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

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Abstract

The reaction of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ with sym-*cis*- and/or sym-*trans*-$[Pt_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ (R' = Et or Pr^i, PR_3 = PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph) in benzene results in the formation of $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ and involves a bimolecular intermediate. The complexes $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ exist in sym-*cis* configuration where phosphine ligands are *trans* to bridging chloride. Their reactions with excess $SnCl_2 \cdot 2H_2O$ in chloroform give sym-*trans*-$[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)(SnCl_3)_2(PR_3)_2]$. Bridge cleavage reactions with various donor ligands have also been investigated. The catalytic activity of the $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]/SnCl_2 \cdot 2H_2O$ system in styrene hydrogenation has been found to be appreciably effective.

Introduction

The geometry [1–5] of dinuclear platinum(II) complexes of the type $[Pt_2(\mu\text{-}X)_2Y_2L_2]$ 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 reactivy of these complexes. For example, the chloro-bridged complexes, when X = Y = Cl, react readily with weak donor ligands such as ethylene to give mono-nuclear complexes of the type $[PtCl_2(CH_2{=}CH_2)L]$ whereas the mercapto-bridged complexes, when X = SR (R = alkyl or aryl), Y = Cl and L = PR_3, are stable and do not undergo bridge cleavage reactions [1].

Mono-nuclear platinum(II) phosphine complexes, in the presence of $SnCl_2 \cdot 2H_2O$ as co-catalyst, have been used as homogeneous catalysts [6–12] in hydrogenation and hydroformylation reactions. The mixed ligand complexes, $[PtCl_2(PR_3)L]$ (L = thio-ether, amine; R = aryl) in the presence of $SnCl_2 \cdot 2H_2O$ were found to be much more active than the corresponding *cis*-$[PtCl_2L_2]/SnCl_2 \cdot 2H_2O$ or $[PtCl_2(PR_3)_2]/SnCl_2 \cdot 2H_2O$ catalyst precursors [1, 11]. Hydrogenation reactions employing dimeric platinum(II) complexes as a homogeneous catalyst are scanty. The homogeneous catalytic systems $[Pt_2(\mu\text{-}X)_2Cl_2(PR_3)_2]/SnCl_2 \cdot 2H_2O$ (X = 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, $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ in the homogeneous hydrogenation of olefins as they are derived by the partial removal of L from the complexes $[PtCl_2(L)(PR_3)]$. In order to investigate the stereochemistry and reactivity of dinuclear platinum(II) complexes containing chloro–mercapto bridges, we have prepared $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ and studied their chemical reactivity, spectroscopic properties and their catalytic activity in homogeneous hydrogenation of styrene as a reference system.

Experimental

The complexes $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ (PR_3 = PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph) [13, 14] and $[Pt_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ (R' = 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 $^{31}P\{^1H\}$ 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

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TABLE I. Physical and Analytical Data for $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ Complexes

Complex	Recrystallization solvent (% Yield)	Melting point (°C)	Analyses, found (calc.) (%)		
			C	H	S
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PEt_3)_2]$	$CHCl_3$ (60)	255 (dec.)	21.10 (21.18)	4.45 (4.44)	4.00 (4.04)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PEt_3)_2]$	$CHCl_3$ (58)	265–67 (dec.)	22.29 (22.30)	4.80 (4.62)	4.25 (3.97)
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PPr^n_3)_2]$	C_6H_6/EtOH/ hexane (90)	212–214	27.55 (27.35)	5.55 (5.39)	3.68 (3.65)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n_3)_2]$	$CHCl_3$/EtOH (82)	217–218	28.67 (28.27)	5.87 (5.54)	3.43 (3.59)
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PBu^n_3)_2]$	EtOH/ hexane (83)	139–140	32.27 (32.45)	6.37 (6.18)	3.27 (3.33)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PBu^n_3)_2]$	EtOH/ hexane (87)	137–138	32.87 (33.22)	6.30 (6.30)	3.18 (3.28)
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PMe_2Ph)_2]$	$CHCl_3$/EtOH (86)	206–209	26.09 (25.92)	3.45 (3.26)	3.90 (3.84)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PMe_2Ph)_2]$	$CHCl_3$/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 $\delta(-CH=CH_2)$ *versus* $\delta(-CH_2-CH_3)$ allowed confirmation and definite identification of products.

