

Mixed Chloro–Mercapto-bridged Dinuclear Platinum(II) Complexes and Their Catalytic Activity in Homogeneous Hydrogenation

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(Received July 14, 1986; revised September 12, 1986)

Abstract

The reaction of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$ with sym-*cis*- and/or sym-*trans*- $[\text{Pt}_2(\mu\text{-SR}')_2\text{Cl}_2(\text{PR}_3)_2]$ ($\text{R}' = \text{Et}$ or Pr^i , $\text{PR}_3 = \text{PEt}_3$, PPr^n_3 , P^nBu_3 , PMe_2Ph) in benzene results in the formation of $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ and involves a bimolecular intermediate. The complexes $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ exist in sym-*cis* configuration where phosphine ligands are *trans* to bridging chloride. Their reactions with excess $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in chloroform give sym-*trans*- $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})(\text{SnCl}_3)_2(\text{PR}_3)_2]$. Bridge cleavage reactions with various donor ligands have also been investigated. The catalytic activity of the $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ system in styrene hydrogenation has been found to be appreciably effective.

Introduction

The geometry [1–5] of dinuclear platinum(II) complexes of the type $[\text{Pt}_2(\mu\text{-X})_2\text{Y}_2\text{L}_2]$ depends on the method of preparation and on the nature of the X, Y or L. In most cases interconversion between the two possible isomers, sym-*cis* and sym-*trans*, occurs readily in solution, so that usually one isomer is obtained on recrystallization. The nature of X, Y and L has a profound influence on the chemical reactivity of these complexes. For example, the chloro-bridged complexes, when $\text{X} = \text{Y} = \text{Cl}$, react readily with weak donor ligands such as ethylene to give mono-nuclear complexes of the type $[\text{PtCl}_2(\text{CH}_2=\text{CH}_2)\text{L}]$ whereas the mercapto-bridged complexes, when $\text{X} = \text{SR}$ ($\text{R} = \text{alkyl}$ or aryl), $\text{Y} = \text{Cl}$ and $\text{L} = \text{PR}_3$, are stable and do not undergo bridge cleavage reactions [1].

Mono-nuclear platinum(II) phosphine complexes, in the presence of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as co-catalyst, have been used as homogeneous catalysts [6–12] in hydrogenation and hydroformylation reactions. The mixed ligand complexes, $[\text{PtCl}_2(\text{PR}_3)\text{L}]$ ($\text{L} = \text{thioether}$, amine ; $\text{R} = \text{aryl}$) in the presence of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were found to be much more active than the corresponding *cis*- $[\text{PtCl}_2\text{L}_2]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or $[\text{PtCl}_2(\text{PR}_3)_2]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ catalyst precursors [1, 11].

Hydrogenation reactions employing dimeric platinum(II) complexes as a homogeneous catalyst are scanty. The homogeneous catalytic systems $[\text{Pt}_2(\mu\text{-X})_2\text{Cl}_2(\text{PR}_3)_2]/\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{Cl}$ or SEt) in dichloromethane showed relatively low activity in styrene hydrogenation [1, 11].

Hence it was decided to study the catalytic activity of dinuclear platinum(II) complexes containing mixed chloro–mercapto bridges, $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ in the homogeneous hydrogenation of olefins as they are derived by the partial removal of L from the complexes $[\text{PtCl}_2(\text{L})(\text{PR}_3)]$. In order to investigate the stereochemistry and reactivity of dinuclear platinum(II) complexes containing chloro–mercapto bridges, we have prepared $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ and studied their chemical reactivity, spectroscopic properties and their catalytic activity in homogeneous hydrogenation of styrene as a reference system.

Experimental

The complexes $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PEt}_3$, PPr^n_3 , P^nBu_3 , PMe_2Ph) [13, 14] and $[\text{Pt}_2(\mu\text{-SR}')_2\text{Cl}_2(\text{PR}_3)_2]$ ($\text{R}' = \text{Et}$ or Pr^i) [1] were prepared by the literature methods. Mercaptans were purchased from Fluka and phosphines were obtained from Strem Chemicals. Styrene was purified by treatment with 5% NaOH solution and then dried over magnesium sulfate and distilled under vacuum at room temperature (35 °C). Analytical grade solvents were used in all reactions. The ^1H NMR spectra were recorded on a Bruker WH-500 NMR spectrometer in CDCl_3 and chemical shifts are relative to external TMS. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were obtained on a Varian FT-80A NMR spectrometer operating at 32.2 MHz. Chemical shifts are relative to external 85% H_3PO_4 , more positive shifts represent deshielding. The errors in J and δ ^{31}P are ± 2 Hz and ± 2 ppm, respectively. Melting points were determined in capillary tubes and are uncorrected.

