_3]$ has been studied in some detail, and a particularly relevant example is the reaction with $C_6F_5SSC_6F_5$ to give the dipalladium(I) complex $[Pd_2(SC_6F_5)_2(\mu\text{-dppm})_2]$.[13—15] In other related reactions, $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with sulphur gives the 'A-frame' complex $[Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2]$,[16] $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with H_2S gives hydrogen and $[Pd_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2]$,[17] $[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$ with methanethiol yields $[Pt_2H_2(\mu\text{-SMe})(\mu\text{-dppm})_2][PF_6]$,[16] and $[Rh_2Cl_2(CO)_2(\mu\text{-dppm})_2]$ with sodium sulphide yields $[Rh_2(\mu\text{-}S)(CO)_2(\mu\text{-dppm})_2]$.[18] Much of this chemistry has been carried out in order better to understand technological processes involving H_2S and RSH.[19,20]

Results

Reaction with H_2S.—A brief survey of the main results is shown in the Scheme. Complex (**1**) reacted rapidly with H_2S(g) to give a yellow precipitate and a light yellow supernatant solution. These fractions were separated and the products were characterized spectroscopically. The yellow precipitate, (**2**), was shown to have the structure $[Pt_2H_2(\mu\text{-}S)(\mu\text{-dppm})_2]$ while the soluble product was shown to contain the known cation $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$,[21] (**3**), presumably as the HS^- salt.

The structure of complex (**2**) was deduced from the i.r., ^1H, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra. The i.r. spectrum contained a peak at 2 090 cm^{-1} due to a terminal metal–hydride bond stretch. The ^1H n.m.r. spectrum confirmed the terminal hydride, which gave a resonance at δ −7.3 with $^1J(PtH)$ = 1 191 Hz. The P_2CH_2 proton signals appeared as two resonances at δ 3.94 and 5.82. The pattern for these signals was very similar to that observed for $[Pt_2Cl_2(\mu\text{-}S)(\mu\text{-dppm})_2]$ and is characteristic for A-frame structures.[16] The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum was typical of a symmetrical A-frame complex,[16] containing a singlet peak at 9.6 p.p.m. with satellites due to both $^1J(PtP)$ and $^2J(PtP)$ couplings and with a $^1J(PtP)$ value of 2 950 Hz characteristic of compounds with trans-$Pt_2(\mu\text{-dppm})_2$ groups. The spectra did not change at low temperatures down to −80 °C.

Complex (**3**), as the PF_6^- salt, has been synthesized previously by the reaction of the triplatinum cluster $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3][PF_6]_2$ with H_2S(g),[21] and the cation was identified by comparison of the ^1H and ^{31}P n.m.r. spectra with those of an authentic sample.

Reactions with Thiols RSH.—Complex (**1**) reacted slowly with excess of methanethiol in toluene solution over a period of several hours to give $[Pt(SMe)_2(dppm)]$ (**4a**). The ^1H n.m.r. spectrum contained a singlet a δ 2.1 due to the SMe protons, and a triplet at 4.3 due to the P_2CH_2 protons with couplings $^2J(PH)$ = 10 Hz and $^3J(PtH)$ = 44 Hz, typical of chelating dppm. The ^{31}P n.m.r. spectrum consists of a singlet at −51.4 p.p.m. with $^1J(PtP)$ = 2 393 Hz, Table 1, only consistent with chelating dppm. Similar reactions occurred with other reagents RSH, in excess, to give the mononuclear products $[Pt(SR)_2(dppm)]$, [R = Et (**4b**), Bu^t (**4c**), CH_2CO_2Et (**4d**), Ph (**4e**), or $4\text{-}MeC_6H_4$ (**4f**)]. All these complexes were air-stable yellow solids. The dithiol $HSCH_2CH_2SH$ gave the analogous chelate derivative, $[Pt(SCH_2CH_2S)(dppm)]$ (**5**).

