Dipalladium and Diplatinum Bis(μ-alkanethiolato) Complexes with a Planar M_2S_2 Ring†

Mercè Capdevila,[a] William Clegg,*[,b] Pilar González-Duarte,*[,a] Bridget Harris,[b] Ignasi Mira,[a] Joan Sola[a] and Ian C. Taylor[b]

[a] *Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain*

[b] *Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, UK*

Mononuclear complexes of formula $[M(SR)_2(dppe)]$ (M = Pd **1** or Pt **2**; R = C_5H_9NMe, dppe = $Ph_2PCH_2CH_2PPh_2$) are formed in reactions of $[MCl_2(dppe)]$ with the sodium salt of 4-mercapto-1-methylpiperidine NaSR in acetonitrile–methanol solution. Subsequent reaction of **1** with $[PdCl_2(dppe)]$ and of **2** with $[PtCl_2(dppe)]$ in acetonitrile solution produces the bridged dinuclear cationic complexes $[M_2(\mu\text{-}SR)_2(dppe)_2]^{2+}$, which are obtained as crystalline salts with tetraphenylborate anions (M = Pd **3** or Pt **4**). An apparently mixed PtPd product **5** is formed in an analogous reaction from **1** and $[PtCl_2(dppe)]$ or from **2** and $[PdCl_2(dppe)]$. The structures of complexes **1**–**5** have been determined crystallographically. Complexes **1** and **2** are isostructural, with a slightly distorted square-planar *cis*-MP_2S_2 co-ordination geometry. The isostructural complexes **3**–**5** also show square-planar co-ordination; the two aminothiolate ligands act as bridges between the metal atoms, giving a precisely planar central M_2S_2 ring. In all five structures the MP_2C_2 chelate rings have a twist conformation. The nitrogen atoms of the aminothiolates are not co-ordinated to the metal atoms. Infrared and ^1H, ^{31}P and ^{195}Pt NMR spectra are presented and discussed. The combined evidence suggests that **5** is essentially a simple solid-solution mixture of pure complexes **3** and **4** in variable proportions, with at most a minor component of a genuinely heterobimetallic complex.

Structural characterization of metal thiolate complexes has been most successful for species of intermediate nuclearity, for which a substantial body of information has been obtained.[1] The investigation of low and very high nuclearity (polymeric) complexes is more difficult because of the high solubility of the former and the well known insolubility of the latter in common solvents. Different approaches are necessary in these cases. Thus, for example, aliphatic mercaptoamines, which can behave as simple thiols with a solubilizing amine group, facilitate solution equilibria studies[2] and the structural characterization of high-nuclearity complexes;[3] they have, however, not yet given mononuclear species, even from a reaction mixture with a very high ligand:metal ratio. The use of additional chelating ligands has enabled us to characterize crystallographically the following dinuclear complexes, in which mercaptoamines act as bridging monodentate thiolate ligands: $[\{M(\mu\text{-}SR)(dppe)\}_2]^{2+}$ [M = Ni, Pd or Pt; R = $(CH_2)_3NMe_2$; dppe = $Ph_2PCH_2CH_2PPh_2$][4] and $[\{Pt(\mu\text{-}SR)(en)\}_2]^{n+}$ [en = ethane-1,2-diamine, R = $(CH_2)_3NMe_2$ or C_5H_9NMe, $n = 2$; R = C_5H_9NHMe, $n = 4$].[5] However, attempts to obtain single crystals of mononuclear mixed-ligand complexes were unsuccessful.

We now report the synthesis and crystal structures of the mononuclear complexes $[M(SC_5H_9NMe)_2(dppe)]$ (M = Pd **1** or Pt **2**) and dinuclear $[M_2(\mu\text{-}SC_5H_9NMe)_2(dppe)_2]^{2+}$ species (M = Pd **3** or Pt **4**). The reaction of **1** with $[PtCl_2(dppe)]$ or of **2** with $[PdCl_2(dppe)]$ has afforded apparently a series of compounds of formula $[Pd_xPt_{2-x}(\mu\text{-}SC_5H_9NMe)_2(dppe)_2]^{2+}$ **5**, the values of x being determined by the solubility of pure **3** and **4** and the concentration of the reactants. Single-crystal diffraction studies together with analytical and $^{31}P\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ NMR data indicate that **5** is always essentially a mixture of **3** and **4**.

Experimental

Synthesis.—General remarks. 4-Mercapto-1-methylpiperidine was synthesised according to a known procedure[6] and purified by vacuum distillation until its purity, checked by iodometric determination of the SH group, was >99%. The corresponding sodium salt was obtained by treatment with NaOMe in methanol.[4] Metal complexes of formula $[MCl_2(dppe)]$ were prepared according to published methods for M = Pd[7] or Pt.[8] Conventionally dried and degassed solvents were used, and standard Schlenk techniques were employed in the following syntheses.

Microanalyses were performed with a Carlo-Erba NA-1500 analyser. Palladium and platinum in complex **5** were analysed by means of an inductively coupled plasma spectrometer, Thermo Jarrell Ash 61E, working at 324.27 and 299.80 nm for Pd and Pt respectively. Samples were dissolved as tetraphenylborate salts in dimethyl sulfoxide. Standard solutions in the same solvent were prepared from **3** and **4**. Infrared spectra in the range 4000–400 cm^{-1} were recorded from KBr discs on a Perkin Elmer 1710 spectrophotometer, proton, $^{31}P\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ NMR spectra on a Bruker AM-400 from samples in $(CD_3)_2SO$ solution with $SiMe_4$, H_3PO_4 or H_2PtCl_6 as reference. In those cases where the tetraphenylborate salt was not sufficiently soluble to obtain the NMR spectra, the hexafluorophosphate salt was used instead.

$[Pd(SC_5H_9NMe)_2(dppe)]$ **1**. A solution of the sodium salt of 4-mercapto-1-methylpiperidine (1.5 mmol) in methanol (6 cm^3) was slowly added with stirring to a suspension of $[PdCl_2(dppe)]$ (0.44 g, 0.76 mmol) in acetonitrile (20 cm^3). Stirring was continued for 24 h. The reaction mixture was then evaporated to dryness and kept under a nitrogen atmosphere for 1 d. Subsequent treatment of the solid residue with acetonitrile allowed us to separate the NaCl formed in the reaction and to obtain 0.52 g (90%) of orange crystals from the filtered and concentrated acetonitrile solution. The quality of these crystals was suitable for X-ray diffraction (Found: C, 59.85; H, 6.25; N,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

3.50; S, 8.45. Calc. for $C_{38}H_{48}N_2P_2PdS_2$: C, 59.60; H, 6.25; N, 3.65; S, 8.35%).

$[Pt(SC_5H_9NMe)_2(dppe)]$ **2**. Analogously, a methanolic solution (10 cm^3) of the sodium salt of 4-mercapto-1-methylpiperidine (7.7 mmol) and a suspension of $[PtCl_2(dppe)]$ (2.53 g, 3.8 mmol) in acetonitrile (60 cm^3) were mixed and stirred for 48 h. The solvent was removed *in vacuo* and the residue was kept under nitrogen for 24 h. Several extractions with acetonitrile yielded after concentration 2.83 g (87%) of yellow crystals suitable for X-ray diffraction (Found: C, 52.70; H, 5.65; N, 3.10; S, 7.80. Calc. for $C_{38}H_{48}N_2P_2PtS_2$: C, 53.40; H, 5.60; N, 3.30; S, 7.50%).

$[\{Pd(SC_5H_9NMe)(dppe)\}_2][BPh_4]_2$ **3**. A solution of complex **1** (0.35 g, 0.46 mmol) in acetonitrile (35 cm^3) was added with stirring to a suspension of $[PdCl_2(dppe)]$ (0.263 g, 0.46 mmol) in acetonitrile (10 cm^3). After some minutes of vigorous stirring the reaction mixture became a clear solution. Sodium tetraphenylborate (0.313 g, 0.91 mmol) in acetonitrile (4 cm^3) was then added. Stirring was continued for 10 min and a yellow solid mixed with sodium chloride separated. The solid mixture was filtered off, washed with water until no chloride ion could be detected and then dried with acetone. It was then recrystallized from acetonitrile solution containing a few drops of dimethylformamide, to give crystals suitable for X-ray diffraction (yield 0.65 g, 75%) (Found: C, 70.30; H, 6.00; N, 1.50; S, 3.20. Calc. for $C_{112}H_{112}B_2N_2P_4Pd_2S_2$: C, 70.40; H, 5.75; N, 1.45; S, 3.35%).

