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DINUCLEAR PLATINUM(II) COMPLEXES WITH A BRIDGING MERCAPTO GROUP: X-RAY CRYSTAL STRUCTURE OF A CHLORO/MERCAPTO-BRIDGED DIMER

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Abstract—$[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-}Y)(PR_3)_2]$ complexes [X = Cl, SPh; X = Y = SPh, Pr^i; PR_3 = PBu_3, PMe_2Ph, PPh_3, $P(p\text{-tol})_3$] have been prepared and characterized by elemental analysis, ^1H and ^{31}P NMR spectroscopy. Bridge cleavage reactions with various donor ligands have been investigated by $^{31}P\{^1H\}$ NMR. The X-ray crystal structure of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PMe_2Ph)_2]$ is reported.

Coordination geometries of dinuclear platinum(II) complexes of the type $[Pt_2(\mu\text{-}X)(\mu\text{-}Y)Z_2L_2]$ depend on the method of preparation and on the nature of the X, Y, Z and L ligands which also influence the chemical reactivity of such complexes. The dimercapto-bridged complexes[1–10] (X = Y = SR) usually prefer a *cis* configuration when R = alkyl, but when R = aryl and L = PPr_3, only the *trans* isomer exists. The monothio-bridged complexes[1,2,9] (X = Z = Cl) adopt a *cis* configuration, however, for Z = $SnCl_3$ the *sym trans* isomer forms.[9] The *cis* and *trans* configurations can readily be identified on the basis of ^3J(Pt—P) and ^4J(P—P) values.[8–10] In continuation of our previous work, we now report the phenyl and isopropyl mercapto-bridged complexes wherein L determines the geometry of the complex, together with the X-ray structure of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PMe_2Ph)_2]$.

RESULTS AND DISCUSSION

Treatment of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with thiophenol in 1 : 2 stoichiometry, in the presence or absence of pyridine, affords the phenylthio-bridged complexes. A similar reaction, in the absence of pyridine, in 1 : 1 stoichiometry in dichloromethane yields the μ-chloro-μ-phenylthio complexes. These can also be obtained by reacting the tetrachloro complex with the dimercapto-bridged compound in dichloromethane. The tetrachloro complex reacts with excess isopropylmercaptan in acetone to give di-μ-isopropylthio complexes. Physical and analytical data of these complexes are given in Table 1.

The ^{31}P NMR data for $[Pt_2Cl_2(\mu\text{-}SPh)_2(PR_3)_2]$ (Table 2) suggest that these complexes adopt a *sym trans* configuration [^3J(Pt—P) = ~50 Hz and ^4J(P—P) = ~12 Hz][8,9] except tris(*p*-tolyl)phosphine which is a mixture of *cis* and *trans* isomers. The latter is in contrast to the observation of Chatt and Hart[1] that with the arylthio ligand the *trans* configuration is preferred. The existence of the *cis* isomer for $P(p\text{-tol})_3$ suggests that phosphine ligands also play a role in determining the geometry of the complex. The magnitude of ^1J(Pt—P) reflects that the chloro/mercapto-bridged complexes adopt a *sym cis* configuration in which the phosphine ligand is *trans* to the bridging chlorine.

The ^1H NMR spectra of the complex $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PMe_2Ph)_2]$ displayed two doublets for

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Table 1. Physical and analytical data for $[Pt_2Cl_2(\mu\text{-}X)(\mu\text{-}SR)(PR_3)_2]$ complexes

Complex	Recrystallization solvent (per cent yield)	Melting point (°C)	Per cent analyses: Found (Calc.)		
			C	H	S
$[Pt_2Cl_2(\mu\text{-}SPh)_2(PBu_3)_2]$	Benzene–hexane (61)	137	39.0 (39.9)	5.6 (5.9)	—
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PBu_3)_2]$	Benzene–hexane (90)	135	35.2 (35.7)	5.8 (5.9)	3.4 (3.2)
$[Pt_2Cl_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$	CH_2Cl_2–methanol (90)	224	34.5 (35.2)	3.1 (3.4)	6.8 (6.7)
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PMe_2Ph)_2]$	CH_2Cl_2–methanol (97)	219–220	29.3 (30.0)	3.0 (3.1)	3.7 (3.6)
$[Pt_2Cl_2(\mu\text{-}SPh)_2(P\text{-}tol_3)_2]$	Benzene–hexane (63)	271–273	50.0 (50.3)	3.8 (4.1)	5.5 (5.0)
$[Pt_2Cl_2(\mu\text{-}SPr^i)_2(P\text{-}tol_3)_2]$	Benzene (43)	253–255	46.9 (47.2)	4.6 (4.6)	5.5 (5.3)
$[Pt_2Cl_2(\mu\text{-}SPr^i)_2(PPh_3)_2]$	Chloroform (65)	264–265	43.9 (44.4)	3.9 (3.9)	—