The reactions of complex (**1**) with the thiols PhSH,

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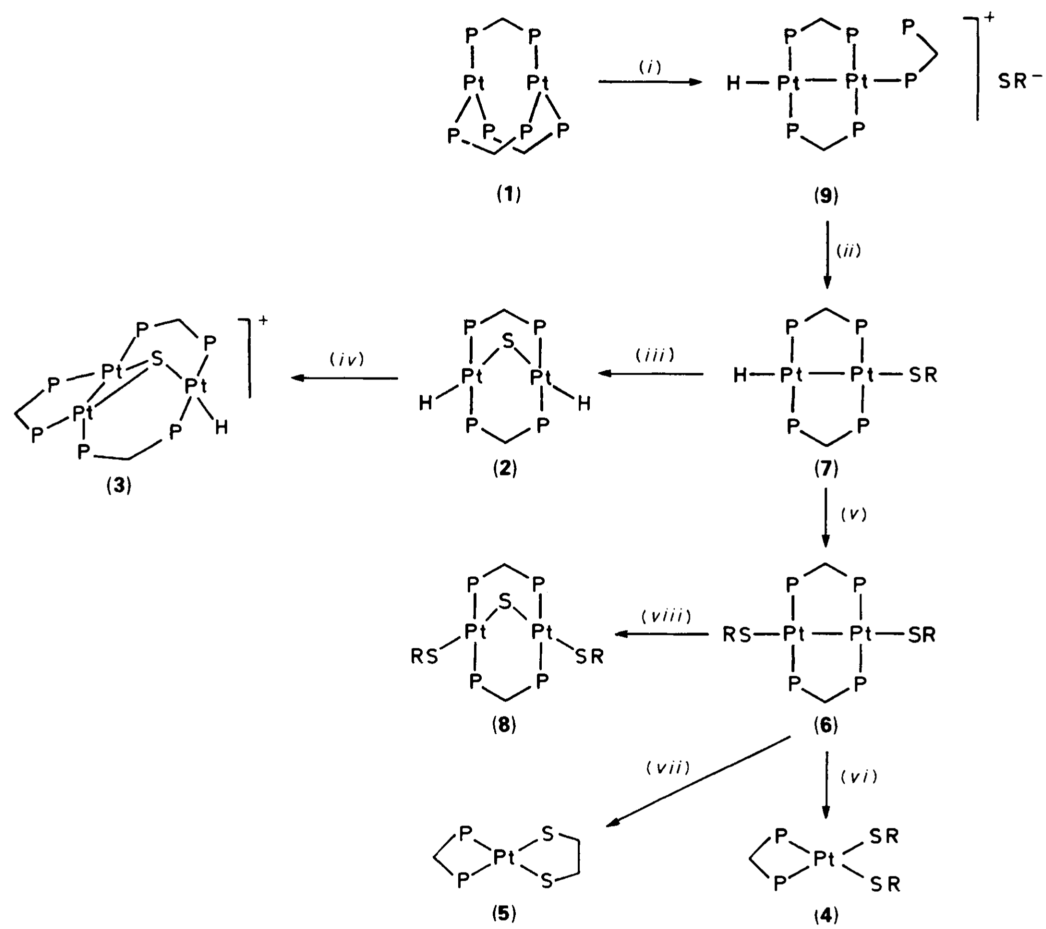
† Bis[μ-bis(diphenylphosphino)methane]-μ-sulphido-bis[benzylthiolatoplatinum(II)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme. A probable reaction sequence for oxidation of $[Pt_2(dppm)_3]$ with thiols. (*i*) RSH; (*ii*) −dppm; (*iii*) R = H; (*iv*) Pt^0(dppm), $-H^+$; (*v*) RSH, $-H_2$; (*vi*) 2RSH, $-H_2$; (*vii*) R = CH_2CH_2SH, $-H_2$; (*viii*) RSH, −RH, R = $PhCH_2$ only

Table 1. $^{31}P-\{^1H\}$ N.m.r. data for complexes $[Pt(SR)_2(dppm)]$

R	Complex	δ(P)/p.p.m.	$^1J(PtP)$/Hz
Me	**(4a)**	−51.4	2 393
Et	**(4b)**	−51.7	2 363
Bu^t	**(4c)**	−54.5	2 300
EtO_2CCH_2	**(4d)**	−51.4	1 994
Ph	**(4e)**	−51.8	2 459
$4-MeC_6H_4$	**(4f)**	−51.5	2 475
CH_2Ph	**(4g)**	−51.7	2 100

Table 2. $^{31}P-\{^1H\}$ N.m.r. data for binuclear platinum complexes

		$^1J(PtP)$	$^2J(PtP)$	$^2J(PP)$	$^3J(PP)$	$J(PtPt)$
Complex	δ(P)/p.p.m.			Hz		
(7)	9.3 (m)	2 850	−80	—	—	4 755
	12.2 (m)	3 000	−89	—	—	4 755
(2)	9.6 (s)	2 950	—	—	—	—
(8)	3.5 (s)	2 950	—	—	—	—
(6a)	7.3 (s)	3 072	−95	65	25	4 760
(6b)	2.2 (s)	3 088	−99	70	26	4 830

$4-MeC_6H_4SH$, and EtSH have been examined in greater detail in order to characterize reaction intermediates. The reactions with arenethiols gave mixtures of complexes **(4e)** and **(4f)** along with the binuclear complexes $[Pt_2(SR)_2(\mu-dppm)_2]$ [R = Ph **(6a)** or $4-MeC_6H_4$ **(6b)**]. The pairs of complexes **(4)** and **(6)** could be separated by recrystallization and the new compounds **(6)** were characterized analytically and spectroscopically. The ^1H and ^{31}P n.m.r. spectra were similar to those reported for other compounds of general formula $[Pt_2X_2(\mu-dppm)_2]$ and are characteristic of the structural type;[22,23] details are given in the Experimental section and Table 2. Treatment of **(6)** with more of the appropriate reagent RSH gave the corresponding complex **(4e)** or **(4f)**.