$[\{Pt(SC_5H_9NMe)(dppe)\}_2][BPh_4]_2$ **4**. A solution of complex **2** (1.0 g, 1.17 mmol) in acetonitrile (100 cm^3) was added with stirring to a suspension of $[PtCl_2(dppe)]$ (0.78 g, 1.17 mmol) in dichloromethane (15 cm^3). Once the reaction mixture became a clear solution potassium hexafluorophosphate (0.43 g, 2.33 mmol) in acetonitrile (10 cm^3) was added. Potassium chloride separated immediately. After some minutes of stirring the solvent was removed *in vacuo* and then acetonitrile (20 cm^3) was added to the solid residue. To the filtered solution sodium tetraphenylborate (0.80 g, 2.33 mmol) in acetonitrile (14 cm^3) was added. After some minutes of stirring a significant amount of a yellow solid separated. It was filtered off and washed with methanol. At this point 1.43 g of solid were collected. Also, several crops of crystals suitable for X-ray diffraction were obtained by slow evaporation of the mother-liquor under a very slow stream of nitrogen. Total yield 1.94 g, 79.5% (Found: C, 64.50; N, 1.25; S, 2.95. Calc. for $C_{112}H_{112}B_2N_2P_4Pt_2S_2$: C, 64.40; N, 1.35; S, 3.05%).

$[Pd_xPt_{2-x}(SC_5H_9NMe)_2(dppe)_2][BPh_4]_2$ **5**. A solution of complex **1** (0.35 g, 0.46 mmol) in acetonitrile (35 cm^3) was added with stirring to a suspension of $[PtCl_2(dppe)]$ (0.304 g, 0.46 mmol) in the same solvent (10 cm^3). Alternatively, a solution of complex **2** (0.15 g, 0.17 mmol) in acetonitrile (10 cm^3) was added with stirring to a suspension of $[PdCl_2(dppe)]$ (0.10 g, 0.17 mmol) in the same solvent (2 cm^3). In each case, after some minutes of stirring the reaction mixture became an almost clear solution, orange in the first case and yellow in the second. The stoichiometrically required amount of sodium tetraphenylborate in acetonitrile (2–4 cm^3) was then added. At this stage both solutions became bright yellow. Stirring was continued for 2 h. The yellow solids formed were filtered off, washed with water to remove sodium chloride, and dried with acetone. By slow evaporation of the mother solution several crops of crystals were obtained. Analytical data for all the solid product crops from several experiments showed that the value of x in the formula of this material was variable, the same pattern of variation being observed in both synthetic procedures. Representative analytical data are given in Table 1. A single crystal from a late crop resulting from the reaction of **1** with $[PtCl_2(dppe)]$ was chosen for X-ray diffraction.

X-Ray Crystallography.— Crystals of complexes **1**–**5**, mounted on glass fibres, were examined on a Stoe-Siemens diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å), at a temperature of 240 K.[9] Crystal data are listed in Table 2, together with other information on the structure determinations. Cell parameters were refined from 2θ values (15–25°) of 32 reflections measured at $\pm\omega$ in each case. Intensities were measured with ω–θ scans and on-line profile fitting.[10] Semiempirical absorption corrections were applied,[11] but no corrections were necessary for crystal decay, because three periodically monitored standard reflections maintained essentially constant intensities for each crystal. Each data set consisted of a complete unique set of reflections, together with part or all of a symmetry-equivalent set.

Atoms were located from Patterson and difference syntheses and refined[11] with anisotropic thermal parameters by blocked-cascade methods to minimize $\Sigma w\Delta^2$, with $\Delta = |F_o| - |F_c|$ and $w^{-1} = \sigma^2(F)$; $\sigma^2(F)$ included contributions from the counting statistics and from an empirical analysis of the variance of observed and calculated data.[12] Isotropic H atoms were constrained to give C–H 0.96 Å, H–C–H 109.5°, aromatic H on ring angle external bisectors, $U(H) = 1.2U_{eq}(C)$. An anisotropic extinction parameter x was refined where necessary, such that $F'_c = F_c/(1 + xF_c^2/\sin 2\theta)^{\frac{1}{4}}$. Atomic scattering factors were taken from ref. 13.

In the refinement of complex **5** each metal atom site was considered to be occupied by a disordered mixture of Pd and Pt, the ratio of the two scattering factors being refined independently for the two sites. Otherwise the treatment was exactly the same as for **3** and **4**.

The principal features in final difference syntheses for complexes **1** and **2** lay close to the metal atoms; for **3**–**5**, two large peaks were found, which corresponded to an image of the two metal atoms shifted along the crystallographic two-fold rotation axis, but other features were insignificant.

Refined coordinates are given in Tables 3 and 4, selected bond lengths and angles in Tables 5 and 6.

Additional material available from the Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis of the Complexes.—The synthetic route followed to obtain complexes **1** and **2** is straightforward and requires no special comment. However, it is the first time that it has been possible to obtain single crystals of mononuclear complexes of formula $[M(SR)_2(dppe)]$ (M = Pd or Pt, SR = a γ-mercaptoamine ligand). In complexes **1** and **2** SR is a cyclic γ-mercaptoamine ligand; for an acyclic ligand, the extreme solubility of the complexes makes structure determination practically impossible. Also in this work a direct route has yielded the dinuclear complexes **3** and **4**. Analogous complexes with acyclic ligands had previously been obtained by a different procedure.[4]

It was expected that the reaction of complex **1** with $[PtCl_2(dppe)]$ and of **2** with $[PdCl_2(dppe)]$ would produce a heteronuclear PdPt complex analogous to the homonuclear Pd_2 (**3**) or Pt_2 (**4**) complexes. However, both reactions afforded apparently a range of products of formula $[Pd_xPt_{2-x}(SC_5H_9NMe)_2(dppe)_2][BPh_4]_2$ **5**, x being in no case equal to 1. The analytical data (Table 1) can be explained on the assumption that **5** is largely a mixture of **3** and **4**, which agrees with the fact that both of these pure homonuclear complexes are slightly soluble in common organic solvents but **3** is considerably less soluble than **4**. Accordingly, the value of x in the initial solid product indicates that it is richer in the less-soluble palladium dimer than in the platinum one, while subsequent crops of crystals obtained from the remaining solution become progressively richer in the more-soluble platinum dimer. Single-crystal X-ray analysis of a late crop of crystals of **5** gives x = 0.15 as one of the refinement results. Moreover, $^{31}P-\{^1H\}$ and $^{195}Pt-\{^1H\}$ NMR data, discussed later, indicate that different solutions of **5** contain essentially **3** and **4**.

The same reactions as those just mentioned were also carried

Table 1 Analytical data for several solids of formula $[Pd_xPt_{2-x}(SC_5H_9NMe)_2(dppe)_2][BPh_4]_2$ **5** obtained from the reaction of $[Pd(SC_5H_9NMe)_2(dppe)]$ **1** with $[PtCl_2(dppe)]$. Calculated values for each value of *x* are given in parentheses

	Analysis (%)					
	C	N	S	Pd	Pt	Pd_xPt_{2-x}
Calc. for $x = 1$	67.30	1.40	3.20	5.35	9.75	PdPt
Found for initial	68.65	1.80	3.20	6.65	8.20	$Pd_{1.20}Pt_{0.80}$
precipitate	(67.95)	(1.40)	(3.25)	(6.40)	(7.90)	
Found for first	67.10	1.60	3.60	5.50	10.95	$Pd_{0.96}Pt_{1.04}$
crop of crystals	(67.15)	(1.40)	(3.20)	(5.10)	(10.15)	
Found for second	65.40	1.40	3.15	2.95	14.95	$Pd_{0.53}Pt_{1.47}$
crop of crystals	(65.90)	(1.35)	(3.15)	(2.75)	(14.05)	
Found for third	64.70	1.45	3.30	1.50	16.35	$Pd_{0.29}Pt_{1.71}$
crop of crystals	(65.10)	(1.35)	(3.10)	(1.60)	(16.60)	

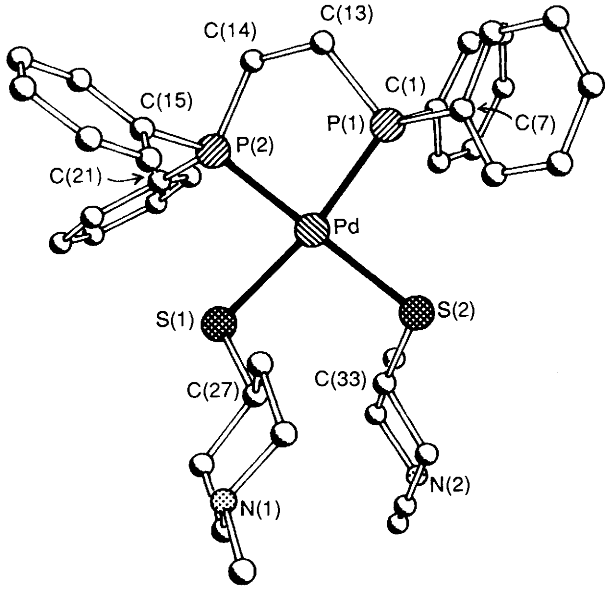

Fig. 1 The structure of complex **1**. Hydrogen atoms are omitted for clarity. The structure of **2** is almost identical

out with the same procedure as described for the synthesis of complex **4**, involving removal of the chloride ions with potassium hexafluorophosphate and subsequent precipitation of **5** with sodium tetraphenylborate rather than a single step of exchange of chloride by tetraphenylborate. When this procedure was followed all solid phases produced had approximately the same composition, with *x* in the range 0.90–1.06. This indicates that the solubilities of **3** and **4** are greater and more nearly equal if sodium hexafluorophosphate is present in the solution.