the methyl protons indicating non-equivalence of the methyl groups on phosphine. The corresponding di-μ-phenylthio complex exhibited only one doublet for the P—Me protons.

Structure of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PMe_2Ph)_2]$

A single-crystal X-ray analysis of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PPhMe_2)_2]$ has confirmed that complexes of this type have a *sym cis* configuration. An ORTEP[11] plot of the molecule, together with the numbering of non-hydrogen atoms, is shown in Fig. 1. Table 3 lists the bond lengths and bond angles in the molecule with their estimated standard deviations. The bond lengths, as shown below, are in good agreement with those reported in the literature.[3,6]

Table 2. ^1H and $^{31}P\{^1H\}$ NMR data for mercapto-bridged dinuclear platinum(II) complexes in $CDCl_3$

Complex	$^{31}P\{^1H\}$ NMR data				^1H NMR data
	δ(Pt—P) (ppm)	^1J(Pt—P) (in Hz)	^3J(Pt—P) (in Hz)	^4J(P—P) (in Hz)	
$[Pt_2Cl_2(\mu\text{-}SPh)_2(PBu^n_3)_2]$	3.1	3160	53	11.5	
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PBu^n_3)_2]$	0.5	3937	—	—	
$[Pt_2Cl_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$	−12.1	3200	52	14	P—Me_2 1.57 (d, 11 Hz)[a] ^3J(Pt—H) 33 Hz
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PMe_2Ph)_2]$	−17.2	4075	—	—	P—Me_2[a] 1.78 (d, 13.7 Hz); 1.66 (d, 13.7 Hz); Ph = 6.99–7.46 (m)
$[Pt_2Cl_2(\mu\text{-}SPh)_2(P\text{-}tol_3)_2]$	12.6 14.9	3325 3276	7.5 42	— 13	P—C_6H_4Me 2.29 s(br)[b]
$[Pt_2Cl_2(\mu\text{-}SPr^i)_2(P\text{-}tol_3)_2]$	14.4	3249	40	12	$SCMe_2$ 1.35 (d, 6 Hz)[b] PC_6H_4Me 2.32 (s)
$[Pt_2Cl_2(\mu\text{-}SPr^i)_2(PPh_3)_2]$	9.7	3255	36	12	$SCMe_2$ 1.40 (d, 6 Hz)[b] SCH 2.35 (m)

[a] Recorded on a Varian VXR 300 S.

[b] Recorded on a Varian FT-80A.