The reaction of complex **(1)** with EtSH occurred much more slowly than with the arenethiols and at intermediate stages of reaction the solutions contained both $[Pt(SEt)_2(dppm)]$ **(4b)** and a new binuclear complex identified as $[Pt_2H(SEt)(\mu-dppm)_2]$ **(7)**. It was not possible to separate these complexes and obtain pure **(7)**, and so **(7)** was characterized by its n.m.r. spectra. The ^{31}P n.m.r. spectrum contained two multiplets at 9.3 [$^1J(PtP)$ = 2 850 Hz, $^2J(PtP)$ = −80 Hz] and 12.2 p.p.m. [$^1J(PtP)$ = 3 000, $^2J(PtP)$ = −89 Hz] and, from analysis of the satellite spectra,[23] $^1J(PtPt)$ = 4 755 Hz. The magnitude of $^1J(PtP)$ indicates a complex with the *trans*-$Pt_2(\mu-dppm)_2$ unit, the values of $^2J(PtP)$ and $^1J(PtPt)$ indicate that a Pt–Pt bond is present, and, together with the presence of two ^{31}P resonances, the data indicate a structure $[Pt_2X(Y)(\mu-dppm)_2]$.[23] The ^1H n.m.r. spectrum of **(7)** contains a terminal hydride resonance at δ −10.74 with $^1J(PtH)$ and $^2J(PtH)$ values of 1 152 and 630 Hz respectively. The relatively large $^2J(PtH)$ again indicates that a Pt–Pt bond is present in the molecule.[24] The presence of the SEt group was shown by signals at δ 0.86 [triplet, $^3J(HH)$ = 8 Hz, Me] and 2.64 [quartet, $^3J(HH)$ = 8, $^3J(PtH)$ = 20 Hz, CH_2]. Thus the structure could be deduced with confidence even

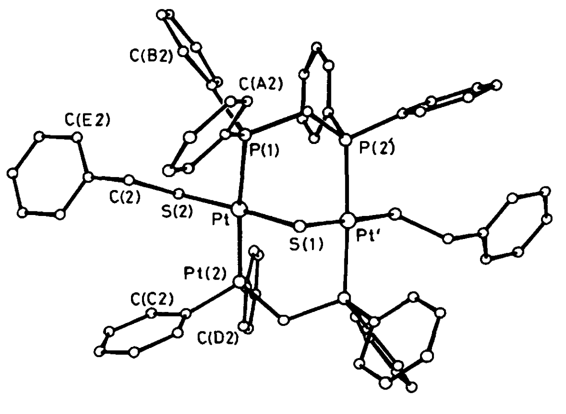


Figure 1. A view of the molecular structure of $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-}dppm)_2]$ (**8**) with atoms represented by spheres of arbitrary size. In the *n* phenyl rings, where *n* is A to E, the atoms are labelled cyclically C(*n*1) to C(*n*6), starting at the site of P and CH_2 substitution; only the labels C(*n*2) are shown, for clarity

Table 3. Selected details (lengths in Å, angles in °) of the molecular geometry of $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-}dppm)_2]$ (**8**) *

Pt–S(1)	2.347(3)	P(1)–C(1)	1.86(1)
Pt–S(2)	2.351(3)	P(1)–C(A1)	1.84(1)
Pt–P(1)	2.280(3)	P(1)–C(B1)	1.85(1)
Pt–P(2)	2.289(3)	P(2)–C(1')	1.84(1)
S(2)–C(2)	1.83(2)	P(2)–C(C1)	1.84(1)
C(2)–C(E1)	1.41(4)	P(2)–C(D1)	1.81(1)
S(1)–Pt–P(1)	80.7(1)	Pt–P(1)–C(A1)	111.7(4)
S(1)–Pt–P(2)	91.4(1)	Pt–P(1)–C(B1)	118.9(5)
S(2)–Pt–P(1)	99.6(1)	Pt–P(2)–C(1')	115.3(4)
S(2)–Pt–P(2)	88.2(1)	Pt–P(2)–C(C1)	112.2(3)
S(1)–Pt–S(2)	176.6(1)	Pt–P(2)–C(D1)	117.7(4)
P(1)–Pt–P(2)	172.0(1)	C(1)–P(1)–C(A1)	103.8(6)
Pt–S(1)–Pt'	84.9(2)	C(1)–P(1)–C(B1)	103.5(6)
Pt–S(2)–C(2)	102.6(7)	C(A1)–P(1)–C(B1)	104.5(6)
S(2)–C(2)–C(E1)	113(2)	C(1')–P(2)–C(C1)	101.4(4)
P(1)–C(1)–P(2')	115.7(6)	C(1')–P(2)–C(D1)	104.2(7)
Pt–P(1)–C(1)	112.9(3)	C(C1)–P(2)–C(D1)	104.3(5)
Torsion angles (°)			
P(1)–Pt–Pt'–P(2')	−24.6(1)	Pt–P(1)–C(1)–P(2')	22.8(4)
S(2)–Pt–S(1)–Pt'	162(2)	Pt'–P(2')–C(1)–P(1)	−52.5(5)
S(1)–Pt–S(2)–C(2)	32(2)		

* The primed atoms are generated from the asymmetric unit by the symmetry operation $-x, y, -\frac{1}{2} - z$.

though the low thermal stability of the complex frustrated efforts at purification.