Structures of Complexes **1** *and* **2**.—The complexes are isostructural and thus can be described together. They consist of mononuclear neutral molecules (Fig. 1) with no significant intermolecular interactions. The metal atom, Pd or Pt, is co-ordinated to two S and two P in a slightly distorted square-planar geometry. Bond lengths involving Pd and Pt atoms (Table 5) are very similar as a consequence of the essential equality of the covalent radii of the two metals. Also, metal–sulfur and -phosphorus bond lengths compare well with the relatively few structural data already established for $[M(SR)_2L_2]$ and similar complexes of Pd and Pt with a phosphine ligand L. Thus, for Pt–$S_{terminal}$, values of 2.360(2) and 2.340(2) Å have been reported for *cis*-$[Pt(SH)_2(PPh_3)_2]$,[14] 2.317(5) and 2.342(5) Å for *cis*-$[\{Pt(SCH_2Ph)(\mu\text{-}SCH_2Ph)(PMePh_2)\}_2]$,[15] and 2.351(3) Å for $[Pt_2(\mu\text{-}S)(SCH_2Ph)_2(\mu\text{-}dppm)_2]$[16] (dppm = $Ph_2PCH_2PPh_2$). For Pd–P, values of 2.233(2) and 2.226(2) Å in $[PdCl_2(dppe)]$, 2.234(1) and 2.250(1) Å in $[PdCl_2(dppm)]$, and 2.244(1) and 2.249(2) Å in $[PdCl_2(dppp)]$ (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) have been given.[17] Also, for Pt–P, values of 2.208(6) Å in $[PtCl_2(dppe)]$,[18] 2.2325(8) and 2.2317(8) Å in $[PtCl_2(dppp)]$,[19] 2.262(3) and 2.265(3) Å in $[PtCl_2(Bu^t_2PCH_2CH_2PBu^t_2)]$,[20] 2.251(2) and 2.265(2) Å in *cis*-$[PtCl_2(PPh_3)_2]$,[21] 2.248(2) and 2.250(2) Å in *cis*-$[PtCl_2(PMePh_2)_2]$,[22] 2.286(2) and 2.279(2) Å in *cis*-$[Pt(SH)_2(PPh_3)_2]$,[14] and 2.250(4) and 2.245(4) Å in *cis*-$[\{Pt(SCH_2Ph)(\mu\text{-}SCH_2Ph)(PMePh_2)\}_2]$[15] have been reported.

Bond angles around the metal atoms in complexes **1** and **2** range between 85.7(1) and 94.7(1)°, the P–M–P angle being in each case about 10° smaller than the S–M–S angle. The former has practically the same value as that found in the corresponding complex $[MCl_2(dppe)]$ (M = Pd[17] or Pt[18]). The main distortion of the square-planar co-ordination is a slight twist of the MS_2 plane relative to the MP_2 plane, by 10.2° in **1** and 10.0° in **2**. As expected, the two carbon atoms of the aliphatic chain of dppe lie one on each side of the MP_2 plane. Thus, C(13) lies 0.354 (M = Pd) or 0.359 Å (M = Pt) to one side, while C(14) lies 0.403 (M = Pd) or 0.380 Å (M = Pt) to the other side of the plane, each MP_2C_2 chelate ring adopting a twist conformation.

The piperidine rings have a chair conformation with both the thiolate S atom and the methyl substituent placed equatorially. These rings avoid mutual steric hindrance by being disposed one on each side of the MS_2 plane. The S(1)–C(27) and S(2)–C(33) bonds subtend angles to the MS_2 mean plane of 45.1 and 40.3°, respectively, for M = Pd (**1**) and 44.7 and 40.2°, respectively, for M = Pt (**2**).

Structures of Complexes **3** *and* **4**.—The crystal structures of the isostructural complexes **3** and **4** consist of discrete dinuclear $[(dppe)M(\mu\text{-}SC_5H_9NMe)_2M(dppe)]^{2+}$ (M = Pd or Pt) cations (Fig. 2) and $[BPh_4]^-$ anions, the latter having an unexceptional structure. The cations and anions have only normal electrostatic interactions.

The cations $[\{M(\mu\text{-}SC_5H_9NMe)(dppe)\}_2]^{2+}$ contain three approximately coplanar rings. A crystallographic two-fold axis passes through both metal atoms and thus the central M_2S_2 ring is exactly planar. Two other non-planar five-membered chelate rings, MP_2C_2, are fused to this central one. The idealized symmetry of the $M_2S_2P_4$ core of the cation (omitting all C, N and H atoms) is D_{2h}. However, the M_2S_2 and MP_2 planes form a dihedral angle of 17.1° for Pd(1) and 12.5° for Pd(2) [17.5° for Pt(1) and 12.9° for Pt(2)], indicating a small twist distortion of the metal square-planar geometry. Also, the C(7) and C(20) atoms are not on the planes defined by MP_2 atoms but deviate from them, respectively, by 0.337 and 0.391 Å in **3**, 0.342 and 0.340 Å in **4**. Analogously, their symmetry-related atoms, C(7′) and C(20′), are also out of the MP_2 planes but in the opposite direction in each case. The non-planarity of the MP_2C_2 ring is a consequence of the tetrahedral geometry at the carbon and phosphorus atoms and of the square-planar co-ordination of the metal. Accordingly, both chelate MP_2C_2 rings in each

Table 2 Crystallographic data

Complex	**1**	**2**	**3**	**4**	**5**[a]
Formula	$C_{38}H_{48}N_2P_2PdS_2$	$C_{38}H_{48}N_2P_2PtS_2$	$C_{112}H_{112}B_2N_2P_4Pd_2S_2$	$C_{112}H_{112}B_2N_2P_4Pt_2S_2$	$C_{112}H_{112}B_2N_2P_4Pd_{0.154}Pt_{1.846}S_2$
M	765.3	854.0	1908.6	2085.9	2072.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$I2/a$[b]	$I2/a$[b]	$I2/a$[b]
a/Å	12.476(2)	12.506(2)	21.568(11)	21.617(6)	21.628(3)
b/Å	11.818(2)	11.928(2)	16.764(4)	16.774(4)	16.772(2)
c/Å	26.183(3)	26.117(5)	26.710(6)	26.725(6)	26.717(3)
β/°	102.82(1)	103.05(2)	100.93(4)	100.88(3)	100.93(1)
U/Å^3	3764.2	3763.2	9481.8	9516.4	9515.3
Z	4	4	4	4	4
D_c/g cm^{-3}	1.350	1.507	1.335	1.454	1.445
μ/mm^{-1}	0.70	3.99	0.53	3.12	2.92
F(000)	1592	1720	3968	4224	4204
Crystal size/mm	0.16 × 0.24 × 0.40	0.22 × 0.24 × 0.34	0.08 × 0.12 × 0.45	0.20 × 0.24 × 0.48	0.12 × 0.16 × 0.52
Transmission factors	0.75–0.78	0.24–0.34	0.84–0.99	0.72–0.90	0.85–0.98
$2\theta_{max}$/°	50	50	45	45	45
Reflections measured	10 279	8320	6647	6800	12 379
Unique reflections	6658	6645	6216	6197	6224
Observed reflections	5455	5447	3758	4561	4655
Observation criterion[c]	$F > 4\sigma_c(F)$	$F > 4\sigma_c(F)$	$F > 3\sigma_c(F)$	$F > 4\sigma_c(F)$	$F > 4\sigma_c(F)$
R_{int}	0.020	0.031	0.034	0.022	0.030
Extinction parameter x	$8(4) \times 10^{-5}$	$1.4(2) \times 10^{-7}$	0	0	0
No. of refined parameters	413	413	560	560	562
R	0.0258	0.0261	0.0754	0.0313	0.0446
$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.0274	0.0291	0.0573	0.0321	0.0387
Goodness of fit	1.07	1.04	1.11	1.08	1.19
Mean, maximum shift/e.s.d.	0.006, 0.031	0.007, 0.034	0.010, 0.045	0.004, 0.019	0.006, 0.021
Maximum, minimum electron density/e Å^{-3}	0.45, −0.31	0.91, −1.08	2.29, −1.06	1.35, −0.47	0.31, −0.96

[a] Crystal data are calculated for the composition indicated by the refinement of site occupancy factors for Pd and Pt. [b] Alternative setting of $C2/c$. [c] $\sigma_c(F)$ estimated from counting statistics only.