Catalytic reactions were carried out at 343 K using a method analogous to that we previously reported [1]. High pressure reactions were carried out in an

TABLE I. Physical and Analytical Data for $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ Complexes

Complex	Recrystallization solvent (% Yield)	Melting point (°C)	Analyses, found (calc.) (%)		
			C	H	S
$[\text{Pt}_2(\mu\text{-SEt})(\mu\text{-Cl})\text{Cl}_2(\text{PEt}_3)_2]$	CHCl_3 (60)	255 (dec.)	21.10 (21.18)	4.45 (4.44)	4.00 (4.04)
$[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PEt}_3)_2]$	CHCl_3 (58)	265–67 (dec.)	22.29 (22.30)	4.80 (4.62)	4.25 (3.97)
$[\text{Pt}_2(\mu\text{-SEt})(\mu\text{-Cl})\text{Cl}_2(\text{PPr}^n_3)_2]$	$\text{C}_6\text{H}_6/\text{EtOH}/$ hexane (90)	212–214	27.55 (27.35)	5.55 (5.39)	3.68 (3.65)
$[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PPr}^n_3)_2]$	$\text{CHCl}_3/\text{EtOH}$ (82)	217–218	28.67 (28.27)	5.87 (5.54)	3.43 (3.59)
$[\text{Pt}_2(\mu\text{-SEt})(\mu\text{-Cl})\text{Cl}_2(\text{PBu}^n_3)_2]$	$\text{EtOH}/$ hexane (83)	139–140	32.27 (32.45)	6.37 (6.18)	3.27 (3.33)
$[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PBu}^n_3)_2]$	$\text{EtOH}/$ hexane (87)	137–138	32.87 (33.22)	6.30 (6.30)	3.18 (3.28)
$[\text{Pt}_2(\mu\text{-SEt})(\mu\text{-Cl})\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$	$\text{CHCl}_3/\text{EtOH}$ (86)	206–209	26.09 (25.92)	3.45 (3.26)	3.90 (3.84)
$[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$	$\text{CHCl}_3/\text{EtOH}$ (80)	242 (dec.)	26.86 (26.91)	3.68 (3.45)	3.71 (3.78)

autoclave. Gas chromatographic analyses were performed on a 6 X 0.25 inch (outside diameter) carbowax 20% column by comparison with known standards. Integration of the ^1H NMR spectra $\delta(-\text{CH}=\text{CH}_2)$ versus $\delta(-\text{CH}_2-\text{CH}_3)$ allowed confirmation and definite identification of products.

Preparation of $[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$

To the benzene solution (15 ml) of $[\text{Pt}_2(\mu\text{-SPr}^i)_2\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$ (265 mg, 0.3 mmol), a solution of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PMe}_2\text{Ph})_2]$ (242 mg, 0.3 mmol) was added and the reaction mixture was heated under reflux with stirring for 5 h. A cream colored precipitate separated out which after cooling was dried under vacuum and recrystallized from chloroform/ethanol mixture as a pale yellow crystalline solid in 88% yield.

Similarly other complexes were prepared and pertinent data are given in Table I.

Reaction of *Sym-trans*- $[\text{Pt}_2(\mu\text{-SPr}^i)_2\text{Cl}_2(\text{PPr}^n_3)_2]$ with $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPr}^n_3)_2]$ in C_6D_6 at Room Temperature

Solutions of *sym-trans*- $[\text{Pt}_2(\mu\text{-SPr}^i)_2\text{Cl}_2(\text{PPr}^n_3)_2]$ (54 mg, 0.06 mmol) and $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPr}^n_3)_2]$ in C_6D_6 were mixed in an NMR tube. The solution thus obtained was studied by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

Reaction of $[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ ($\text{R} = \text{Pr}^n, \text{Bu}^n$) with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$

To a CDCl_3 solution (4 ml) of $[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PPr}^n_3)_2]$ (104 mg, 0.12 mmol) excess of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (200 mg, 0.89 mmol) was added and stirred for 2 h. Unreacted $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was filtered

off. Filtrate was studied by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. A similar reaction was carried out when $\text{R} = \text{Bu}^n$.

Reaction of $[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ with Pyridine

A solution of pyridine (0.8 ml) in CDCl_3 was added to a solution of $[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ ($\text{R} = \text{Pr}^n$ or Bu^n) (70–90 mg, 0.07–0.1 mmol) in an NMR tube and progress of the reaction was examined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

A similar reaction with triphenylphosphine was also carried out.