Reaction with $PhCH_2SH$.—Complex (**1**) in toluene solution reacted with a 2 molar excess of benzenethiol over a period of several hours to yield a mixture of a sparingly soluble yellow complex, identified as $[Pt(SCH_2Ph)_2(dppm)]$ (**4g**), and a more soluble orange complex, identified as $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-}dppm)_2]$ (**8**). The new product (**8**) was purified and fully characterized by n.m.r. spectroscopy and *X*-ray crystallography.

The 'A-frame' structure of (**8**) was suggested by the characteristic appearance of the resonances in the ^1H n.m.r. spectrum due to the P_2CH_2 protons, which appeared as two sets of multiplets at δ 2.98 and 5.11. The patterns of these resonances are typical of methylene protons of dppm ligands in A-frame complexes.[22,23] The presence of the terminal benzyl groups was also indicated by the ^1H n.m.r. signal due to the $PhCH_2$ protons [δ 2.4, $^3J(PtH) = 24$ Hz]. The ^{31}P n.m.r. spectrum contained a singlet at δ 3.48 p.p.m. with satellites due to coupling to ^{195}Pt, with $^1J(PtP) = 2\,950$ Hz, fully consistent with an 'A-frame' structure.[22,23]

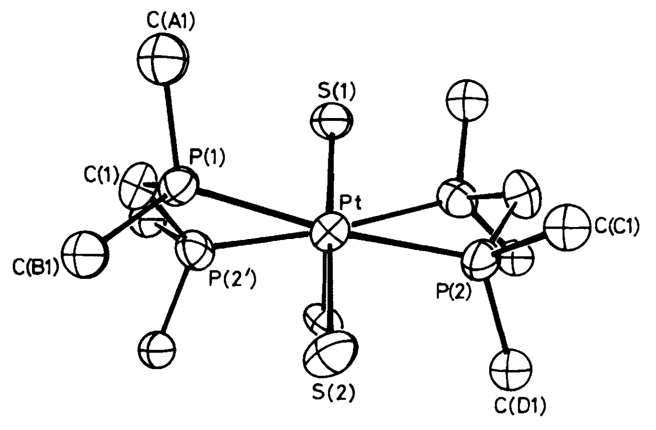


Figure 2. Conformation of the $Pt_2P_4C_2$ ring in $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-}dppm)_2]$ (**8**), viewed along the Pt ··· Pt' vector. The CH_2Ph groups are omitted and only the *ipso*-carbon atoms of the phenyl rings A—D are shown, for clarity

A single-crystal *X*-ray diffraction study confirmed the 'A-frame'-type structure and established the presence of sulphur at the apex of the 'A' (Figure 1). An inspection of non-bonding interatomic distances revealed no anomalously short intermolecular contacts.

The molecular structure of (**8**) displays crystallographically imposed C_2 symmetry, with the diad axis passing through the S(1) atom and bisecting the Pt ··· Pt' distance of 3.1682(4) Å. Metal–metal separations larger than 3.1 Å have also been observed in the isoelectronic, sulphur-bridged 'A-frames' $[Rh_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$[18] and $[Pd_2Cl_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$.[25] As is evident from the bond angles and torsion angles listed in Table 3, the distortion of the molecular geometry of (**8**) from an idealized 'A-frame' is high and similar to that previously found in the complex $[Rh_2(CO)_2(\mu\text{-}S)(\mu\text{-}dppm)_2]$. Thus, the eight-membered $Pt_2P_4C_2$ dimetallacycle shows a twisted boat conformation (Figure 2), characterized by the P(1)–Pt–Pt'–P(2)' torsion angle of −24.6(1)°; the metal centres lie in substantially distorted square-planar environments.

In the $Pt_2(SCH_2Ph)_2(\mu\text{-}S)$ fragment the Pt–S bond lengths are 2.347(3) and 2.351(3) Å and the S–Pt–S and Pt–S–Pt' bond angles are 176.6(1) and 84.9(2)°, respectively. The Pt–P distances, 2.280(3) and 2.289(3) Å, are within the range of those usually found in diplatinum 'A-frames'.[26]

Discussion

The reaction of $[Pt_2(\mu\text{-}dppm)_3]$ (**1**) with thiols results in the formation of binuclear platinum(I) and platinum(II) complexes as well as monomeric platinum(II) species. In some cases intermediate complexes have been characterized and, based on this and previous studies of the reactivity of complex (**1**), it is possible to propose a reasonable sequence of reactions shown in the Scheme.