Table 3 Atomic coordinates for complexes **1** and **2**

	1			**2**		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
M	0.390 19(1)	0.852 09(1)	0.153 18(1)	0.390 60(1)	0.849 91(1)	0.153 92(1)
P(1)	0.320 44(5)	0.806 38(5)	0.224 12(2)	0.320 67(8)	0.805 63(9)	0.223 95(4)
P(2)	0.403 45(5)	0.664 06(5)	0.141 66(2)	0.404 42(8)	0.663 04(8)	0.142 48(4)
C(1)	0.171 8(2)	0.821 6(2)	0.216 6(1)	0.172 4(3)	0.821 0(3)	0.216 6(2)
C(2)	0.110 2(2)	0.878 5(2)	0.174 0(1)	0.110 7(4)	0.877 9(4)	0.173 7(2)
C(3)	−0.002 6(3)	0.890 0(3)	0.168 5(1)	−0.002 0(4)	0.890 1(5)	0.168 2(2)
C(4)	−0.053 1(2)	0.844 2(3)	0.205 5(1)	−0.052 3(4)	0.844 0(4)	0.205 4(2)
C(5)	0.007 5(2)	0.786 7(3)	0.247 6(1)	0.009 1(4)	0.787 2(4)	0.247 6(2)
C(6)	0.119 2(2)	0.775 1(2)	0.253 6(1)	0.119 7(3)	0.775 5(4)	0.253 2(2)
C(7)	0.380 7(2)	0.873 2(2)	0.286 7(1)	0.381 5(3)	0.873 3(3)	0.286 7(1)
C(8)	0.433 6(2)	0.977 1(2)	0.288 0(1)	0.434 8(3)	0.976 8(4)	0.288 4(2)
C(9)	0.476 4(2)	1.029 5(2)	0.335 7(1)	0.476 0(4)	1.029 3(4)	0.335 9(2)
C(10)	0.467 2(2)	0.978 5(2)	0.381 8(1)	0.466 5(3)	0.979 0(4)	0.382 3(2)
C(11)	0.415 9(2)	0.875 3(2)	0.381 3(1)	0.414 7(4)	0.875 7(4)	0.381 7(2)
C(12)	0.373 1(2)	0.822 1(2)	0.333 9(1)	0.373 2(3)	0.822 2(4)	0.333 9(2)
C(13)	0.344 8(2)	0.653 7(2)	0.236 3(1)	0.344 9(3)	0.653 9(3)	0.237 0(2)
C(14)	0.323 1(2)	0.592 7(2)	0.183 4(1)	0.325 3(3)	0.591 4(3)	0.184 6(2)
C(15)	0.536 0(2)	0.593 5(2)	0.157 8(1)	0.536 7(3)	0.592 7(3)	0.158 6(2)
C(16)	0.542 2(2)	0.477 2(2)	0.149 7(1)	0.544 7(4)	0.477 1(4)	0.150 7(2)
C(17)	0.642 8(3)	0.422 8(3)	0.162 7(1)	0.644 4(5)	0.422 9(4)	0.163 6(2)
C(18)	0.736 7(3)	0.482 7(3)	0.183 9(2)	0.737 2(5)	0.482 6(5)	0.184 5(2)
C(19)	0.730 5(3)	0.595 4(4)	0.192 2(2)	0.731 6(5)	0.596 1(6)	0.192 9(3)
C(20)	0.630 6(2)	0.651 9(3)	0.179 1(1)	0.631 6(4)	0.651 3(4)	0.180 0(2)
C(21)	0.341 1(2)	0.625 4(2)	0.074 5(1)	0.342 1(4)	0.625 1(3)	0.075 1(2)
C(22)	0.405 1(3)	0.602 9(2)	0.038 3(1)	0.406 6(4)	0.600 9(4)	0.039 2(2)
C(23)	0.354 6(3)	0.585 1(3)	−0.014 1(1)	0.354 6(5)	0.584 1(4)	−0.013 7(2)
C(24)	0.242 6(3)	0.590 0(3)	−0.030 7(1)	0.244 2(5)	0.588 6(5)	−0.030 2(2)
C(25)	0.179 2(3)	0.614 4(4)	0.004 4(1)	0.180 2(5)	0.614 0(6)	0.004 6(2)
C(26)	0.228 2(2)	0.632 4(3)	0.056 9(1)	0.229 6(4)	0.632 2(5)	0.057 3(2)
S(1)	0.480 24(5)	0.870 42(5)	0.083 81(2)	0.481 06(8)	0.871 38(8)	0.084 48(4)
C(27)	0.572 1(2)	0.991 4(2)	0.102 4(1)	0.572 8(3)	0.993 0(3)	0.103 3(2)
C(28)	0.660 0(3)	0.970 7(3)	0.151 6(1)	0.663 0(4)	0.970 5(4)	0.151 6(2)
C(29)	0.742 2(3)	1.069 0(3)	0.161 4(1)	0.744 9(4)	1.068 4(4)	0.161 4(2)
N(1)	0.792 7(2)	1.086 0(2)	0.117 6(1)	0.792 7(3)	1.087 4(4)	0.117 0(2)
C(30)	0.710 0(3)	1.113 7(3)	0.071 3(1)	0.708 3(4)	1.115 9(5)	0.071 6(2)
C(31)	0.625 7(3)	1.019 2(3)	0.057 4(1)	0.623 6(4)	1.021 6(5)	0.057 4(2)
C(32)	0.877 0(3)	1.174 2(3)	0.129 1(2)	0.878 0(5)	1.173 9(5)	0.127 9(3)
S(2)	0.348 37(6)	1.046 98(5)	0.156 18(2)	0.349 38(9)	1.045 15(9)	0.156 74(4)
C(33)	0.303 1(2)	1.093 0(2)	0.087 7(1)	0.304 9(3)	1.091 6(3)	0.088 2(2)
C(34)	0.329 6(2)	1.218 8(2)	0.083 1(1)	0.328 5(4)	1.217 4(4)	0.083 7(2)
C(35)	0.282 7(3)	1.260 8(2)	0.027 7(1)	0.283 8(5)	1.259 9(4)	0.027 7(2)
N(2)	0.165 3(2)	1.238 5(2)	0.010 1(1)	0.166 7(4)	1.237 4(3)	0.010 5(2)
C(36)	0.143 2(2)	1.117 4(3)	0.011 4(1)	0.144 5(4)	1.116 6(4)	0.011 2(2)
C(37)	0.181 6(2)	1.069 7(2)	0.066 0(1)	0.183 0(4)	1.068 4(4)	0.066 0(2)
C(38)	0.125 3(5)	1.281 3(4)	−0.043 0(2)	0.127 6(7)	1.280 5(6)	−0.043 5(3)

structure, as well as those found in complexes **1** and **2**, have a twist conformation.

The co-ordination around M(1) and M(2) is essentially square planar, the *cis* bond angles at M ranging between 83.5(1) and 96.9(1)°. On comparison of the S–M–S and P–M–P bond angles around the metal atoms in complexes **1**–**4**, the main difference is that the former are about 10° smaller in the dinuclear species. This clearly reflects the different behaviour of the sulfur atom in these complexes, as it belongs to a terminal ligand in the mononuclear molecues **1** and **2**, and to a bridging ligand in the dinuclear cations **3** and **4**. The geometry around the bridging sulfur atom is pseudo-tetrahedral (pyramidal) as indicated by the angles at S in **3** and **4** [93.2(1)–106.0(2)°].

The piperidinic rings in complexes **3** and **4**, which have the same conformation and geometry features as those found in **1** and **2**, give rise to an *anti* conformation of the bridging M_2S_2 unit. Their disposition with respect to the $M_2S_2P_4$ central core, as well as those of the phenyl groups, can be expressed by the angle subtended by the S–C(1) bond, and those of P(1)–C(8), P(1)–C(14), P(2)–C(21) and P(2)–C(27), to the relevant M_2S_2 or MP_2 plane. These values are, respectively, 72.3, 37.4, 68.7, 38.5 and 69.4° for **3** and 70.5, 37.8, 68.8, 38.9 and 67.5° for **4**.

A comparison of the main geometric parameters in thiolate-bridged dinuclear palladium(II) or platinum(II) complexes with different terminal ligands containing phosphorus or nitrogen donor atoms is given in Table 7. The following features can be deduced from the values and references given there. (*a*) Complexes of formula [(L–L)M(μ-SR)$_2$M(L–L)], where L–L represents a chelating ligand which gives rise to a five-membered ring, show many structural similarities independently of the metal atom (M = Pd or Pt), the nature of the mercapto-amine [SR = SC_5H_9NHMe, SC_5H_9NMe or $S(CH_2)_3NMe_2$], or the nature of the chelating ligand (dppe or en) (complexes **I**–**IV** and **XIII**–**XV**). The similarity still holds if the nickel(II) complex $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$ is included.[4] (*b*) Complexes **I**–**XV** can be divided into two sets: one formed by **I**–**VII** and **XIII**–**XV**, where the M_2S_2 ring is perfectly planar, and the other formed by **VIII**–**XII**, where the dihedral angle along the S···S line varies from 121 to 141°. Factors determining which of the two distinct geometries, flat or hinged square planar, is adopted are not obvious, as has already been pointed out.[25,29] Recent attempts to find an explanation apply only to mono(μ-thiolato) complexes.[27] However, a non-planar M_2S_2 ring is the only geometry found among previously