Results and Discussion

Halogen-bridged dinuclear platinum(II) complexes $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PEt}_3, \text{PPr}^n_3, \text{PBu}^n_3, \text{PMe}_2\text{Ph}$) react with mercapto-bridged dinuclear platinum(II) complexes $[\text{Pt}_2(\mu\text{-SR}')_2\text{Cl}_2(\text{PR}_3)_2]$ ($\text{R}' = \text{Et}, \text{Pr}^i$) in 1:1 stoichiometry in refluxing benzene to afford dinuclear platinum(II) complexes containing both chloro- and mercapto-bridges, $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$. The reactions were slow in benzene at room temperature and took 3–5 days for completion; however in chloroform they were relatively fast and completed in a few hours (4–8 h). Thus the progress of the reaction of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PR}_3)_2]$ with *sym-trans*- $[\text{Pt}_2(\mu\text{-SPr}^i)_2\text{Cl}_2(\text{PR}_3)_2]$ in benzene- d_6 was monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum obtained immediately after mixing the benzene solutions containing equimolar amounts of *sym-trans*- $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPr}^n_3)_2]$ and *sym-trans*- $[\text{Pt}_2(\mu\text{-SPr}^i)_2\text{Cl}_2(\text{PPr}^n_3)_2]$ at room

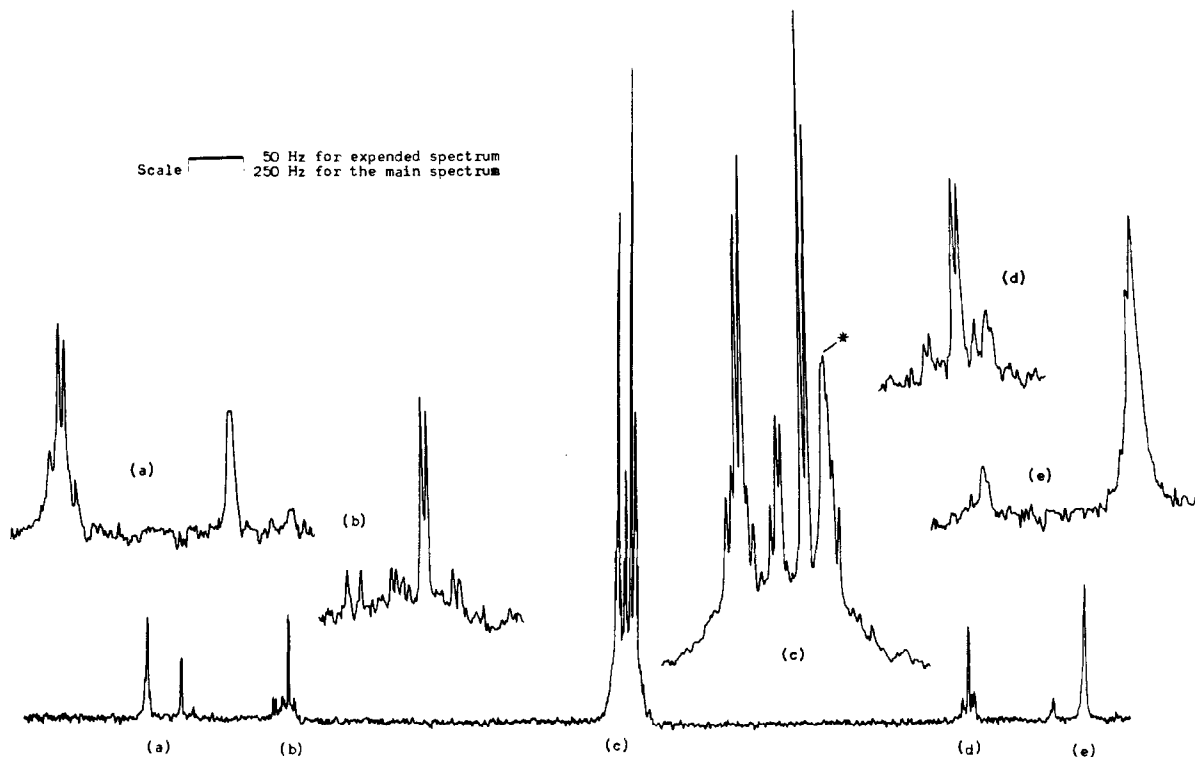


Fig. 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a 1:1 mixture of $[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{PPr}^n_3)_2]$ and $[\text{Pt}_2(\mu\text{-SPr}^i)_2\text{Cl}_2(\text{PPr}^n_3)_2]$ recorded in C_6D_6 immediately after mixing at room temperature. Expansions for the regions a, b, c, d and e are shown in the figure and labelled respectively. * Due to $[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PPr}^n_3)_2]$.

temperature displayed resonances attributable to two molecular species, none of them belonging to the starting dimers. Of the two species, the one present in small amounts can be identified as the redistribution product, $\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PPr}^n_3)_2$ (*vide infra*). The other one was a reaction intermediate with a complex $^{31}\text{P}\{^1\text{H}\}$ NMR pattern. The resonances due to this intermediate gradually reduced in their intensities and finally disappeared after 72 h from the spectrum leaving only $[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})\text{Cl}_2(\text{PPr}^n_3)_2]$ as the final product.