Preparation of $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PMe_2Ph)_2]$

To the benzene solution (15 ml) of $[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PMe_2Ph)_2]$ (265 mg, 0.3 mmol), a solution of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PMe_2Ph)_2]$ (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-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PPr^n_3)_2]$ with $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPr^n_3)_2]$ in C_6D_6 at Room Temperature

Solutions of sym-*trans*-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PPr^n_3)_2]$ (54 mg, 0.06 mmol) and $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPr^n_3)_2$ in C_6D_6 were mixed in an NMR tube. The solution thus obtained was studied by $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PR_3)_2]$ ($R = Pr^n$, Bu^n) with $SnCl_2 \cdot 2H_2O$

To a $CDCl_3$ solution (4 ml) of $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n_3)_2]$ (104 mg, 0.12 mmol) excess of $SnCl_2 \cdot 2H_2O$ (200 mg, 0.89 mmol) was added and stirred for 2 h. Unreacted $SnCl_2 \cdot 2H_2O$ was filtered off. Filtrate was studied by $^{31}P\{^1H\}$ NMR spectroscopy. A similar reaction was carried out when $R = Bu^n$.

Reaction of $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PR_3)_2]$ with Pyridine

A solution of pyridine (0.8 ml) in $CDCl_3$ was added to a solution of $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PR_3)_2]$ ($R = Pr^n$ or Bu^n) (70–90 mg, 0.07–0.1 mmol) in an NMR tube and progress of the reaction was examined by $^{31}P\{^1H\}$ NMR spectroscopy.

A similar reaction with triphenylphoshine was also carried out.

Results and Discussion

Halogen-bridged dinuclear platinum(II) complexes $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ ($PR_3 = PEt_3$, PPr^n_3, PBu^n_3, PMe_2Ph) react with mercapto-bridged dinuclear platinum(II) complexes $[Pt_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ ($R' = Et$, Pr^i) in 1:1 stoichiometry in refluxing benzene to afford dinuclear platinum(II) complexes containing both chloro- and mercapto-bridges, $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$. 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 $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ with sym-*trans*-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PR_3)_2]$ in benzene-d_6 was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum obtained immediately after mixing the benzene solutions containing equimolar amounts of sym-*trans*-$[Pt_2(\mu\text{-}Cl)_2Cl_2(PPr^n_3)_2]$ and sym-*trans*-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PPr^n_3)_2]$ at room