Table 4 Atomic coordinates for complexes **3**–**5**

	3			**4**			**5**		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
M(1)	0.25	0.481 77(5)	0.5	0.25	0.481 17(2)	0.5	0.25	0.481 11(2)	0.5
M(2)	0.25	0.690 26(5)	0.5	0.25	0.692 78(2)	0.5	0.25	0.692 33(2)	0.5
S	0.327 97(8)	0.587 7(2)	0.515 30(7)	0.325 50(6)	0.587 7(1)	0.514 77(5)	0.326 04(7)	0.587 4(1)	0.514 64(6)
C(1)	0.349 4(4)	0.595 4(6)	0.585 8(3)	0.349 7(3)	0.596 5(5)	0.585 6(2)	0.349 0(3)	0.595 6(6)	0.585 0(3)
C(2)	0.417 8(4)	0.574 0(6)	0.605 8(3)	0.416 8(3)	0.573 0(4)	0.603 8(3)	0.416 4(4)	0.573 6(6)	0.603 9(3)
C(3)	0.433 7(4)	0.578 8(7)	0.662 7(3)	0.434 3(3)	0.576 9(5)	0.661 0(3)	0.434 2(4)	0.577 0(6)	0.661 2(3)
N	0.391 7(4)	0.533 3(6)	0.687 0(3)	0.392 4(3)	0.533 1(4)	0.686 4(3)	0.392 6(4)	0.532 6(5)	0.686 5(3)
C(4)	0.327 5(5)	0.560 1(6)	0.670 8(4)	0.328 9(4)	0.561 7(5)	0.671 8(3)	0.328 2(4)	0.560 7(6)	0.670 8(3)
C(5)	0.304 8(4)	0.550 8(6)	0.613 4(3)	0.305 1(3)	0.554 3(5)	0.614 2(3)	0.306 0(4)	0.553 2(6)	0.614 4(3)
C(6)	0.410 1(8)	0.537 6(10)	0.743 5(5)	0.413 1(5)	0.535 7(7)	0.742 1(3)	0.412 9(6)	0.535 7(9)	0.741 9(4)
P(1)	0.319 8(1)	0.381 3(1)	0.496 86(9)	0.319 67(6)	0.381 49(8)	0.496 46(6)	0.319 79(8)	0.381 3(1)	0.496 62(7)
C(7)	0.287 9(5)	0.287 3(5)	0.511 3(4)	0.284 9(3)	0.286 9(3)	0.511 4(3)	0.284 6(3)	0.286 3(4)	0.511 6(3)
C(8)	0.398 2(4)	0.381 2(5)	0.535 7(3)	0.398 1(3)	0.380 4(3)	0.535 5(2)	0.397 6(3)	0.381 0(4)	0.535 5(3)
C(9)	0.405 2(5)	0.361 3(6)	0.587 8(4)	0.405 3(3)	0.361 0(4)	0.587 0(3)	0.405 8(4)	0.361 1(5)	0.587 2(3)
C(10)	0.466 8(5)	0.357 8(7)	0.618 4(4)	0.465 0(4)	0.358 3(5)	0.617 2(3)	0.464 6(5)	0.358 3(6)	0.617 8(4)
C(11)	0.517 2(5)	0.376 7(7)	0.595 9(4)	0.516 3(3)	0.375 7(5)	0.596 4(4)	0.516 1(4)	0.376 1(6)	0.597 0(4)
C(12)	0.511 3(4)	0.397 8(6)	0.546 5(4)	0.510 0(3)	0.397 0(5)	0.546 4(3)	0.511 1(4)	0.399 4(7)	0.547 0(4)
C(13)	0.451 5(4)	0.400 3(5)	0.515 7(3)	0.450 9(2)	0.399 8(4)	0.515 5(3)	0.451 4(3)	0.400 5(5)	0.515 4(3)
C(14)	0.330 5(4)	0.379 1(5)	0.431 9(3)	0.329 7(2)	0.377 4(3)	0.430 4(2)	0.330 4(3)	0.377 6(4)	0.430 5(3)
C(15)	0.324 7(4)	0.307 8(6)	0.402 8(4)	0.325 3(3)	0.308 3(4)	0.402 0(3)	0.324 5(3)	0.307 3(5)	0.402 2(3)
C(16)	0.332 7(4)	0.309 3(6)	0.352 0(4)	0.333 7(3)	0.310 0(5)	0.352 4(3)	0.333 2(4)	0.311 0(6)	0.351 4(4)
C(17)	0.346 3(6)	0.381 0(7)	0.330 2(4)	0.346 0(4)	0.380 2(5)	0.330 0(3)	0.346 3(5)	0.379 7(7)	0.330 1(3)
C(18)	0.351 8(5)	0.449 5(7)	0.357 8(4)	0.352 0(4)	0.449 2(5)	0.357 3(3)	0.350 9(5)	0.448 7(6)	0.357 1(4)
C(19)	0.343 0(4)	0.450 0(6)	0.408 3(4)	0.343 4(3)	0.449 5(4)	0.407 5(3)	0.343 1(4)	0.448 4(5)	0.407 4(3)
P(2)	0.320 7(1)	0.791 6(1)	0.501 58(9)	0.320 60(7)	0.792 62(8)	0.501 07(6)	0.320 73(8)	0.792 8(1)	0.501 41(7)
C(20)	0.285 3(4)	0.887 2(5)	0.515 6(4)	0.284 0(3)	0.888 1(3)	0.513 4(3)	0.285 2(3)	0.886 8(4)	0.514 1(3)
C(21)	0.395 3(4)	0.787 1(5)	0.546 0(3)	0.394 7(3)	0.787 2(3)	0.545 2(2)	0.394 5(3)	0.787 0(4)	0.545 7(3)
C(22)	0.396 5(4)	0.802 1(5)	0.597 3(4)	0.395 2(3)	0.801 4(3)	0.596 1(3)	0.396 3(4)	0.801 4(5)	0.596 8(3)
C(23)	0.453 2(4)	0.797 6(6)	0.632 1(4)	0.452 0(3)	0.795 5(4)	0.631 8(3)	0.451 5(4)	0.796 0(5)	0.631 3(3)
C(24)	0.508 2(4)	0.777 7(6)	0.615 6(4)	0.506 6(3)	0.776 6(4)	0.615 2(3)	0.506 2(4)	0.776 4(5)	0.615 7(4)
C(25)	0.507 5(4)	0.762 3(7)	0.565 3(4)	0.505 4(3)	0.761 2(4)	0.565 4(3)	0.506 4(3)	0.762 6(5)	0.565 4(3)
C(26)	0.450 3(4)	0.768 5(6)	0.530 1(4)	0.450 2(2)	0.766 5(4)	0.529 8(3)	0.451 4(3)	0.766 6(4)	0.529 5(3)
C(27)	0.336 4(4)	0.801 0(5)	0.437 9(3)	0.338 7(3)	0.801 5(3)	0.437 7(2)	0.338 0(3)	0.801 2(4)	0.437 5(3)
C(28)	0.366 0(5)	0.866 9(6)	0.423 0(4)	0.370 0(4)	0.869 2(4)	0.424 8(3)	0.369 1(5)	0.869 3(5)	0.424 8(4)
C(29)	0.377 7(7)	0.873 2(8)	0.375 3(5)	0.383 8(6)	0.873 2(6)	0.376 2(4)	0.382 7(6)	0.873 3(7)	0.376 5(4)
C(30)	0.359 9(7)	0.810 6(7)	0.339 5(4)	0.364 1(6)	0.814 9(6)	0.341 1(4)	0.364 0(7)	0.813 2(7)	0.340 8(4)
C(31)	0.330 8(6)	0.746 2(8)	0.354 6(4)	0.333 8(5)	0.750 5(6)	0.354 3(3)	0.333 0(6)	0.748 9(7)	0.353 6(4)
C(32)	0.319 2(5)	0.741 9(7)	0.403 2(4)	0.320 4(4)	0.743 8(5)	0.401 9(3)	0.320 6(4)	0.743 3(6)	0.402 2(3)
B	0.342 2(4)	0.082 3(7)	0.658 5(3)	0.341 4(3)	0.082 5(5)	0.658 3(2)	0.340 8(3)	0.083 4(6)	0.658 5(3)
C(33)	0.352 0(5)	0.002 3(6)	0.693 3(4)	0.350 7(3)	0.002 1(4)	0.693 2(2)	0.351 0(4)	0.002 4(6)	0.692 7(3)
C(34)	0.404 0(5)	−0.010 3(7)	0.733 5(4)	0.402 2(4)	−0.010 6(5)	0.732 8(3)	0.402 2(5)	−0.011 2(6)	0.732 9(4)
C(35)	0.417 6(6)	−0.080 0(10)	0.758 1(4)	0.416 5(6)	−0.080 5(8)	0.757 9(4)	0.415 6(6)	−0.080 2(8)	0.758 4(4)
C(36)	0.379 5(6)	−0.145 3(8)	0.746 1(5)	0.379 9(6)	−0.142 8(9)	0.747 0(4)	0.378 9(6)	−0.144 6(8)	0.746 4(5)
C(37)	0.326 3(6)	−0.139 7(8)	0.710 4(5)	0.325 3(5)	−0.138 1(6)	0.709 1(5)	0.324 6(6)	−0.137 9(7)	0.708 4(6)
C(38)	0.312 6(5)	−0.067 2(6)	0.683 9(4)	0.312 7(4)	−0.065 1(4)	0.682 1(4)	0.313 1(5)	−0.065 6(6)	0.682 7(4)
C(39)	0.363 7(5)	0.164 5(6)	0.691 4(3)	0.364 1(3)	0.163 8(4)	0.691 8(2)	0.363 4(4)	0.164 7(5)	0.691 6(3)
C(40)	0.428 4(5)	0.179 0(7)	0.710 2(4)	0.428 2(3)	0.178 4(5)	0.710 0(3)	0.428 4(4)	0.179 3(6)	0.710 3(3)
C(41)	0.449 6(6)	0.246 1(8)	0.737 3(4)	0.450 6(4)	0.245 3(6)	0.736 7(3)	0.450 6(6)	0.246 0(7)	0.737 1(4)
C(42)	0.408 4(7)	0.303 5(8)	0.746 1(5)	0.409 0(6)	0.304 5(5)	0.745 2(4)	0.410 3(7)	0.303 8(7)	0.745 5(4)
C(43)	0.346 3(6)	0.293 0(7)	0.727 2(4)	0.347 5(5)	0.293 5(5)	0.728 4(4)	0.346 2(6)	0.294 7(6)	0.727 2(4)
C(44)	0.323 5(5)	0.222 7(6)	0.701 0(4)	0.324 1(4)	0.224 8(5)	0.701 3(3)	0.324 7(4)	0.225 3(6)	0.701 6(3)
C(45)	0.386 7(3)	0.076 7(6)	0.614 8(3)	0.386 6(2)	0.076 6(4)	0.615 4(2)	0.386 6(3)	0.077 3(5)	0.615 2(2)
C(46)	0.400 9(4)	0.144 1(6)	0.589 2(3)	0.400 1(3)	0.145 4(4)	0.588 9(2)	0.400 2(4)	0.145 3(5)	0.589 0(3)
C(47)	0.440 0(4)	0.142 4(6)	0.554 1(4)	0.438 6(3)	0.142 6(4)	0.553 2(3)	0.439 3(4)	0.143 8(6)	0.553 5(3)
C(48)	0.467 1(4)	0.070 7(5)	0.543 1(3)	0.465 4(3)	0.071 9(5)	0.542 5(3)	0.465 3(4)	0.073 1(6)	0.541 9(4)
C(49)	0.451 9(5)	0.005 7(6)	0.566 8(4)	0.452 5(3)	0.004 8(4)	0.566 5(3)	0.453 8(4)	0.005 0(6)	0.566 4(4)
C(50)	0.415 4(4)	0.007 9(6)	0.603 4(4)	0.414 3(3)	0.007 7(4)	0.602 4(3)	0.413 1(4)	0.008 6(5)	0.602 5(4)
C(51)	0.267 0(3)	0.087 3(6)	0.630 3(3)	0.267 0(3)	0.088 1(4)	0.630 2(2)	0.267 3(3)	0.088 1(5)	0.630 5(2)
C(52)	0.245 9(4)	0.087 6(6)	0.577 4(3)	0.245 7(2)	0.088 2(4)	0.577 9(2)	0.245 2(3)	0.089 4(5)	0.577 7(2)
C(53)	0.181 5(4)	0.085 4(7)	0.554 5(3)	0.182 0(3)	0.088 8(4)	0.555 4(2)	0.181 4(3)	0.088 0(5)	0.554 9(3)
C(54)	0.137 8(4)	0.087 3(7)	0.584 5(3)	0.136 9(3)	0.088 7(5)	0.585 3(3)	0.137 3(3)	0.087 7(5)	0.585 5(3)
C(55)	0.155 1(4)	0.087 2(7)	0.637 5(3)	0.156 1(3)	0.087 9(5)	0.637 6(3)	0.155 9(4)	0.087 4(6)	0.637 8(3)
C(56)	0.217 8(4)	0.087 2(7)	0.658 7(3)	0.218 4(3)	0.088 3(5)	0.659 1(2)	0.218 8(3)	0.087 2(6)	0.659 0(3)