Although a number of mechanisms have been proposed [15–17] for the redistribution reactions of transition metal complexes, the observed $^{31}\text{P}\{^1\text{H}\}$ NMR pattern (Fig. 1) due to the intermediate clearly demonstrates a bimolecular mechanism. Thus a tetranuclear species is formed by the interaction of dichloro- and dimercapto-bridged dinuclear platinum-(II) complexes as an intermediate (Fig. 2). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum due to this species displayed two main lines both showing platinum couplings. One of them can be attributed to the interacting chloro-bridged dimer ($\delta \text{Pt-P}$, -8.8 (doublet, $^4J(\text{P-P}') = \sim 5$ Hz); $^1J(\text{Pt-P})$, 4231 Hz, $^3J(\text{Pt-P})$, 19 Hz; $^4J(\text{P-P})$, < 2 Hz) and the other one to the mercapto-bridged dimer ($\delta \text{Pt-P}$, -11.8 (doublet, $^4J(\text{P-P}') = \sim 5$ Hz); $^1J(\text{Pt-P})$, 3073 Hz; $^3J(\text{Pt-P})$, 47 Hz, $^4J(\text{P-P}$

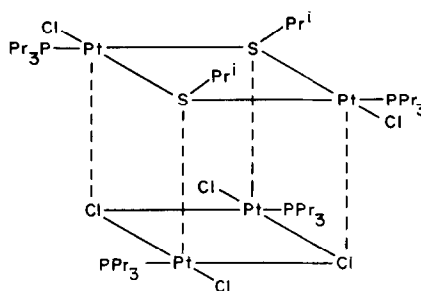


Fig. 2. Tetranuclear reaction intermediate $[\text{Pt}_4(\mu\text{-SPr}^i)_2(\mu\text{-Cl})_2\text{Cl}_4(\text{PPr}^n_3)_2]$.

P), ~ 4 Hz) of a tetranuclear species. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum due to this tetranuclear intermediate showed the following interesting features:

(i) Shielding of the ^{31}P NMR chemical shifts for the two interacting dimers of the tetranuclear species has been observed compared to the free dimers.

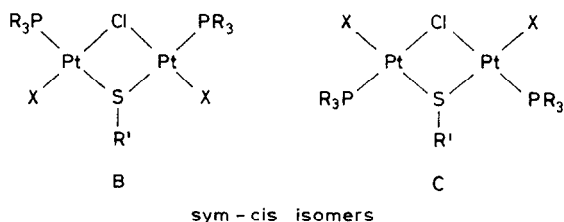
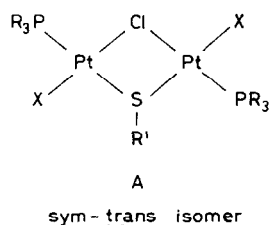
(ii) Small couplings ($^4J(\text{P-P}') = \sim 5$ Hz) between the phosphorus nuclei of the mercapto-bridged dimer and the chloro-bridged dimer have been observed.

(iii) The $^1J(\text{Pt-P})$, $^3J(\text{Pt-P})$ and $^4J(\text{P-P})$ have been reduced for the mercapto-bridged dimer while

for chloro-bridged dimer the magnitude of these couplings has increased*. The changes in coupling constants reflect the changes in bonding [18]. Accordingly the bridging Pt—Cl bond *trans* to phosphine in the chloro-bridged dimer and the Pt—SP^ri bond *trans* to chloride in mercapto-bridged dimer of the tetranuclear intermediate weaken and finally after their cleavage afford stable dinuclear platinum(II) complexes containing both chloro- and mercapto-bridges. Disproportionation of such a tetranuclear species (Fig. 2) would yield sym-*cis* isomer. The observed sym-*cis* configuration for chloro-mercapto-bridged complexes supports the above proposal. Although ³¹P NMR data support the existence of tetranuclear intermediate, ¹⁹⁵Pt NMR and X-ray data would prove its nature unambiguously.

A similar tetranuclear intermediate has been proposed for the exchange of 2-methylallylpalladium groups in thiocyno- and halogeno-bridged [19] dimers of the type $[\eta^3\text{-MeC}_3\text{H}_3\text{PdX}]_2$ (X = Cl, I, SCN) and for the formation of mixed metal complexes [17, 20] $[\text{PdPtCl}_4(\text{PBU}_3)_2]$ from $[\text{Pd}_2\text{Cl}_4(\text{PBU}_3)_2]$ and $[\text{Pt}_2\text{Cl}_4(\text{PBU}_3)_2]$.