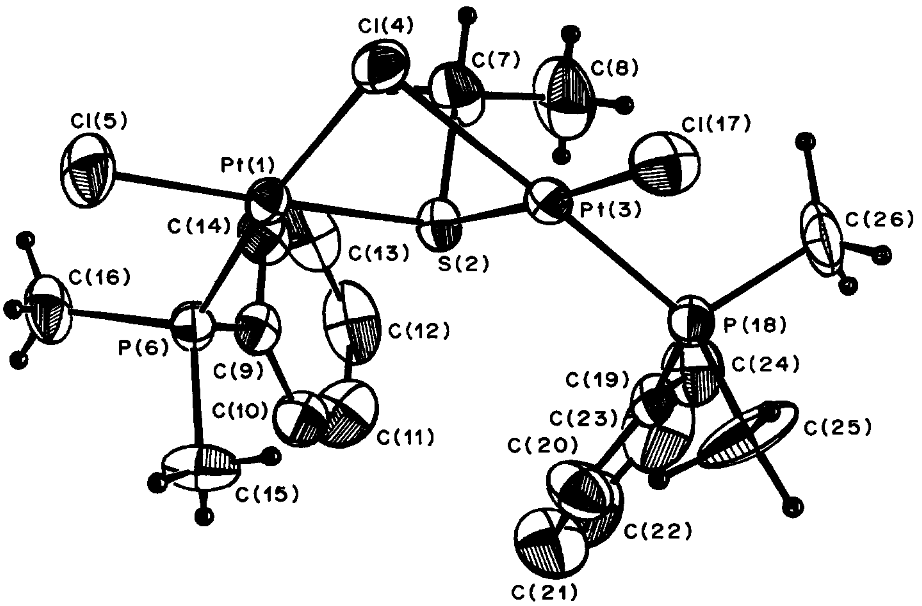

Fig. 1. ORTEP view of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PMe_2Ph)_2]$.

Bond	*trans* group	Bond length (Å) Expected[3,6]	Bond length (Å) ⟨observed⟩$_{av}$
⟨Pt—P⟩	Cl	2.23	2.222(4)
⟨Pt—S⟩	Cl	2.27	2.271(4)
⟨Pt—Cl⟩$_{terminal}$	SR	2.34	2.334(5)
⟨Pt—Cl⟩$_{bridging}$	PR_3	2.43	2.452(5)

The terminal Pt—Cl distances are shorter than the bridging distances. The Pt—P and Pt—S distances are considerably shorter than their radius sum of 2.42 and 2.36 Å, respectively. The bond lengths are thus in keeping with the usual *trans* influence order $P \gg S > Cl$. The shortening of the Pt—S bond has been attributed to a strong π-bond character.[3] The possibility of forming two strong bonds at sulphur, as suggested by Hall *et al.*,[3] results in a P—Pt—S—Pt—P chain and stabilizes the *cis* configuration. The *trans* configuration would lead to weakening of one of the Pt—S bonds due to the strong *trans* influence of the phosphine ligand, thereby destabilizing the bridge framework. The Pt···Pt distance [3.299(1) Å] lies within the expected[6,12] range, 3.18–3.48 Å.

The angles around both the platinum atoms are normal and fall within the expected range. The S—Pt—P angle is larger than the ideal 90° [91.8(2) and 95.9(2)°, respectively], which results in minimization of the crowding of the alkyl and aryl groups on the sulphur and phosphorus atoms, respectively. Further, the Pt—Cl—Pt angle which lies in the range 94–96° in di-μ-chloro-bridged complexes[12–16] shows a significantly smaller value of 84.5(2)° in the present case. The angle around the bridging sulphur atom [Pt(1)—S(2)—Pt(3)] is significantly larger [93.1(2)°] than that reported for any sulphur-bridged dinuclear platinum(II) complex[6] [85.5–92.0°]. Although a wide variation in the angle at the bridging sulphur (79–98°)[17,18a] has been observed with different metal ions, the reason for this, except due to the ionic radii variation, is not clear.

The conformations of the two PMe_2Ph ligands are different. The methyl carbon [C(15)] attached to P(6) nearly lies in the plane defined by C(9), C(10), C(11), C(12), C(13), C(14) [deviation ~ 0.16(2) Å], and in the plane defined by P(6), C(9), C(10), C(11), C(12), C(13), C(14) [deviation ~ 0.11(2) Å], while deviations of −1.63(2) and −1.59(2) Å occur for C(16). The respective values for C(25) and C(26) from the planes defined by C(19), C(20), C(21), C(22), C(23), C(24), and P(18), C(19), C(20), C(21), C(22), C(23), C(24) in the other phosphine ligand are −1.31(2), −1.35(2) Å and −0.46(3), −0.50(3) Å, respectively. These deviations are also reflected in the corresponding torsion angles C(15)—P(6)—C(9)—C(10) [0.7 (2.0)°], C(15)—P(6)—C(9)—C(14) [−176.7 (1.7)°], C(16)—P(6)—C(9)—C(10) [109.6 (1.8)°], C(16)—P(6)—C(9)—C(14) [72.9 (1.8)°], C(25)—P(18)—C(19)—C(20) [53.3 (2.0)°], C(25)—P(18)—C(19)—C(24) [−127.6 (1.9)°], C(26)—

Table 3. Selected bond lengths (Å) and angles (°)