The initial step in the reaction of complex (**1**) with thiols is suggested to involved protonation of (**1**) by the thiol, which would lead to a diplatinum(I) complex (**9**). Complex (**9**) was not detected in any of the reactions but is proposed by analogy with the products formed from (**1**) and stronger protic acids.[8–10] Since the thiolate anion is a good ligand for platinum and substitution reactions of diplatinum(I) complexes are rapid, (**9**) is expected to undergo loss of a dppm ligand with formation of (**7**). Complex (**7**) was detected in the case where R = Et. At this stage the course which the reaction takes depends chiefly on the nature and the concentration of the thiol and the length of time for which the reaction is allowed to continue.

In the case of the reaction with H_2S where, in structure (**7**), R = H, this complex can undergo an intramolecular oxidation to give the A-frame complex, (**2**). Further reaction of (**2**) with a $\mathrm{Pt^0}$(dppm) fragment derived from complex (**1**) may result in the formation of the stable trinuclear cluster (**3**). We have shown previously that $\mathrm{Pt_3}$ clusters may be derived from combination of $\mathrm{Pt^I{}_2}$ and $\mathrm{Pt^0}$ units.[27,28] When R is an alkyl or aryl group, complex (**7**) may undergo a reaction with a second molecule of thiol, resulting in the elimination of hydrogen and formation of the symmetrical $\mathrm{Pt^I}$–$\mathrm{Pt^I}$ dimer with structure (**6**). This structure was characterized when R = aryl, but not when R = alkyl. The more acidic arenethiols are expected to give a more rapid conversion of (**7**) into (**6**) and this may rationalize the different behaviour of the alkane- and arene-thiols. Finally, further oxidation is accompanied by fragmentation and the complexes (**4**) and (**5**) are formed.

There is an exception only where R is a benzyl group. In this case the reaction of the thiol with the complex of structure (**6**) appears to result in the elimination of toluene and formation of the A-frame complex, (**8**). This is presumably due to the fact that the benzyl group is a better leaving group than the other alkyl substituents that were used.

Thus it is shown that the reaction of complex (**1**) with thiols involves a stepwise oxidation of the platinum(0) centres first to $\mathrm{Pt^I}$ and later to $\mathrm{Pt^{II}}$.

Experimental

Proton n.m.r. spectra were recorded on a Varian XL-200 spectrometer, $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ spectra on a Varian XL-300 spectrometer. Proton chemical shifts were measured relative to $\mathrm{SiMe_4}$, ^{31}P chemical shifts relative to $\mathrm{H_3PO_4}$.

$[\mathrm{Pt_2H_2}(\mu\text{-S})(\mu\text{-dppm})_2]$ (**2**) *and* $[\mathrm{Pt_3H}(\mu_3\text{-S})(\mu\text{-dppm})_3][\mathrm{HS}]$ (**3**).—Hydrogen sulphide was slowly bubbled through a solution of complex (**1**) (100 mg, 0.065 mmol) in toluene (10 $\mathrm{cm^3}$) under an atmosphere of nitrogen. A reaction was apparent from the immediate colour change of the solution from red to orange and then yellow. After 1 h the mixture consisted of a yellow precipitate and a yellow supernatant. These fractions were separated, washed with pentane (10 $\mathrm{cm^3}$), and dried to give complexes (**2**) (20 mg, 0.02 mmol) and (**3**) (50 mg, 0.03 mmol). Complex (**2**) (Found: C, 49.9; H, 4.1. Calc. for $\mathrm{C_{50}H_{46}P_4Pt_2S}$: C, 50.3; H, 3.9%): i.r., ν(PtH) 2 090 $\mathrm{cm^{-1}}$; n.m.r. (in $\mathrm{CD_2Cl_2}$), ^{1}H δ −7.3 [s, 2 H, $^1J(\mathrm{PtH})$ = 1 191, PtH], 3.94 [m, 2 H, $^2J(\mathrm{PH})$ = 10, $^3J(\mathrm{PtH})$ = 60 Hz, $\mathrm{P_2CH^aH^b}$], 5.82 (m, 2 H, $\mathrm{P_2CH^aH^b}$), and 6.8—7.4 (m, 40 H, Ph); $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ 9.6 p.p.m. [m, $^1J(\mathrm{PtP})$ = 2 950 Hz, PPt]. Complex (**3**): i.r., ν(PtH) 2 146 $\mathrm{cm^{-1}}$; n.m.r. (in $\mathrm{CD_2Cl_2}$), ^{1}H, δ −9.2 [t of t, $^1J(\mathrm{PtH})$ = 1 106, $^2J(\mathrm{PH})$ = 13, $^4J(\mathrm{PH})$ = 3 Hz, PtH]; $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$, δ −12.7 [m, 2 P, $^1J(\mathrm{PtP})$ = 3 887, $\mathrm{P^a}$], 5.0 [t, 2 P, $^1J(\mathrm{PtP})$ = 3 110, $^2J(\mathrm{PtP})$ = 222, $^2J(\mathrm{PP})$ = 27, $^3J(\mathrm{PP})$ = 170, $\mathrm{P^b}$], and 25.2 p.p.m. [t, 2 P, $^1J(\mathrm{PtP})$ = 2 992 Hz, $\mathrm{P^c}$].