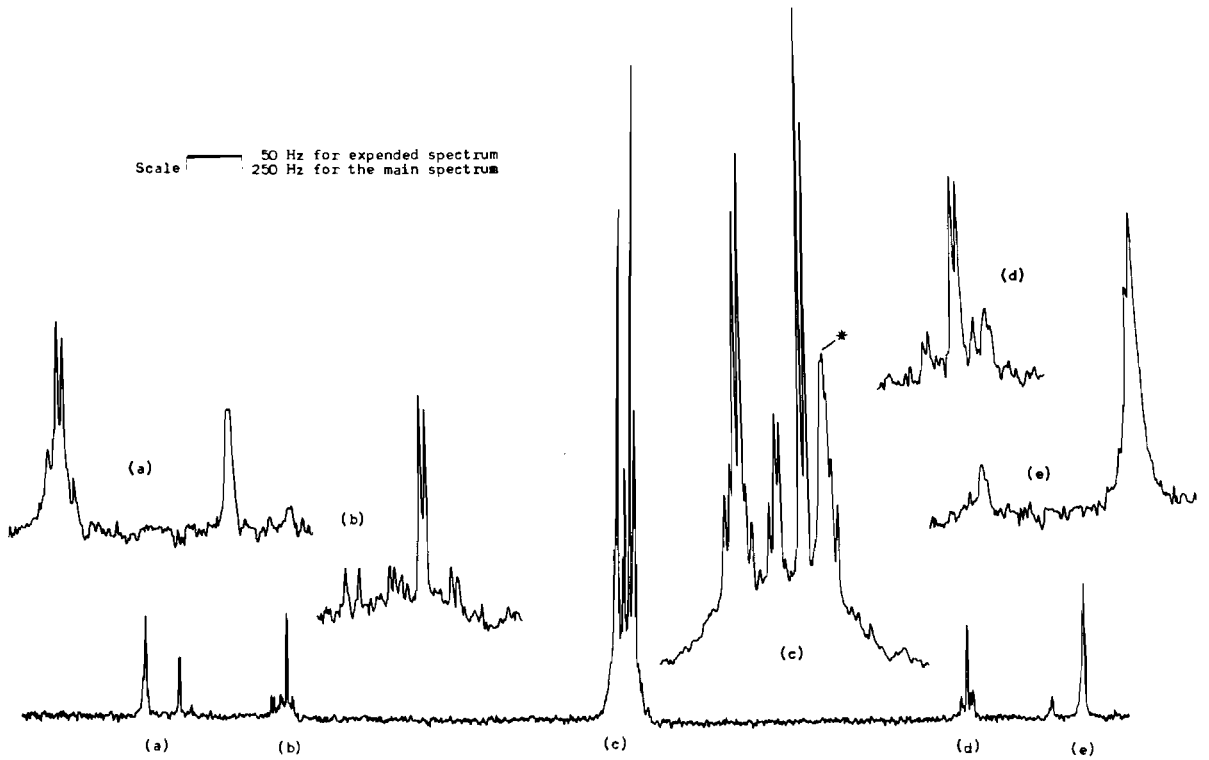


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of a 1:1 mixture of $[Pt_2(\mu\text{-}Cl)_2Cl_2(PPr^n{}_3)_2]$ and $[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PPr^n{}_3)_2]$ recorded in C_6D_6 immediately after mixing at room temperature. Expansions for the regions a, b, c, d and e are shown in the figure and labelled respectively. *Due to $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$.

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, $Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$ (*vide infra*). The other one was a reaction intermediate with a complex $^{31}P\{^1H\}$ NMR pattern. The resonances due to this intermediate gradually reduced in their intensities and finally disappeared after 72 h from the spectrum leaving only $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$ as the final product.

Although a number of mechanisms have been proposed [15–17] for the redistribution reactions of transition metal complexes, the observed $^{31}P\{^1H\}$ 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 $^{31}P\{^1H\}$ 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 (δ Pt–P, −8.8 (doublet, $^4J(P\text{–}P') \simeq$ ~5 Hz); $^1J(Pt\text{–}P)$, 4231 Hz, $^3J(Pt\text{–}P)$, 19 Hz; $^4J(P\text{–}P)$, <2 Hz) and the other one to the mercapto-bridged dimer (δ Pt–P, −11.8 (doublet, $^4J(P'\text{–}P) \simeq$ ~5 Hz); $^1J(Pt\text{–}P)$, 3073 Hz; $^3J(Pt\text{–}P)$, 47 Hz, $^4J(P\text{–}P)$, ~4 Hz) of a tetranuclear species. The $^{31}P\{^1H\}$ NMR spectrum due to this tetranuclear intermediate showed the following interesting features:

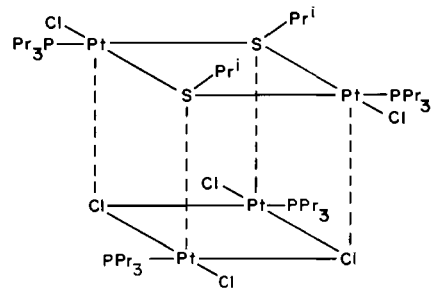


Fig. 2. Tetranuclear reaction intermediate $[Pt_4(\mu\text{-}SPr^i)_2(\mu\text{-}Cl)_2Cl_4(PPr^n{}_3)_2]$.

(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.

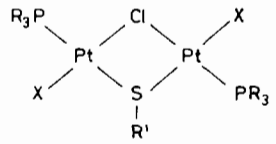
(ii) Small couplings ($^4J(P\text{–}P') \simeq$ ~5 Hz) between the phosphorus nuclei of the mercapto-bridged dimer and the chloro-bridged dimer have been observed.

(iii) The $^1J(Pt\text{–}P)$, $^3J(Pt\text{–}P)$ and $^4J(P\text{–}P)$ 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–SPr^i 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 ^{31}P NMR data support the existence of tetranuclear intermediate, ^{195}Pt NMR and X-ray data would prove its nature unambiguously.

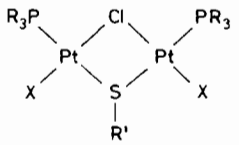
A similar tetranuclear intermediate has been proposed for the exchange of 2-methylallylpalladium groups in thiocyano- and halogeno-bridged [19] dimers of the type $[\eta^3\text{-}MeC_3H_3PdX]_2$ (X = Cl, I, SCN) and for the formation of mixed metal complexes [17, 20] $[PdPtCl_4(PBu_3)_2]$ from $[Pd_2Cl_4(PBu_3)_2]$ and $[Pt_2Cl_4(PBu_3)_2]$.

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 ^{31}P NMR spectra.