Pt(1)—Cl(4)	2.442(5)	P(6)—C(9)	1.797(16)
Pt(1)—Cl(5)	2.332(5)	P(6)—C(15)	1.815(25)
Pt(1)—S(2)	2.275(4)	P(6)—C(16)	1.818(27)
Pt(1)—P(6)	2.214(5)	P(18)—C(19)	1.802(17)
Pt(3)—Cl(4)	2.463(4)	P(18)—C(25)	1.779(14)
Pt(3)—Cl(17)	2.334(5)	P(18)—C(26)	1.809(27)
Pt(3)—S(2)	2.267(4)	S(2)—C(7)	1.823(18)
Pt(3)—P(18)	2.230(4)	C(7)—C(8)	1.517(37)
Pt(1)—Pt(3)	3.299(1)		
Cl(4)—Pt(1)—S(2)	83.0(2)	Cl(4)—Pt(3)—S(2)	82.7(2)
Cl(5)—Pt(1)—P(6)	92.5(2)	Cl(17)—Pt(3)—P(18)	88.5(2)
S(2)—Pt(1)—P(6)	91.8(2)	S(2)—Pt(3)—P(18)	95.9(2)
Cl(4)—Pt(1)—Cl(5)	92.5(5)	Cl(4)—Pt(3)—Cl(17)	93.0(2)
Pt(1)—P(6)—C(9)	114.0(7)	Pt(3)—P(18)—C(19)	115.5(7)
Pt(1)—P(6)—C(15)	109.1(8)	Pt(3)—P(18)—C(25)	116.1(9)
Pt(1)—P(6)—C(16)	116.8(8)	Pt(3)—P(18)—C(26)	110.2(9)
C(9)—P(6)—C(15)	107.4(9)	C(19)—P(18)—C(25)	103.6(10)
C(9)—P(6)—C(16)	104.3(9)	C(19)—P(18)—C(26)	107.1(10)
C(15)—P(6)—C(16)	104.6(10)	C(25)—P(18)—C(26)	103.2(12)
Pt(1)—S(2)—C(7)	102.4(8)	Pt(3)—S(2)—C(7)	103.3(8)
Pt(1)—Cl(4)—Pt(3)	84.5(2)	Pt(1)—S(2)—Pt(3)	93.1(2)
S(2)—C(7)—C(8)	108.1(16)		

$\langle C—C \rangle_{av}$ bond length in phenyl rings 1.370(33) Å.

P(18)—C(19)—C(20) [162.8 (1.7)°] and C(26)—P(18)—C(19)—C(24) [−18.1 (2.0)°]. A similar conformation has been reported for di-μ-chlorodi(propionyl) bis (dimethylphenylphosphine)diplatinum (II).[16] These values show that the deviations of one of the methyl groups from the PPh plane are different at the two ends of the molecule, one end being distinctly more planar than the other. The two phenyl rings are inclined to each other at 129.6(9)°. The ethyl group on S(2) adopts the axial position relative to the mean plane through the Pt(1), Cl(4), S(2), Pt(3) atoms with the methylene carbon [C(7)] staggered with respect to Pt(3), as reflected by the values of the torsion angles. The Pt—S—Cl—Pt bridge is non-planar with an interplanar angle between the two platinum coordination planes of 135.6(5)°. This is in agreement with the value observed for $[Pt_2Cl_2(\mu\text{-SEt})_2(PPr_3)_2]$ where the corresponding angle[3] is 130°. An ORTEP view of the unit cell contents is shown in Fig. 2. Most of the aforementioned results are analogous to those of the palladium derivative[18b] and the two structures appear to be isomorphous.

A few bridge cleavage reactions of phenylthio-bridged complexes have been carried out and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The products formed were identified by comparison of the observed chemical shifts and coupling constants with those reported previously.[8,9,15] The phenylthio-bridged complexes undergo bridge cleavage reactions more readily than the corresponding alkylthio complexes. Pyridine cleaves the μ-chloro-μ-phenylthio bridge readily. The $^{31}P\{^1H\}$ NMR spectra of the reactions of pyridine with $[Pt_2Cl_2(\mu\text{-Cl})(\mu\text{-SPh})(PR_3)_2]$ ($PR_3 = PBu_3$, PMe_2Ph) in $CDCl_3$, obtained immediately after mixing, showed resonances assignable to three molecular species, viz. $[Pt_2Cl_2(\mu\text{-SPh})_2(PR_3)_2]$, *trans*-$[PtCl_2(py)(PR_3)]$ and $[PtCl(SPh)(py)(PR_3)]$. The concentration of *trans*-$[PtCl_2(py)(PR_3)]$ did not change with time, but the mononuclear complex $[PtCl(SPh)(py)(PR_3)]$, phosphine *trans* to pyridine [PBu_3: δ −4.6 ppm, ^1J(Pt—P) 3502 Hz; PMe_2Ph: δ −20.8 ppm, ^1J(Pt—P) 3580 Hz], established equilibrium within 10–15 h with the di-μ-phenylthio complex, since even after a week no change in their concentrations was noticed. The relative ratio of the three species from ^{31}P NMR integration was approximately 2.7 : 1.7 : 1.0 (PBu_3) and 2.5 : 1.1 : 1.2 (PMe_2Ph).