$[\mathrm{Pt(SMe)_2(dppm)}]$ (**4a**).—To a solution of complex (**1**) (95 mg, 0.06 mmol) in toluene (10 $\mathrm{cm^3}$) under an atmosphere of nitrogen, MeSH(g) was added and the mixture was stirred for 1 h, during which time the solution changed from red to orange and then yellow. The volume of the solution was reduced and the yellow product was precipitated by addition of pentane (10 $\mathrm{cm^3}$) and recrystallized from $\mathrm{CH_2Cl_2}$–pentane. Yield 50 mg, 0.07 mmol, 60% (Found: C, 47.9; H, 4.8. Calc. for $\mathrm{C_{27}H_{28}P_2Pt_2S_2}$: C, 48.1; H, 4.2%). ^{1}H N.m.r. (in $\mathrm{CDCl_3}$): δ 2.1 (m, 6 H, MeS), 4.3 [t, 2 H, $^2J(\mathrm{PH})$ = 10, $^3J(\mathrm{PtH})$ = 44 Hz, $\mathrm{P_2CH_2}$], and 6.8—7.5 (m, 20 H, Ph).

$[\mathrm{Pt(SEt)_2(dppm)}]$ (**4b**) *and* $[\mathrm{Pt_2H(SEt)}(\mu\text{-dppm})_2]$ (**7**).—Ethanethiol (8 mg, 0.14 mmol) was added to a solution of complex (**1**) (106 mg, 0.07 mmol) in toluene (10 $\mathrm{cm^3}$) under an atmosphere of nitrogen. After 4 h the final mixture consisted of a precipitate and a supernatant. These were separated, washed with pentane (10 $\mathrm{cm^3}$), and dried *in vacuo* to yield complexes (**4b**) (40 mg, 0.06 mmol; 43%) and (**7**), which contained *ca.* 10% (**4b**) and could not be isolated in analytically pure form. Complex (**4b**) (Found: C, 50.2; H, 5.0. Calc. for $\mathrm{C_{29}H_{32}P_2PtS_2}$: C, 49.7; H, 4.6%): ^{1}H n.m.r. (in $\mathrm{CDCl_3}$), δ 1.11 [t, 6 H, $^3J(\mathrm{HH})$ = 8, $\mathrm{SCH_2}\mathit{C}\mathrm{H_3}$], 2.68 [q, 4 H, $^3J(\mathrm{PtH})$ = 20, $\mathrm{S}\mathit{C}\mathrm{H_2CH_3}$], 4.3 [t, 2 H, $^2J(\mathrm{PH})$ = 10, $^4J(\mathrm{PtH})$ = 44 Hz, $\mathrm{P_2CH_2}$], and 6.8—7.4 (m, 20 H, Ph). Complex (**7**); ^{1}H n.m.r. (in $\mathrm{CDCl_3}$), δ −10.74 [m, 1 H, $^1J(\mathrm{PtH})$ = 1 152, $^2J(\mathrm{PtH})$ = 630, PtH], 0.86 [t, 3 H, $^3J(\mathrm{HH})$ = 8, $\mathrm{SCH_2}\mathit{C}\mathrm{H_3}$], 2.64 [q, 2 H, $^3J(\mathrm{PtH})$ = 20 Hz, $\mathrm{SC}\mathit{H}_2\mathrm{CH_3}$], 3.7 (m, 4 H, $\mathrm{P_2CH_2}$), and 6.8—7.3 (m, 40 H, Ph).

Complexes (**4c**) and (**4d**) were prepared similarly.

$[\mathrm{Pt(SCH_2CH_2S)(dppm)}]$ (**5**).—To a solution of complex (**1**) (142 mg, 0.09 mmol) in toluene (10 $\mathrm{cm^3}$) under nitrogen was added $\mathrm{HSCH_2CH_2SH}$ (8 mg, 0.09 mmol). After 4 h the product (**5**) was isolated by the same procedure as before. Yield 85 mg, 0.13 mmol, 70% (Found: C, 48.6; H, 4.3. Calc. for $\mathrm{C_{27}H_{26}P_2PtS_2}$: C, 48.3; H, 3.9%). ^{1}H N.m.r. (in $\mathrm{CDCl_3}$): δ 2.26 (m, 4 H, $\mathrm{SCH_2CH_2S}$), 4.6 [t, 2 H, $^2J(\mathrm{PH})$ = 10, $^3J(\mathrm{PtH})$ = 44 Hz, $\mathrm{P_2CH_2}$], and 6.9—7.3 (m, 20 H, Ph).