reported dipalladium and diplatinum complexes containing either mono-[27] or bis(μ-alkanethiolato) groups, as evidenced in Table 7. The central planar ring, up to now restricted to μ-arenethiolato complexes, is the geometry found for all complexes with bridging aliphatic γ-mercaptoamine ligands. A common factor for these complexes is the presence of five-membered chelate rings with terminal ligands. Although it is difficult to explain this apparent relation between the nature of the terminal ligands and the hinge angle in dinuclear d^8 metal complexes, it has also been found that among [Ni_2(μ-

Table 5 Selected bond lengths (Å) and angles (°) for complexes **1** (M = Pd) and **2** (M = Pt)

	1	**2**
M–P(1)	2.284(1)	2.260(1)
M–P(2)	2.254(1)	2.242(1)
M–S(1)	2.348(1)	2.358(1)
M–S(2)	2.367(1)	2.371(1)
P(1)–C(1)	1.829(2)	1.830(4)
P(1)–C(7)	1.824(2)	1.829(4)
P(1)–C(13)	1.846(2)	1.839(4)
P(2)–C(14)	1.844(3)	1.843(5)
P(2)–C(15)	1.816(3)	1.815(4)
P(2)–C(21)	1.816(3)	1.813(4)
C(13)–C(14)	1.529(3)	1.526(6)
S(1)–C(27)	1.830(2)	1.836(4)
S(2)–C(33)	1.837(3)	1.834(4)
P(1)–M–P(2)	85.9(1)	86.3(1)
P(1)–M–S(1)	170.0(1)	171.1(1)
P(2)–M–S(1)	85.7(1)	86.5(1)
P(1)–M–S(2)	94.4(1)	94.2(1)
P(2)–M–S(2)	170.9(1)	171.2(1)
S(1)–M–S(2)	94.7(1)	93.7(1)
M–P(1)–C(1)	116.7(1)	117.4(1)
M–P(1)–C(7)	118.2(1)	117.7(1)
C(1)–P(1)–C(7)	105.1(1)	104.9(2)
M–P(1)–C(13)	107.1(1)	107.4(1)
C(1)–P(1)–C(13)	103.8(1)	103.7(2)
C(7)–P(1)–C(13)	104.4(1)	104.1(2)
M–P(2)–C(14)	107.8(1)	107.8(1)
M–P(2)–C(15)	120.8(1)	121.0(1)
C(14)–P(2)–C(15)	103.8(1)	103.6(2)
M–P(2)–C(21)	110.5(1)	110.1(1)
C(14)–P(2)–C(21)	106.7(1)	107.2(2)
C(15)–P(2)–C(21)	106.4(1)	106.3(2)
P(1)–C(13)–C(14)	108.3(2)	108.6(3)
P(2)–C(14)–C(13)	108.2(2)	108.3(3)
M–S(1)–C(27)	104.2(1)	104.9(1)
M–S(2)–C(33)	106.1(1)	106.4(1)

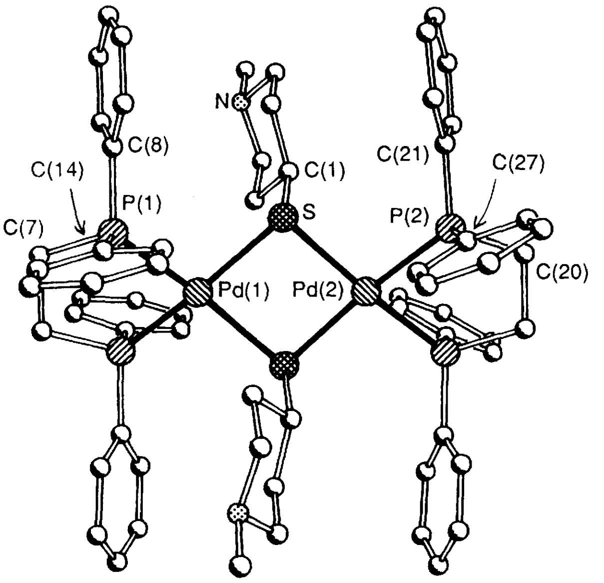

Fig. 2 The structure of the cation of complex **3**. Hydrogen atoms are omitted for clarity. The structures of **4** and **5** are almost identical

SR)$_2$L$_4$] complexes only [{Ni[μ-S(CH$_2$)$_3$NMe$_2$](dppe)}$_2$]$^{2+}$ and [Ni$_2$(μ-SEt)$_2$(SEt)$_4$]$^{2-}$ have a Ni$_2$S$_2$ planar ring,[4,30] while [Ni$_2$(μ-SEt)$_2$(S$_2$CSEt)$_2$], with the same bridging unit, but with terminal four-membered chelate rings, has a hinge angle of 110.2°.[31] (*c*) The planarity of the M$_2$S$_2$ ring (M = Pd or Pt) in complexes **I–VII** and **XIII–XV** causes the M–M distances and M–S$_b$–M angles to be greater than those of the other set of complexes. (*d*) In all complexes the M–S$_b$ bond lengths (M = Pd or Pt) are sensitive to the nature of the terminal ligands. Thus, by comparing complexes **I–IV** with **XIII–XV**, we find that the metal–sulfur bond length is greater when the terminal ligands have phosphorus (**I–IV**) rather than nitrogen (**XIII–XV**) donor atoms. Also, in complexes **I–IV** the M–S$_b$ bond length is much closer to that found in **VII**, **VIII** and **XI** with *trans*- than with *cis*-PR$_3$ ligands. (*e*) In contrast to M–S$_b$, metal–phosphorus (**I–XII**) and metal–nitrogen (**XIII–XV**) bond lengths vary very little, with ranges 2.25–2.30 and 2.06–2.12 Å, respectively.