A similar bridge cleavage reaction of $[Pt_2Cl_2(\mu\text{-SPh})_2(PBu_3)_2]$ with 2 mole equivalents of $AsPh_3$ in $CDCl_3$ gave four products, *trans*- and *cis*-$[PtCl_2(AsPh_3)(PBu_3)]$ [δ 3.4 ppm, ^1J(Pt—P) 3054 Hz; δ −3.3 ppm, ^1J(Pt—P) 3341 Hz], [PtCl(SPh)

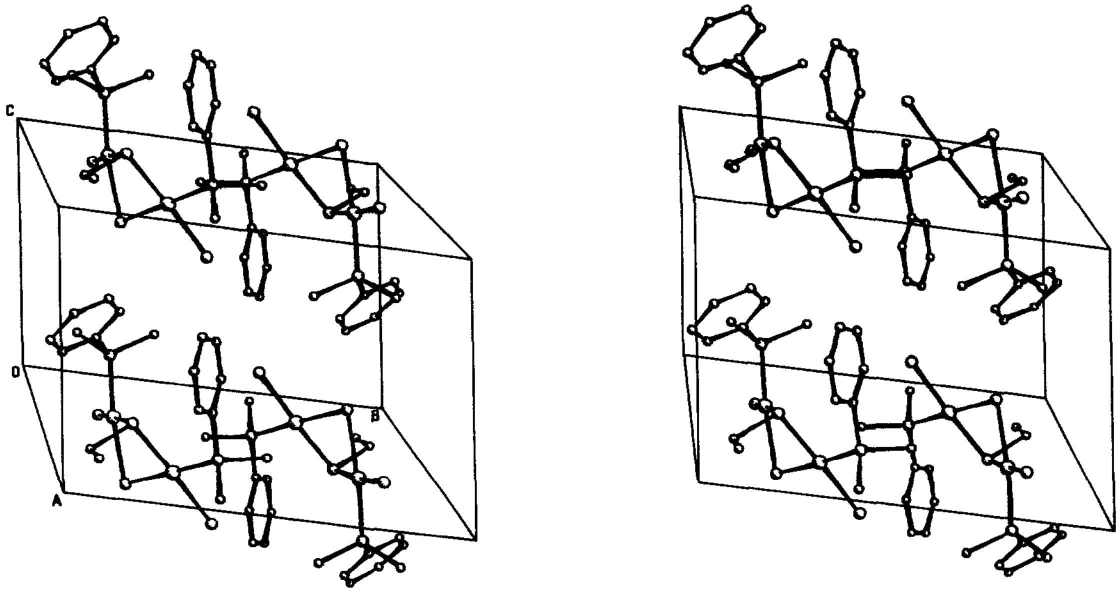

Fig. 2. ORTEP view of the unit cell contents.

$(AsPh_3)(PBu_3)]$ [δ 6.6; 0.4 ppm, ^1J(Pt—P) 3937 Hz]. After 20 h only three products, the former two and *sym trans*-$[Pt_2Cl_2(\mu\text{-}SPh)_2(PBu_3)_2]$, existed in solution and no further change was noticed even after 3 days.