The mixed chloro-mercapto-bridged dinuclear platinum(II) complexes may exist in the following (A–C) three configurations which can be identified by their ¹H and ³¹P NMR spectra.



The sym-*cis* configurations **B** and **C** can be differentiated by the magnitude of ¹J(Pt—P), in **B** phosphine ligands are *trans* to a high *trans* influencing [21] group SR' (¹J(Pt—P) would be ~3100 Hz) [1] while in **C** they are *trans* to a bridging chloride (¹J(Pt—P) would be ~3900 Hz) [2, 17, 22]. For the

sym-*trans* isomer **A** two PR₃ resonances would appear in the ³¹P NMR spectra with two different ¹J(Pt—P) values, one *trans* to SR' (~3100 Hz) and another *trans* to chloride (~3900 Hz). The ³¹P NMR spectra of our complexes displayed a single Pt—P resonance with ¹J(Pt—P) ~4100 Hz clearly indicating configuration **C** in solution. The ³J(Pt—P) values are surprisingly small (~6 Hz) compared to those of either of the dimers sym-*trans*-[Pt₂(μ-Cl)₂Cl₂(PR₃)₂] [22] or sym-*cis*-[Pt₂(μ-SR')₂Cl₂(PR₃)₂] [1] and could be resolved in a few cases only.

The ¹H NMR spectra of these complexes displayed a single type of SR' (R' = Et or Prⁱ) resonance. Couplings between SR' protons and ³¹P for ¹⁹⁵Pt nuclei were not observed for our complexes, although such couplings have been reported previously [23, 24] when R' = Me. It has also been reported [23, 24] that a methyl thio group *cis* to phosphine ligand did not show ⁴J(P—H) and appeared as a singlet while the SMe group *trans* to phosphine showed couplings with phosphorus nucleus (~5 Hz). The [Pt₂(μ-SR')-(μ-Cl)Cl₂(PMe₂Ph)₂] (R' = Et or Prⁱ) displayed two doublets for P—Me protons indicating that these complexes are not planar; presumably the lack of symmetry at Pt—P axis is leading to non-equivalence of the methyl group on each phosphine [25]. The ¹H and ³¹P{¹H} NMR spectral data for these complexes are given in Table II.

The dimeric complexes [Pt₂(μ-SP^ri)(μ-Cl)Cl₂(PR₃)₂] (R = Prⁿ or Buⁿ) react with excess SnCl₂·2H₂O in chloroform via a simple insertion of SnCl₂ into terminal Pt—Cl bonds to yield the corresponding trichlorostannate complexes, [Pt₂(μ-SP^ri)(μ-Cl)-(SnCl₃)₂(PR₃)₂]. The trichlorostannate complexes exist exclusively in sym-*trans* configuration **A**, as two resonances with two different values of ¹J(Pt—P) appeared in the ³¹P{¹H} NMR spectra. The upfield resonance with a higher value of ¹J(Pt—P) 3705 ± 1 Hz is assigned for the phosphine ligand *trans* to bridging chloride. The other one appearing at a downfield with a smaller value of ¹J(Pt—P) is due to the phosphine ligand *trans* to SR'. The spectra showed following remarkable features:

(i) The ³J(Pt—P) for the ligand *trans* to Cl is smaller (11.5 Hz) than that of the ligand *trans* to SR' (~33 Hz).

(ii) The ⁴J(P—P) for the ligand *trans* to Cl is slightly higher than that of the *trans* SR' ligand. It appears that ³J(Pt—P) and ⁴J(P—P) couplings take place via two independent routes (one via Cl and another via SR') and their magnitudes reflect the bond strength; the Pt—Cl—Pt in chloro-mercapto-bridged complexes being slightly longer than the one observed in [Pt₂(μ-Cl)₂Cl₂(PR₃)₂].

A few bridge cleavage reactions of [Pt₂(μ-SR')-(μ-Cl)Cl₂(PR₃)₂] by neutral donor ligands have also been investigated. Pyridine slowly reacts with [Pt₂(μ-SP^ri)(μ-Cl)Cl₂(PR₃)₂] (R = Prⁿ or Buⁿ) in chloro-

**trans*-[Pt₂(μ-Cl)₂Cl₂(PPrⁿ)₂] δ(Pt—P), -7.75, ¹J(Pt—P) 3891 Hz, ³J(Pt—P) 19 Hz, ⁴J(P—P) <2 Hz; *trans*-[Pt₂(μ-SP^ri)₂Cl₂(PPrⁿ)₂] δ(Pt—P) -8.4, ¹J(Pt—P) 3136 Hz, ³J(Pt—P) 51 Hz, ⁴J(P—P) 12 Hz. Spectra were recorded in C₆D₆.