Table 6 Selected bond lengths (Å) and angles (°) for complexes **3** (M = Pd), **4** (M = Pt) and **5**

	3	**4**	**5**
M(1)–S	2.427(2)	2.402(2)	2.406(2)
M(1)–P(1)	2.271(2)	2.264(2)	2.267(2)
M(2)–S	2.385(2)	2.384(2)	2.390(2)
M(2)–P(2)	2.278(2)	2.262(2)	2.271(2)
S–C(1)	1.856(8)	1.873(6)	1.857(8)
P(1)–C(7)	1.790(10)	1.832(6)	1.842(7)
P(1)–C(8)	1.808(9)	1.816(6)	1.803(7)
P(1)–C(14)	1.793(9)	1.821(7)	1.825(8)
C(7)–C(7′)	1.631(19)	1.519(11)	1.510(13)
P(2)–C(20)	1.844(9)	1.843(6)	1.814(7)
P(2)–C(21)	1.810(8)	1.805(6)	1.799(7)
P(2)–C(27)	1.803(10)	1.815(7)	1.820(9)
C(20)–C(20′)	1.591(16)	1.510(11)	1.567(14)
S–M(1)–P(1)	96.1(1)	96.9(1)	96.5(1)
S–M(1)–S′	85.9(1)	83.9(1)	84.4(1)
P(1)–M(1)–S′	168.4(1)	168.3(1)	168.5(1)
P(1)–M(1)–P(1′)	84.2(1)	84.8(1)	84.8(1)
S–M(2)–P(2)	95.0(1)	96.1(1)	95.9(1)
S–M(2)–S′	87.8(1)	84.6(1)	85.1(1)
P(2)–M(2)–S′	171.3(1)	171.3(1)	171.7(1)
P(2)–M(2)–P(2′)	83.5(1)	84.5(1)	84.2(1)
M(1)–S–M(2)	93.2(1)	95.7(1)	95.2(1)
M(1)–S–C(1)	104.7(3)	106.0(2)	105.3(3)
M(2)–S–C(1)	98.9(3)	99.2(2)	98.9(3)
M(1)–P(1)–C(7)	111.1(3)	109.1(2)	109.0(2)
M(1)–P(1)–C(8)	122.2(3)	122.7(2)	122.3(2)
C(7)–P(1)–C(8)	103.4(4)	104.1(3)	104.6(3)
M(1)–P(1)–C(14)	105.0(3)	105.7(2)	105.7(2)
C(7)–P(1)–C(14)	108.5(4)	107.9(3)	108.3(4)
C(8)–P(1)–C(14)	106.1(4)	106.7(3)	106.4(3)
P(1)–C(7)–C(7′)	108.6(4)	109.2(3)	109.2(4)
M(2)–P(2)–C(20)	110.5(3)	109.5(2)	109.9(2)
M(2)–P(2)–C(21)	119.3(3)	119.0(2)	118.8(2)
C(20)–P(2)–C(21)	104.7(4)	106.6(3)	106.1(3)
M(2)–P(2)–C(27)	107.0(3)	108.2(2)	107.4(2)
C(20)–P(2)–C(27)	106.0(4)	105.7(3)	106.1(4)
C(21)–P(2)–C(27)	108.6(4)	107.1(3)	107.9(4)
P(2)–C(20)–C(20′)	106.6(4)	109.1(3)	108.5(4)

Symmetry operator for primed atoms: $\frac{1}{2} - x, y, 1 - z$.

Structure of Complex **5**.—Complex **5** is isostructural with **3** and **4**; their almost identical cell parameters reflect the equivalence in size of the Pd and Pt atoms. The two metals have, however, very different atomic scattering factors for X-rays, allowing a clear distinction between them in an ordered structure, and a relatively precise determination of the Pd:Pt occupancy ratio for the metal sites in a substitutionally disordered structure, as part of the least-squares refinement of the crystal structure. We find in the case of **5** that both metal sites in the dinuclear cation are disordered but that Pt predominates strongly over Pd, unequally so for the two sites. The determined Pd:Pt ratio is 11.4:88.6(7) for one site and 4.0:96.0(8) for the other, giving an effective formulation of Pd$_{0.154}$Pt$_{1.846}$ rather than PdPt for the dinuclear species. It

Table 7 Structural data[a] (Å and °) for dinuclear complexes of Pd or Pt with a central M_2S_2 ring

Complex		$M-S_b$[b]	M–L[c]	M···M	$M-S_b-M$	S_b-M-S_b	φ[d]	L–M–L[e]	Ref.
I	$[\{Pd(\mu\text{-}SC_5H_9NMe)(dppe)\}_2]^{2+}$	2.436(3) 2.381(3)	2.267(2) 2.280(2)	3.497	93.1(1)	85.7(1) 88.2(1)	180	83.4(1) 84.3(1)	This work
II	$[\{Pt(\mu\text{-}SC_5H_9NMe)(dppe)\}_2]^{2+}$	2.402(2) 2.384(2)	2.264(2) 2.262(2)	3.550	95.7(1)	83.9(1) 84.6(1)	180	84.8(1) 84.5(1)	This work
III	$[\{Pd[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$	2.386(5)	2.263(5) 2.275(6)	3.504	94.4(3)	85.6(3)	180	84.7(2)	23
IV	$[\{Pt[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2]^{2+}$	2.377(5)	2.242(5) 2.259(7)	3.556	96.7(3)	83.3(3)	180	85.2(2)	23
V	$[\{Pd(\mu\text{-}SPh)(SPh)_2\}_2]^{2-}$	2.345(4)		3.505	96.7(2)	83.3(2)	180	93.2(2)	24
VIa[f]	*trans*-$[\{Pd(SC_6F_5)(\mu\text{-}SC_6F_5)(PPh_3)\}_2]$	2.37	2.28	*g*	*g*	87.6			26*a*
VIb[f]	*trans*-$[\{Pd(SC_6F_5)(\mu\text{-}SC_6F_5)(PPh_3)\}_2]$	2.39	2.25	*g*	*g*	80.6	180		26*b*
VII	*trans*-$[\{PdCl(\mu\text{-}SPh)(PEt_3)\}_2]$	2.289(2)[h] 2.382(2)[i]	2.266(2)	3.463	95.7(1)	84.3(1)	180		27
VIII	*cis*-$[\{PtCl(\mu\text{-}SEt)(PPr^n{}_3)\}_2]$	2.274(7)[h] 2.371(7)[i]	2.262(5)	3.206	87.0(20)	80.2(3)	130		28
IX	$[\{Pt(\mu\text{-}S)(PMe_2Ph)_2\}_2]$	2.340(8)	2.265(7)	3.175	85.5(4)	81.6(4)	121	*g*	25
X	$[Pt_2(\mu\text{-}S)(\mu\text{-}SMe)(PPh_3)_4]^+$	2.320(8) 2.363(11)	2.276(7)	3.306	90.0(10)	81.6(1)	138	102.3(2) 99.0(2)	25
XI	*cis*-$[\{Pt(NO_2)(\mu\text{-}SMe)(PPh_3)\}_2]$	2.294(3)[h] 2.354(2)[i]	2.266(1)	3.342	92.0(15)	81.7(1)	141		25
XII	*cis*-$[\{Pt(SCH_2Ph)(\mu\text{-}SCH_2Ph)(PMePh_2)\}_2]$	2.322(4)	2.250(4)	*g*	91.0	80.3(1)	138.8		15
XIII	$[\{Pt(\mu\text{-}SC_5H_9NMe)(en)\}_2]^{2+}$[j]	2.299(2)	2.066(6) 2.075(6)	3.452	97.3(1)	82.7(1)	180	82.8(2)	5
XIV	$[\{Pt(\mu\text{-}SC_5H_9NHMe)(en)\}_2]^{4+}$	2.296(2)	2.071(5) 2.074(5)	3.448	97.0(1)	83.0(1)	180	82.2(2)	5
XV	$[\{Pt[\mu\text{-}S(CH_2)_3NMe_2](en)\}_2]^{2+}$	2.292(3)	2.111(8) 2.066(8)	3.425	96.9(1)	83.1(1)	180	83.3(3)	5