A ^{31}P NMR spectrum obtained immediately after mixing an excess of pyridine with a $CDCl_3$ solution of $[Pt_2Cl_2(\mu\text{-}SPh)_2(PBu_3)_2]$ showed the formation of $[PtCl(SPh)(py)(PBu_3)]$ [δ −4.6 ppm, ^1J(Pt—P) 3504 Hz] and within a few hours (4–6) an equilibrium was established, the two being in an approximately 1:2.8 ratio, as no change was observed even after 4 days. Removal of pyridine *in vacuo* gave the parent complex quantitatively. This is in contrast to the alkylthio-bridged dinuclear platinum(II) compounds which are inert to such ligands.[1,8,9]

EXPERIMENTAL

The complexes $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ [PR_3 = PBu_3, PMe_2Ph, PPh_3, $P(p\text{-}tol)_3$] were prepared according to literature methods.[19–21] Methods and spectroscopic techniques are similar to those described previously.[9,10]

Preparation of $[Pt_2Cl_2(\mu\text{-}SPh)_2(PR_3)_2]$

(a) To a benzene solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ (406 mg, 0.43 mmol), excess pyridine (0.2 cm^3) was added and the reaction mixture was stirred at room temperature for 30 min. To this, a benzene solution (~ 5 cm^3) of benzenethiol (95 mg, 0.86 mmol) was added and the mixture was heated at ~ 60°C with stirring for 2 h. After cooling, the solvents were stripped off *in vacuo* leaving a pasty mass which was extracted from benzene, and recrystallized from benzene–hexane in 62% yield (289 mg).

(b) To a dichloromethane solution (20 cm^3) of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (142 mg, 0.17 mmol), benzenethiol (39 mg, 0.35 mmol) was added and the reactants were stirred at room temperature for 2 h. The solvent was reduced to 5 cm^3, and an equal amount of methanol was added to give pale yellow crystals (141 mg, 84%).

Similar reactions in 1:1 stoichiometry gave chloro/phenylthio-bridged complexes. The di-μ-SPr^i complexes were prepared by a method similar to the one described previously.[8,9]

Preparation of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SPh)(PBu_3)_2]$

Benzene solutions containing $[Pt_2Cl_2(\mu\text{-}SPh)_2(PBu_3)_2]$ (120 mg, 0.11 mmol) and $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu_3)_2]$ (106 mg, 0.11 mmol) were mixed and heated under reflux for 3 h. Concentrating to 5 cm^3 under reduced pressure and addition of 10 cm^3 of hexane gave pale yellow crystals in 90% yield (205 mg). Similarly, the complex $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SEt)(PMe_2Ph)_2]$ was prepared and characterizing data are reported elsewhere.[9]

Bridge cleavage reactions

Pyridine (0.5 cm^3) or a $CDCl_3$ solution of 2 mole equivalents of $AsPh_3$ was added to a $CDCl_3$ solution of dinuclear platinum(II) complexes (90–120 mg) in an NMR tube and the progress of the reaction was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy.

Crystal data

$C_{18}H_{27}Cl_3P_2SPt_2$, Mol. wt 833.4, triclinic, space group $P\bar{1}$, $a = 10.412(1)$, $b = 13.782(1)$, $c = 9.325(1)$ Å, $\alpha = 98.00(1)$, $\beta = 112.26(2)$, $\gamma = 80.29(1)°$, $V = 1219.2$ Å^3, $Z = 2$, $D_c = 2.264$ g cm^{-3}, $D_m = 2.273$ g cm^{-3} (flotation technique, solvents: $CHBr_3$ and CH_3I), $\mu = 126.9$ cm^{-1}, $F(000) = 767.9$.

Data collection

Intensity data for 4290 reflections (crystal size: 0.3 × 0.32 × 0.34 mm) were collected on an Enraf–Nonius CAD-4 diffractometer using graphite monochromatized Mo-K_α ($\lambda = 0.71068$ Å) radiation in the range $3 < 2\theta < 53°$ employing zigzag mode of data collection. Three control reflections were monitored after every 200 reflections (maximum decay = 0.70% during data collection which was corrected during data reduction). Data were corrected for Lorentz, polarization and absorption effects. The unit cell dimensions were refined using 25 arbitrarily chosen higher order reflections around θ of 15–16°.