$[\mathrm{Pt(SCH_2Ph)_2(dppm)}]$ (**4g**) *and* $[\mathrm{Pt_2}(\mu\text{-S})(\mathrm{SCH_2Ph})_2(\mu\text{-dppm})_2]$ (**8**).—To a solution of complex (**1**) (147 mg, 0.09 mmol) in toluene (10 $\mathrm{cm^3}$) under nitrogen was added $\mathrm{PhCH_2SH}$ (23 mg, 0.18 mmol) and the solution was stirred for 4 h. The final mixture consisted of a yellow precipitate and a supernatant. These fractions were separated and the products were isolated, complex (**4g**) (44 mg, 0.05 mmol, 30%), and (**8**) (55 mg, 0.04 mmol, 44%). ^{1}H N.m.r. (in $\mathrm{CDCl_3}$): δ 2.4 [m, 4 H, $^3J(\mathrm{PtH})$ = 24, $\mathrm{SCH_2Ph}$], 2.98 [m, 2 H, $^2J(\mathrm{PH})$ = 10, $^3J(\mathrm{PtH})$ = 60 Hz, $\mathrm{P_2CH_2}$], 5.11 (m, 2 H, $\mathrm{P_2CH_2}$), and 6.7—7.9 (m, 50 H, Ph).

$[\mathrm{Pt(SPh)_2(dppm)}]$ (**4e**) *and* $[\mathrm{Pt_2(SPh)_2}(\mu\text{-dppm})_2]$ (**6a**).—To a solution of complex (**1**) (171 mg, 0.11 mmol) in toluene (10 $\mathrm{cm^3}$) was added PhSH (24 mg, 0.22 mmol) and the mixture was stirred for 4 h to yield a precipitate and a supernatant. These fractions were separated and the products were washed with pentane (15 $\mathrm{cm^3}$) and dried *in vacuo*. Complex (**4e**): yield 52 mg, 0.06 mmol, 29% (Found: C, 56.3; H, 4.4. Calc. for $\mathrm{C_{37}H_{32}P_2PtS_2}$: C, 55.7; H, 4.0%). Complex (**6a**): yield 85 mg, 0.06 mmol, 54% (Found: C, 52.9; H, 4.2. Calc. for $\mathrm{C_{62}H_{54}P_4Pt_2S_2}$: C, 54.1; H, 3.9%). ^{1}H N.m.r. (in $\mathrm{CDCl_3}$): δ 4.7 [qnt of qnt, 4 H, $^2J(\mathrm{PH})$ = 4, $^3J(\mathrm{PtH})$ = 55 Hz, $\mathrm{P_2CH_2}$] and 6.7—7.9 (m, 50 H, Ph).

$[\mathrm{Pt(SC_6H_4Me\text{-}4)_2(dppm)}]$ (**4f**) *and* $[\mathrm{Pt_2(SC_6H_4Me\text{-}4)_2}(\mu\text{-dppm})_2]$ (**6b**).—These complexes were prepared as described above: (**4f**), yield 20% (Found: C, 56.8; H, 5.1. Calc. for $\mathrm{C_{39}H_{36}P_2PtS_2}$: C, 56.7; H, 4.4%); (**6b**), yield 54% (Found: C, 55.9; H, 4.7. $\mathrm{C_{64}H_{58}P_2Pt_2S_2}$: C, 55.8; H, 4.3%). ^{1}H N.m.r. (in $\mathrm{CDCl_3}$): δ 2.3 (m, 6 H, Me), 4.8 [qnt of qnt, 4 H, $^2J(\mathrm{PH})$ = 4, $^3J(\mathrm{PtH})$ = 55 Hz, $\mathrm{P_2CH_2}$], and 6.7—7.9 (m, 48 H, Ph, $\mathrm{C_6H_4}$).

X-Ray Structure Analysis of $[\mathrm{Pt_2}(\mu\text{-S})(\mathrm{SCH_2Ph})_2(\mu\text{-dppm})_2]$ (**8**).—Orange, needle-like crystals were grown from an acetone–diethyl ether mixture.

Crystal data. $\mathrm{C_{64}H_{58}P_4Pt_2S_3}$, M = 1 437.4, monoclinic, space group $C2/c$, a = 11.744(1), b = 18.531(2), c = 26.841(3) Å, β = 98.021(8)°, U = 5 784(1) Å^3, Z = 4, D_c = 1.651 g $\mathrm{cm^{-3}}$, $F(000)$ = 2 824, μ(Mo-K_α) = 51.34 $\mathrm{cm^{-1}}$, 24 °C.

Measurements. A crystal of approximate dimensions 0.16 × 0.16 × 0.20 mm was mounted on an Enraf-Nonius CAD4

Table 4. Fractional atomic co-ordinates (with standard deviations in parentheses) for $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-dppm})_2]$ (**8**)