TABLE II. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR Data $[\text{Pt}_2(\mu\text{-SR})(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ Complexes in CDCl_3 at Room Temperature

Complex	³¹ P{ ¹ H} NMR data			¹ H NMR data ^f		
	δ(Pt–P) (ppm)	¹ J(Pt–P) (Hz)	² J(Pt–Pt) (Hz)	SR' Protons		PR ₃ Protons
				S–CH(CH ₃)	S–C–CH ₃	
[Pt ₂ (μ–SEt)(μ–Cl)Cl ₂ (PEt ₃) ₂]	5.0	4057	–	2.97(q, 7.4)	1.46(t, 7.4)	P–CH ₂ , 1.93(m) P–C–CH ₃ , 1.19(m)
[Pt ₂ (μ–SP [†])(μ–Cl)Cl ₂ (PEt ₃) ₂]	0.7	4088	–	3.66(m)	1.51(d, 6.8)	P–CH ₂ , 1.97(m) P–C–CH ₃ , 1.19(m)
[Pt ₂ (μ–SEt)(μ–Cl)Cl ₂ (PPt ⁿ ₃) ₂]	–12.2	4034	399	2.95(q, 7.3)	1.44(t, 7.4)	1.06(t, 7.2), 1.66(m), 1.88(m)
[Pt ₂ (μ–SP [†])(μ–Cl)Cl ₂ (PPt ⁿ ₃) ₂]	–13.4	4066	284	3.63(m)	1.50(d, 6.7)	1.07(t, 7.4), 1.66(m), 1.90(m)
[Pt ₂ (μ–SEt)(μ–Cl)Cl ₂ (PBu ⁿ ₃) ₂]	–11.2	4032	424	2.96(q, 7.3)	e	0.96(t, 7.3), 1.46(m), 1.58(m), 1.90(m)
[Pt ₂ (μ–SP [†])(μ–Cl)Cl ₂ (PBu ⁿ ₃) ₂]	–12.6	4065	321	3.63(m)	e	0.96(t, 7.2), 1.46(m), 1.59(m), 1.92(m)
[Pt ₂ (μ–SEt)(μ–Cl)Cl ₂ (PMe ₂ Ph) ₂]	–23.8	4149	–	2.47(q, 7.3)	1.02(t, 7.3)	P–Me, 2.48(d, 7.3); 2.45(d, 7.2) P–Ph, 7.68(m), 7.44(m)
[Pt ₂ (μ–SP [†])(μ–Cl)Cl ₂ (PMe ₂ Ph) ₂]	–26.8	4187	326	3.34(m)	1.14(d, 6.8)	P–Me, 1.91(d, 12.0); 1.83(d, 12) P–Ph, 7.72(m), 7.43(m)
[Pt ₂ (μ–SP [†])(μ–Cl)(SnCl ₃) ₂ (PPt ⁿ ₃) ₂]	–5.1 ^a –3.5 ^b	3706 2869	–	–	–	–
[Pt ₂ (μ–SP [†])(μ–Cl)(SnCl ₃) ₂ (PBu ⁿ ₃) ₂]	–4.1 ^c –2.3 ^d	3704 2866	–	–	–	–

^a *trans* to Cl; ³ $J(\text{Pt}-\text{P})$ 11.5 Hz; ⁴ $J(\text{P}-\text{P})$ 3.9 Hz; ² $J(^{195}\text{Pt}-^{119}\text{Sn})$ 263 Hz; ² $J(^{195}\text{Pt}-^{117}\text{Sn})$ 253 Hz. ^b *trans* to SP^i ; ³ $J(\text{Pt}-\text{P})$ 33 Hz; ⁴ $J(\text{P}-\text{P})$ 3.7 Hz; ² $J(^{195}\text{Pt}-^{119}\text{Sn})$ 230 Hz; ² $J(^{195}\text{Pt}-^{117}\text{Sn})$ 220 Hz. ^c *trans* to Cl; ³ $J(\text{Pt}-\text{P})$ 11.5 Hz; ⁴ $J(\text{P}-\text{P})$ 3.9 Hz; ² $J(^{195}\text{Pt}-^{119}\text{Sn})$ 259 Hz; ² $J(^{195}\text{Pt}-^{117}\text{Sn})$ 251 Hz. ^d *trans* to SP^i ; ³ $J(\text{Pt}-\text{P})$ 33 Hz; ⁴ $J(\text{P}-\text{P})$ 3.6 Hz; ² $J(^{195}\text{Pt}-^{119}\text{Sn})$ 227 Hz; ² $J(^{195}\text{Pt}-^{117}\text{Sn})$ 218 Hz. ^e Merged in phosphine proton resonances. ^f Values given in parenthesis represent coupling constants in Hz; m = multiplet, d = doublet, q = quartet, t = triplet.