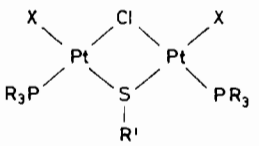


A

sym-trans isomer



B



C

sym-cis isomers

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 PR_3 resonances would appear in the ^{31}P NMR spectra with two different ^1J(Pt–P) values, one *trans* to SR′ (~3100 Hz) and another *trans* to chloride (~3900 Hz). The ^{31}P 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*-$[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$ [22] or sym-*cis*-$[Pt_2(\mu\text{-}SR')_2Cl_2(PR_3)_2]$ [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 Pr^i) resonance. Couplings between SR′ protons and ^{31}P for ^{195}Pt 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 $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PMe_2Ph)_2]$ (R′ = Et or Pr^i) 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 $^{31}P\{^1H\}$ NMR spectral data for these complexes are given in Table II.

The dimeric complexes $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PR_3)_2]$ (R = Pr^n or Bu^n) react with excess $SnCl_2 \cdot 2H_2O$ in chloroform via a simple insertion of $SnCl_2$ into terminal Pt–Cl bonds to yield the corresponding trichlorostannate complexes, $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)(SnCl_3)_2(PR_3)_2]$. The trichlorostannate complexes exist exclusively in sym-*trans* configuration A, as two resonances with two different values of ^1J(Pt–P) appeared in the $^{31}P\{^1H\}$ 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 $[Pt_2(\mu\text{-}Cl)_2Cl_2(PR_3)_2]$.

A few bridge cleavage reactions of $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ by neutral donor ligands have also been investigated. Pyridine slowly reacts with $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PR_3)_2]$ (R = Pr^n or Bu^n) in chloro-

*sym-*trans*-$[Pt_2(\mu\text{-}Cl)_2Cl_2(PPr^n{}_3)_2]$ δ(Pt–P), −7.75, ^1J(Pt–P) 3891 Hz, ^3J(Pt–P) 19 Hz, ^4J(P–P) <2 Hz; *trans*-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PPr^n{}_3)_2]$ δ (Pt–P) −8.4, ^1J(Pt–P) 3136 Hz, ^3J(Pt–P) 51 Hz, ^4J(P–P) 12 Hz. Spectra were recorded in C_6D_6.

TABLE II. ^{1}H and $^{31}P\{^{1}H\}$ NMR Data $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ 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_2)	S–C–CH_3	
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PEt_3)_2]$	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)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PEt_3)_2]$	0.7	4088	–	3.66(m)	1.51(d, 6.8)	P–CH_2, 1.97(m) P–C–CH_3, 1.19(m)
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$	−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)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$	−13.4	4066	284	3.63(m)	1.50(d, 6.7)	1.07(t, 7.4), 1.66(m), 1.90(m)
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PBu^n{}_3)_2]$	−11.2	4032	424	2.96(q, 7.3)	[e]	0.96(t, 7.3), 1.46(m), 1.58(m), 1.90(m)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PBu^n{}_3)_2]$	−12.6	4065	321	3.63(m)	[e]	0.96(t, 7.2), 1.46(m), 1.59(m), 1.92(m)
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PMe_2Ph)_2]$	−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)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PMe_2Ph)_2]$	−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)
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)(SnCl_3)_2(PPr^n{}_3)_2]$	−5.1[a] −3.5[b]	3706 2869	–			
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)(SnCl_3)_2(PBu^n{}_3)_2]$	−4.1[c] −2.3[d]	3704 2866	– –			

[a] *trans* to Cl; ^{3}J(Pt–P) 11.5 Hz; ^{4}J(P–P) 3.9 Hz; $^{2}J(^{195}Pt-^{119}Sn)$ 263 Hz; $^{2}J(^{195}Pt-^{117}Sn)$ 253 Hz. [b] *trans* to SPr^i; ^{3}J(Pt–P) 33 Hz; ^{4}J(P–P) 3.7 Hz, $^{2}J(^{195}Pt-^{119}Sn)$ 230 Hz; $^{2}J(^{195}Pt-^{117}Sn)$ 220 Hz. [c] *trans* to Cl; ^{3}J(Pt–P) 11.5 Hz; ^{4}J(P–P) 3.9 Hz; $^{2}J(^{195}Pt-^{119}Sn)$ 259 Hz; $^{2}J(^{195}Pt-^{117}Sn)$ 251 Hz. [d] *trans* to SPr^i; ^{3}J(Pt–P) 33 Hz; ^{4}J(P–P) 3.6 Hz; $^{2}J(^{195}Pt-^{119}Sn)$ 227 Hz; $^{2}J(^{195}Pt-^{117}Sn)$ 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*-$[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)X_2(PR_3)_2]$ Complexes in the Hydrogenation of Styrene in Chloroform[a]