Structure solution and refinement

A three-dimensional sharpened origin removed Patterson map yielded the positions of the platinum atoms. The least-squares method alternated with difference Fourier synthesis gave the positions of all the non-hydrogen atoms. A weighted anisotropic refinement of all the non-hydrogen atoms using BLOKLS, while keeping the hydrogen atoms in stereochemically acceptable positions, with a unit weighting scheme modified by the Dunitz–Seiler weighting scheme, gave final R and R_w values of 0.055 and 0.067, respectively. The refinement was deemed to be over when the shift-to-error ratio in scale and, positional and thermal parameters of non-hydrogen atoms reached 0.01. The final difference map has ripples of 1.68–1.00 Å around the heavy atoms. The scattering factors for platinum, phosphorus, sulphur and chlorine were taken from Vol. IV of the *International Tables for X-ray Crystallography*,[22] while those of hydrogen were taken from Stewart *et al.*[23] All the computations were carried out using the SDP package available for PDP-11/73.[24]*

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REFERENCES

1. J. Chatt and F. A. Hart, *J. Chem. Soc.* 1953, 2363; 1960, 2807; J. Chatt and J. M. Davidson, *J. Chem. Soc.* 1964, 2433.
2. P. L. Goggin, R. J. Goodfellow and F. J. S. Reed, *J. Chem. Soc. A* 1971, 2031.
3. M. C. Hall, J. A. S. Jarvis, B. T. Kilbourn and P. G. Owston, *J. Chem. Soc., Dalton Trans.* 1972, 1544.
4. P. H. Bird, U. Siriwardane, R. D. Lai and A. Shaver, *Can. J. Chem.* 1982, **60**, 2075; J. Soulie, J. Y. Lallemand and R. C. Rao, *Org. Magn. Res.* 1979, **12**, 67.
5. K. R. Dixon, K. C. Moss and M. A. R. Smith, *J. Chem. Soc., Dalton Trans.* 1974, 971.
6. C. E. Briant, C. J. Gardner, T. S. A. Hor, N. D. Howells and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.* 1984, 2645.
7. M. P. Brown, R. J. Puddephatt and C. E. E. Upton, *J. Chem. Soc., Dalton Trans.* 1976, 2490.
8. H. C. Clark, V. K. Jain and G. S. Rao, *J. Organomet. Chem.* 1985, **279**, 181.
9. V. K. Jain and G. S. Rao, *Inorg. Chim. Acta* 1987, **127**, 161.
10. V. K. Jain, *Inorg. Chim. Acta* 1987, **133**, 261.
11. C. K. Johnson, ORTEP II, Report ORNL-3794. Oak Ridge National Laboratory, Tennessee (1970).
12. S. F. Watkins, *J. Chem. Soc. A* 1970, 168.
13. M. Black, R. H. B. Mais and P. G. Owston, *Acta Cryst.* 1969, **B25**, 1760.
14. R. Mason, M. Textor, N. Al-Saleem and B. L. Shaw, *J. Chem. Soc., Chem. Commun.* 1976, 292; A. B. Goel, S. Goel and D. Vanderveer, *Inorg. Chim. Acta* 1981, **51**, 1267.
15. H. C. Clark, G. Ferguson, V. K. Jain and M. Parvez, *Inorg. Chem.* 1981, **24**, 1477.
16. G. K. Anderson, R. J. Cross, L. Manojlovic-Muir, K. W. Muir and T. Solomun, *J. Organomet. Chem.* 1979, **170**, 385.
17. D. L. Sales, J. Stokes and P. Weedward, *J. Chem. Soc. A* 1968, 1858.
18. (a) A. T. McPhail and G. A. Sim, *J. Chem. Soc. A* 1968, 1858; (b) V. K. Jain, R. P. Patel, K. V. Muralidharan and R. Bohra, *Polyhedron* 1989, **8**, 2151.

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*Tables of fractional coordinates, anisotropic thermal parameters, hydrogen atom parameters, torsion angles, planes and F_o/F_c data have been deposited with the Editor.

19. R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.* 1965, 7533.
20. A. C. Smithies, M. Rycheck and M. Orchin, *J. Organomet. Chem.* 1968, **12**, 199.
21. F. R. Hartley and G. W. Searle, *Inorg. Chem.* 1973, **12**, 1949.
22. *International Tables for X-ray Crystallography*, Vol. IV. Kynoch Press, Birmingham (1974). (Present Distributor: D. Reidel, Dordrecht.)
23. R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.* 1965, **42**, 3175.
24. Enraf–Nonius, Structure Determination Package. Enraf-Nonius, Delft, The Netherlands (1983).