[a] Mean values for chemically equivalent bonds and angles in previously published structures. [b] S_b denotes bridging sulfur atom. [c] L denotes terminal ligand; M–L bond distances are given only if the L donor atom is nitrogen or phosphorus. [d] Dihedral angle between the two S_b-M-S_b planes. [e] This angle is given only for chelating or equal unidentate ligands L. [f] Two crystalline modifications of the same chemical complex. [g] Value not reported. [h] *cis* to phosphine. [i] *trans* to phosphine. [j] en = Ethane-1,2-diamine.

must be pointed out that this empirically determined 'analysis' applies only to the particular single crystal selected for X-ray study, these mixed PdPt products not necessarily being homogeneous. With this formulation the crystal studied contains mainly homonuclear Pt_2 cation species. As a check on the validity of this treatment we have also refined a Pd:Pt disorder ratio for each of the metal atom sites in the pure homonuclear complexes **3** and **4**. Refinement gives occupancy factors of 0.998 2(61) and 1.003 3(3) for Pd in **3**, and of 1.013 65(5) and 1.010 76(6) for Pt in **4**. These factors, which are all essentially unity but have extremely small estimated standard deviations, indicate that the occupancy factors obtained for **5** are reliable, but that their standard deviations are rather underestimated. The inequality of the Pd:Pt disorder ratios for the two metal atom sites in **5**, which indicates that a very small proportion of the cations are heteronuclear PdPt species, should therefore be interpreted with caution. A few heteronuclear PdPt complexes are known, in which Pd and Pt occupy chemically equivalent positions; in all cases for which crystal structures have been reported there is disorder of the metal atom sites.[32]

The geometrical results for complex **5** are essentially identical to those of **3** and **4** discussed above (see Table 6).

Infrared Data.—The IR spectra of the solid complexes **1** and **2** are very similar, one of their main features being two intense and resolved bands in the region 3000–2700 cm^{-1}, which indicate that the complexed ligand is in the anionic form co-ordinating through the sulfur atom exclusively.[33] Those of **3**–**5**, which are practically identical, have the same basic features as that of the complex $[\{Ni[\mu\text{-}S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$, the structure of which was already known.[4]

Proton, $^{31}P\text{-}\{^1H\}$ and $^{195}Pt\text{-}\{^1H\}$ NMR Studies.—The most important features of the ^1H NMR spectra of complexes **1**–**5** are the sharp singlet peak corresponding to the protons of the *N*-methyl group of 4-mercapto-1-methylpiperidine and the two multiplets corresponding to the aromatic protons of dppe. For complexes **3**–**5** these two multiplets practically overlap and another multiplet at higher field and with a 2:2:1 pattern, due to the protons of the tetraphenylborate anion, is also apparent. Based on reported information on aliphatic mercaptoamine complexes,[3d,33] the position of the singlet, for all complexes at δ 2.0 ± 0.1 indicates that the nitrogen has a free pair of electrons and thus the mercaptoamine ligand co-ordinates only through sulfur. The relative areas under the peaks agree well in each case with the empirical formula of the corresponding complex.

An important evidence of the purity of the complexes **1** and **2** is obtained from the $^{31}P\text{-}\{^1H\}$ NMR spectra, each of them showing that the solution contains only one complex species and that it is free of dppe oxide (which gives a signal at δ *ca.* 31). Thus, for complex **1** one singlet is observed, while the spectrum of **2** consists only of a 1:4:1 triplet, as expected for $^{31}P-^{195}Pt$ coupling with a 34% natural abundance of ^{195}Pt. The positions of these peaks and the observed $^1J(Pt-P)$ coupling constants are given in Table 8, where data for closely related complexes are also included. Values found for complexes **1** and **2** are very close to those obtained for complexes with the same formula but with the 3-dimethylaminopropane-1-thiolate ligand. The similarity of corresponding values, together with the X-ray crystal structures of **1** and **2**, clearly indicate that complexes of formula $[M(SR)_2(dppe)]^x$ [M = Pd or Pt; $x = 0$, R = $(CH_2)_3NMe_2$; $x = +2$, R = $(CH_2)_3NHMe_2$] also have a mononuclear structure.

The $^{31}P\text{-}\{^1H\}$ NMR data for the dinuclear complexes **3** and **4** and closely related compounds are also included in Table 8. The spectra of **3** and **4** consist of a singlet at δ 62.31 and a 1:4:1 triplet at δ 47.06 with $^1J(Pt-P)$ = 2934 Hz, respectively. These values compare very well with those found for complexes with the same structure but with 3-dimethylaminopropane-1-thiolate instead of 4-mercapto-1-methylpiperidine. The presence of

Table 8 ^{31}P-$\{^1H\}$ and ^{195}Pt-$\{^1H\}$ NMR data for complexes **1**–**5** and closely related complexes

Complex		Solvent	$\delta(^{31}P)$	$\delta(^{195}Pt)$	$^1J(Pt-P)$/Hz	Ref.
1	$[Pd(SC_5H_9NMe)_2(dppe)]$	dmso	54.4			This work
	$[Pd\{S(CH_2)_3NMe_2\}_2(dppe)]$	dmso	53.4			4
	$[Pd\{S(CH_2)_3NHMe_2\}_2(dppe)][BPh_4]_2$	dmso	55.5			4
2	$[Pt(SC_5H_9NMe)_2(dppe)]$	dmso	48.1 (t)	−4701.5 (t)	2788	This work
	$[Pt\{S(CH_2)_3NMe_2\}_2(dppe)]$		47.7 (t)[a]	−4713.6 (t)[b]	2811,[a] 2782[b]	23
	$[Pt\{S(CH_2)_3NHMe_2\}_2(dppe)][BPh_4]_2$	dmso	47.5 (t)		2805	4
	$[Pt(SPh)_2(dppe)]$	CD_2Cl_2	92.7 (t)		3047	34
	$[Pt(SCH_2Ph)_2(dppe)]$	$CDCl_3$	47.2 (t)		2798	35
	cis-$[Pt(SMe)_2(PPh_3)_2]$	CD_2Cl_2	25.5 (t)		2862	14
	$[PtCl_2(dppe)]$	dmso	43.8 (t)	−4554 (t)	3600	36
3	$[\{Pd(SC_5H_9NMe)(dppe)\}_2][BPh_4]_2$	dmso	62.3			This work
	$[\{Pd[S(CH_2)_3NMe_2](dppe)\}_2][BPh_4]_2$	dmso	63.4			4
4,4′	$[\{Pt(SC_5H_9NMe)(dppe)\}_2]X_2$	dmso	47.1 (t)[c]	−4503.6 (t)[d]	2934	This work
	$[\{Pt[S(CH_2)_3NMe_2](dppe)\}_2][PF_6]_2$	$CDCl_3$	46.6 (t)	−4560 (t)	3046	4, 23
5,5′	$[Pd_xPt_{2-x}(SC_5H_9NMe)_2(dppe)_2]X_2$	dmso	62.3, 47.1 (t)[c]	−4525 (t)[d]	2952	This work

[a] In $CDCl_3$. [b] In dmso. [c] $X = BPh_4$ (**4**, **5**). [d] $X = PF_6$ (**4′**, **5′**); PF_6^- signal in ^{31}P NMR spectra is not reported.

other peaks of very low intensity suggests that not only the corresponding dinuclear complex is present in solution. These additional signals, which are reproducible, cannot be attributed to impurities from the synthesis because the spectra are obtained from **3** and **4** which have been isolated as pure crystalline products and then redissolved.

The spectrum of complex **5**, regardless of the Pd : Pt ratio for the particular crop of product taken, is apparently the sum of the spectra of **3** and **4** in appropriate relative proportions, showing the same signals at the same chemical shifts. It essentially contains a singlet peak at δ 62.31 and a 1:4:1 triplet at δ 47.16 with $^1J(Pt-P) = 2952$ Hz. This similarity was one of the reasons that first led us to assume that **5** was mainly a mixture of **3** and **4**. The spectra of **5** for different Pd:Pt ratios reinforce the previous assumption, as they vary only in the relative intensities of the peaks: that is, the singlet peak decreases and the triplet increases in going from the spectrum of **5** with $x > 1$ to that of **5** with $x \ll 1$.

The ^{195}Pt-$\{^1H\}$ NMR spectrum of complex **2** consists only of a 1:2:1 triplet centred at δ −4701.5 with $^1J(Pt-P) = 2787$ Hz, which agrees very well with that calculated from the ^{31}P-$\{^1H\}$ spectrum of the same compound (2788 Hz) and with those found for similar platinum complexes, as indicated in Table 8. The hexafluorophosphate salt of complex **4** also shows only one 1:2:1 triplet centred at δ −4503.6, with $^1J(Pt-P) = 2934$ Hz. The ^{195}Pt-$\{^1H\}$ NMR spectrum of **5** has exactly the same features as that of **4**, consisting of only one 1:2:1 triplet centred at δ −4525, with $^1J(Pt-P) = 2952$ Hz. This similarity, together with the absence of any other peaks, confirms the existence of the homonuclear diplatinum complex **4** in the apparently heteronuclear PdPt compound **5**.

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