Complex	n-$SnCl_2 \cdot 2H_2O$ n =	n Styrene n =	Turnover number[b]
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$	0	5986	18
	1	6279	27
	2	6325	32
	5	5355	348
	10	6889	1221
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)(SnCl_3)_2(PPr^n{}_3)_2]$	0	8157	49
$[Pt_2(\mu\text{-}SEt)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$	11	4140	748
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PEt_3)_2]$	11	4490	724
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PBu^n{}_3)_2]$	11	6977	1322
$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PMe_2Ph)_2]$	10	6910	271

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

form to yield *trans*-$[PtCl_2(PR_3)py]$ and $[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PR_3)_2]$ (sym-*trans* isomer when R = Bu^n and a mixture of sym-*cis* and sym-*trans* isomers when R = Pr^n). These reactions were monitored by $^{31}P\{^1H\}$ 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*-$[PtCl_2(PR_3)(py)]$ (**1**) (R = Pr^n– δ Pt–P, –15.8; ^1J(Pt–P) 3355 Hz R = Bu^n δ (Pt–P) –24.8, ^1J(Pt–P) 3362 Hz) [22, 26] and $[Pt(SPr^i)Cl(PR_3)(py)]$ in which the phosphine ligand is *trans* to the halide, (**IIa**) or to the pyridine ligand (**IIb**). The complex $[Pt(SPr^i)Cl(PR_3)(py)]$ slowly rearranges, probably due to lack of symmetry [27–29], to more stable dinuclear mercapto-bridged platinum complexes. Thus the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture containing $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PR_3)_2]$ and excess pyridine after 20 h displayed five resonances due to **I**, **IIa**, **IIb** and sym-*cis*- and sym-*trans*-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PR_3)_2]$ (**III**). The mononuclear complex **IIb** appears to contain the phoshine 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 $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PBu^n{}_3)_2]$ with excess pyridine proceeds similarly except the intermediate complex **IIb** does not form and hence the sym-*cis*-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PBu^n{}_3)_2]$ is absent in the final products. The $^{31}P\{^1H\}$ NMR spectrum of the reaction after 24 h displayed only three resonances due to **I**, **IIa** (R = Bu^n, δ (Pt–P), –17.95, ^1J(Pt–P) 3617 Hz) and sym-*trans*-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PBu^n{}_3)_2]$ (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*-$[Pt_2(\mu\text{-}SPr^i)_2Cl_2(PBu^n{}_3)_2]$.

Triphenylphosphine also reacts with sym-*cis*-$[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$ to give a complex mixture of mononuclear platinum(II) complexes, containing *cis*-$[PtCl_2(PPr_3)(PPh_3)]$ (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*-$[PtCl_2(PPr_3)_2]$, *cis*-$[PtCl_2(PPh_3)_2]$, *trans*-$[PtCl(SPr^i)(PPr_3)_2]$ 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 $[Pt_2[(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ 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 $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)X_2(PR_3)_2]$ (X = Cl or $SnCl_3$) in the presence of $SnCl_2 \cdot 2H_2O$ 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 $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)Cl_2(PPr^n{}_3)_2]$ in the absence of $SnCl_2 \cdot 2H_2O$ 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 $SnCl_2 \cdot 2H_2O$. A sudden increase in

activity has been observed on addition of 5 equivalents of $SnCl_2 \cdot 2H_2O$ which further increased on addition of 10 equivalents of $SnCl_2 \cdot 2H_2O$. If the active precursor in these reactions is $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)(SnCl_3)_2(PR_3)_2]$ (*vide supra*) the catalytic activity of the preformed precursor and the precursor generated *in situ* on addition of two or more equivalents of $SnCl_2 \cdot 2H_2O$ must be comparable. This was so when only two equivalents of $SnCl_2 \cdot 2H_2O$ were added. However the activity of a catalyst formed *in situ* by the addition of 5 or 10 equivalents of $SnCl_2 \cdot 2H_2O$ was far greater. Evidently, a simple catalyst precursor such as $[Pt_2(\mu\text{-}SPr^i)(\mu\text{-}Cl)(SnCl_3)_2(PPr^n{}_3)_2]$ is not the sole product under operating conditions. It has been suggested [11] that a multicomponent 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 $[Pt_2(\mu\text{-}SR')(\mu\text{-}Cl)Cl_2(PR_3)_2]$ 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: $PBu^n{}_3 \sim PPr^n{}_3 \sim PEt_3 > PMe_2Ph$ 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 containining $PBu^n{}_3$. 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.

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