TABLE III. Catalytic Activity of *cis*-[Pt₂(μ-SR')(μ-Cl)X₂(PR₃)₂] Complexes in the Hydrogenation of Styrene in Chloroform^a

Complex	<i>n</i> -SnCl ₂ ·2H ₂ O <i>n</i> =	<i>n</i> Styrene <i>n</i> =	Turnover number ^b
[Pt ₂ (μ-SPr ⁱ)(μ-Cl)Cl ₂ (PPr ⁿ ₃) ₂]	0	5986	18
	1	6279	27
	2	6325	32
	5	5355	348
	10	6889	1221
[Pt ₂ (μ-SPr ⁱ)(μ-Cl)(SnCl ₃) ₂ (PPr ⁿ ₃) ₂]	0	8157	49
[Pt ₂ (μ-SEt)(μ-Cl)Cl ₂ (PPr ⁿ ₃) ₂]	11	4140	748
[Pt ₂ (μ-SPr ⁱ)(μ-Cl)Cl ₂ (PEt ₃) ₂]	11	4490	724
[Pt ₂ (μ-SPr ⁱ)(μ-Cl)Cl ₂ (PBu ⁿ ₃) ₂]	11	6977	1322
[Pt ₂ (μ-SPr ⁱ)(μ-Cl)Cl ₂ (PMe ₂ Ph) ₂]	10	6910	271

^aCatalysis by the named complex in 30 ml chloroform containing ~10 ml styrene at 343 K under 800 psi of hydrogen. ^bMoles of styrene converted to ethylbenzene per mole of platinum (*i.e.*, half a dimeric unit) per hour.

form to yield *trans*-[PtCl₂(PR₃)py] and [Pt₂(μ-SPrⁱ)₂Cl₂(PR₃)₂] (sym-*trans* isomer when R = Buⁿ and a mixture of sym-*cis* and sym-*trans* isomers when R = Prⁿ). These reactions were monitored by ³¹P{¹H} NMR and products formed were identified by comparison of the observed chemical shifts and coupling constants with those reported previously [1, 18–22]. Excess pyridine cleaves the bridge slowly in 10 to 15 h and generates mononuclear complexes *trans*-[PtCl₂(PR₃)(py)] (**1**) (R = Prⁿ, δ (Pt–P), –15.8; ¹J(Pt–P) 3355 Hz; R = Buⁿ, δ (Pt–P) –24.8, ¹J(Pt–P) 3362 Hz) [22, 26] and [Pt(SPⁱ)Cl(PR₃)(py)] in which the phosphine ligand is *trans* to the halide, (**IIa**) or to the pyridine ligand (**IIb**). The complex [Pt(SPⁱ)Cl(PR₃)(py)] slowly rearranges, probably due to lack of symmetry [27–29], to more stable dinuclear mercapto-bridged platinum complexes. Thus the ³¹P{¹H} NMR spectrum of the reaction mixture containing [Pt₂(μ-SPrⁱ)(μ-Cl)Cl₂(PR₃)₂] and excess pyridine after 20 h displayed five resonances due to **I**, **IIa**, **IIb** and sym-*cis*- and sym-*trans*-[Pt₂(μ-SPrⁱ)₂Cl₂(PR₃)₂] (**III**). The mononuclear complex **IIb** appears to contain the phosphine ligand *trans* to pyridine (δ (Pt–P), –6.55 ppm) rearranged relatively faster than **IIa** to the sym-*cis* isomer of **III** and disappeared from the spectrum in less than 40 h. The **IIa** phosphine ligand *trans* to chloride (δ (Pt–P), –10.9 ppm; ¹J(Pt–P) 3607 Hz), however, rearranged slowly to the sym-*trans* isomer of **III** and took about three weeks for complete conversion to **III** (sym-*trans*). Thus after three weeks only three resonances due to **I** and sym-*cis* and sym-*trans* **III** (sym-*cis* **III**, δ (Pt–P), –8.45; ¹J(Pt–P) 3156 Hz, ³J(Pt–P) 16 Hz; sym-*trans* **III**, δ (Pt–P), –6.0, ¹J(Pt–P) 3136 Hz, ³J(Pt–P) 51 Hz, ⁴J(P–P) 12 Hz) appeared in the spectrum.

The reaction of [Pt₂(μ-SPrⁱ)(μ-Cl)Cl₂(PBuⁿ₃)₂] with excess pyridine proceeds similarly except the intermediate complex **IIb** does not form and hence

the sym-*cis*-[Pt₂(μ-SPrⁱ)₂Cl₂(PBuⁿ₃)₂] is absent in the final products. The ³¹P{¹H} NMR spectrum of the reaction after 24 h displayed only three resonances due to **I**, **IIa** (R = Buⁿ, δ (Pt–P), –17.95, ¹J(Pt–P) 3617 Hz) and sym-*trans*-[Pt₂(μ-SPrⁱ)₂Cl₂(PBuⁿ₃)₂] (δ (Pt–P) –8.4, ¹J(Pt–P) 3142 Hz, ³J(Pt–P) 50 Hz, ⁴J(P–P) 12 Hz. **IIa** vanishes with time and finally converts to sym-*trans*-[Pt₂(μ-SPrⁱ)₂Cl₂(PBuⁿ₃)₂].