Atom	X/a	Y/b	X/c
Pt	−0.027 59(3)	0.270 69(2)	−0.193 89(1)
P(1)	0.155 00(18)	0.237 71(16)	−0.161 79(8)
P(2)	−0.210 82(18)	0.289 99(14)	−0.233 24(9)
S(1)	0.0000	0.177 2(2)	−0.2500
S(2)	−0.060 6(2)	0.359 3(2)	−0.134 9(1)
C(1)	0.253 9(7)	0.234 9(7)	−0.210 3(3)
C(2)	−0.051(2)	0.308(1)	−0.076(1)
C(A1)	0.160 3(9)	0.145 0(5)	−0.136 5(6)
C(A2)	0.252 9(6)	0.099 4(5)	−0.137 5(4)
C(A3)	0.250 4(9)	0.030 6(6)	−0.118 1(6)
C(A4)	0.155 3(8)	0.007 3(5)	−0.097 6(5)
C(A5)	0.062 7(7)	0.052 9(5)	−0.096 7(4)
C(A6)	0.065 2(10)	0.121 7(7)	−0.116 1(7)
C(B1)	0.234 5(13)	0.292 4(7)	−0.110 7(2)
C(B2)	0.293 0(10)	0.263 7(4)	−0.067 1(4)
C(B3)	0.353 8(6)	0.308 4(6)	−0.031 8(4)
C(B4)	0.356 1(11)	0.381 8(6)	−0.040 1(2)
C(B5)	0.297 5(8)	0.410 5(4)	−0.083 7(4)
C(B6)	0.236 7(8)	0.365 9(7)	−0.119 1(4)
C(C1)	−0.319 7(7)	0.263 9(3)	−0.193 7(3)
C(C2)	−0.364 8(9)	0.314 2(4)	−0.163 9(4)
C(C3)	−0.433 8(11)	0.292 1(4)	−0.129 2(4)
C(C4)	−0.457 8(6)	0.219 7(3)	−0.124 2(3)
C(C5)	−0.412 7(10)	0.169 5(4)	−0.154 0(4)
C(C6)	−0.343 7(12)	0.191 6(4)	−0.188 7(5)
C(D1)	−0.249 9(8)	0.381 2(5)	−0.253 1(6)
C(D2)	−0.361 3(9)	0.397 2(5)	−0.273 8(3)
C(D3)	−0.390 2(6)	0.466 8(7)	−0.288 9(5)
C(D4)	−0.307 8(7)	0.520 4(5)	−0.283 2(5)
C(D5)	−0.196 4(8)	0.504 4(6)	−0.262 5(3)
C(D6)	−0.167 5(6)	0.434 8(8)	−0.247 5(6)
C(E1)	−0.085(4)	0.347(1)	−0.036(1)
C(E2)	−0.011(2)	0.393(2)	−0.007(1)
C(E3)	−0.048(3)	0.431(2)	0.032(1)
C(E4)	−0.159(4)	0.423(1)	0.042(1)
C(E5)	−0.234(2)	0.377(2)	0.013(1)
C(E6)	−0.196(4)	0.339(2)	−0.026(1)

diffractometer and exposed to graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å).

The unit-cell dimensions were determined by a least-squares treatment of 25 reflections with $12 \leqslant \theta(\text{Mo-}K_\alpha) \leqslant 16°$. An investigation of the diffraction pattern established $2/m$ Laue symmetry. The observed systematic absences were compatible with the space groups Cc and $C2/c$, but the latter was confirmed by the successful structure analysis.

Intensities of 4 387 reflections with $2 \leqslant \theta(\text{Mo-}K_\alpha) \leqslant 22°$ were measured by continuous θ—2θ scans of 0.72° in θ. Scan speeds were adjusted to give $\sigma(I)/I \leqslant 0.03$, subject to a time limit of 180 s. Two strong reflections, remeasured ever 2 h, revealed no systematic variation of intensity during the experiment. Intensities of all reflections were corrected for background, Lorentz, polarization, and absorption effects. The absorption factors (0.89—1.23) were calculated by an empirical method.[29] Intensities of 3 546 reflections related by symmetry were averaged to yield 1 692 independent structure amplitudes and gave R(internal) of 0.045 before, and 0.032 after, absorption correction. Only 2 456 unique reflections, for which $I \geqslant 3\sigma(I)$, were used in the structure analysis.

Structure solution and refinement. The positions of the platinum atoms were obtained from a Patterson function and those of phosphorus, sulphur, and carbon atoms from Fourier difference syntheses. Only platinum, phosphorus, sulphur, and CH_2-carbon atoms were allowed anisotropic displacement parameters. Many hydrogen atoms were found in a low-angle difference map. All hydrogens were included in the structural model in calculated positions and constrained to C–H 1.0 Å and $U(H) = 1.2\ U_{iso}(C)$, where for CH_2-carbon atoms $U_{iso}(C) = \frac{1}{3}(U_{11} + U_{22} + U_{33})$. The CH_2 hydrogens were allowed to ride on the carbon atoms to which they are bonded, and the phenyl rings were treated as rigid bodies of D_{6h} symmetry (C–C 1.38 Å).

The structure was refined by full-matrix least squares, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^{-2}(|F_o|)]\exp(15\sin^2\theta/\lambda^2)$. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref. 30. The refinement of 120 parameters converged at $R = 0.036$ and $R' = 0.039$, with a maximum parameter shift/error ratio of 0.04. In the final difference electron-density map the function values ranged from −0.6 to 1.1 e Å^{-3}, the highest peaks lying close to the phenyl rings of idealized geometry. The final atomic co-ordinates are shown in Table 4.

All calculations were performed on a GOULD SEL 32/27 computer, using the GX program package.[31]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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