Triphenylphosphine also reacts with sym-*cis*-[Pt₂(μ-SPrⁱ)(μ-Cl)Cl₂(PPrⁿ₃)₂] to give a complex mixture of mononuclear platinum(II) complexes, containing *cis*-[PtCl₂(PPr₃)(PPh₃)] (δ (Pt–P), –9.0, ¹J(Pt–P) 3368 Hz, ²J(P–P) 15.6 Hz; δ (Pt–P) 6.8, ¹J(Pt–P) 3822 Hz, ²J(P–P) 15.6 Hz), *cis*-[PtCl₂(PPr₃)₂], *cis*-[PtCl₂(PPh₃)₂], *trans*-[PtCl(SPⁱ)(PPr₃)₂] as assessed from the known spectra [27–30] along with some other products in small concentrations.

From the above bridge cleavage reactions it is clear that the bridge in [Pt₂(μ-SR')(μ-Cl)Cl₂(PR₃)₂] is of intermediate stability between the very reactive halogen-bridge in the tetrachloro complexes and the stable dimercapto complexes. Thus under catalytic conditions the cleavage reactions may generate mixed ligand catalyst precursors, which have been shown [10, 11] to be generally more active. In order to assess the catalytic activity of such complexes, hydrogenation of styrene employing [Pt₂(μ-SR')(μ-Cl)X₂(PR₃)₂] (X = Cl or SnCl₃) in the presence of SnCl₂·2H₂O as a homogeneous catalyst system, has been carried out. The results of catalytic hydrogenation of styrene to ethylbenzene in chloroform are summarised in Table III.

The complex [Pt₂(μ-SPrⁱ)(μ-Cl)Cl₂(PPrⁿ₃)₂] in the absence of SnCl₂·2H₂O showed little catalytic activity in the hydrogenation of styrene in chloroform at 800 psi hydrogen pressure at 343 K which however increased on addition of one or two equivalents of SnCl₂·2H₂O. A sudden increase in

activity has been observed on addition of 5 equivalents of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ which further increased on addition of 10 equivalents of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. If the active precursor in these reactions is $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})(\text{SnCl}_3)_2(\text{PR}_3)_2]$ (*vide supra*) the catalytic activity of the preformed precursor and the precursor generated *in situ* on addition of two or more equivalents of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ must be comparable. This was so when only two equivalents of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were added. However the activity of a catalyst formed *in situ* by the addition of 5 or 10 equivalents of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was far greater. Evidently, a simple catalyst precursor such as $[\text{Pt}_2(\mu\text{-SPr}^i)(\mu\text{-Cl})(\text{SnCl}_3)_2(\text{PPr}^n_3)_2]$ is not the sole product under operating conditions. It has been suggested [11] that a multi-component system is involved in the generation of the catalytic cycle.

In order to examine the effect of varying the ligands, PR_3 or SR' in complexes $[\text{Pt}_2(\mu\text{-SR}')(\mu\text{-Cl})\text{Cl}_2(\text{PR}_3)_2]$ on the catalytic activity, we have tested the activity of a range of complexes. The effect which a PR_3 ligand exerts upon the reactions of its complexes can often be attributed to either steric or electronic effects or to a combination of both [31]. From the cone angle data of Tolman [31], which give a rough measure of relative size, the steric effects of our chosen phosphines lie in the order: $\text{PBu}^n_3 \sim \text{PPr}^n_3 \sim \text{PEt}_3 > \text{PMe}_2\text{Ph}$ and so their basicities, which describe electronic effects.

The data in Table III indicate that hydrogenation of styrene is favoured by ligands which are more basic and bulky in nature. Thus the highest turnover number (1322) is observed by the complex containing PBu^n_3 . It has been shown previously [11] that the catalytic activity increases with the electron donating ability of the PR_3 ligand. The effect of the SR' ligand on activity is also evident from the data shown in Table III. The sterically demanding R' group such as Pr^i on the SR' ligand favoured hydrogenation of styrene.

Acknowledgements

Thanks are expressed to Dr. R. M. Iyer, Head of the Chemistry Division for his interest in this work and to Mr. N. V. Ayer for his help in gas chromatographic analyses. Thanks are also due to the National NMR Facility at TIFR for recording the ^1H NMR

spectra and the Analytical chemistry division, BARC for microanalyses.

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