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PREPARATION AND CHARACTERIZATION OF MERCAPTO-BRIDGED DINUCLEAR PLATINUM(II) COMPLEXES. CATALYTIC ACTIVITY OF $[(PEt_3)PtCl(\mu\text{-}SEt)]_2/SnCl_2 \cdot 2H_2O$ SYSTEM IN HYDROGENATION AND HYDROFORMYLATION OF STYRENE *

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Summary

A series of complexes $[(PR_3)PtX(\mu\text{-}SR')]_2$ ($PR_3 = PEt_3$, PPr^n_3, PBu^t_3 or PMe_2Ph; X = Cl, $SnCl_3$, Me, Ph or COPh; R′ = Et or Pr^i) and $[(P\text{–}C)Pt(\mu\text{-}SR')]_2$ (P–C = metalated tri-t-butylphosphine; R′ = Et, Pr^n, Pr^i, Bu^n, Bu^i) has been prepared and characterized by elemental analyses, ^1H, ^{31}P, ^{13}C and ^{119}Sn NMR spectroscopy. The stereochemistry of the complexes in solution and the *trans* influence of the SR′ ligands are discussed. The catalytic activity of the $[(PEt_3)PtCl(\mu\text{-}SEt)]_2/SnCl_2 \cdot 2H_2O$ system in styrene hydrogenation and hydroformylation has been described.

Introduction

Dinuclear platinum(II) complexes of the type $[L_2Pt_2(\mu\text{-}X)_2Y_2]$ can exist in *cis* or *trans* configuration with the overall geometry depending on the method of preparation and on the nature of the L, X or Y group. In most cases interconversion between the two isomers occurs readily in solution, so that usually only one isomer is obtained on crystallization. Thus halogen or thiocyanate bridged complexes, $[L_2Pt_2(\mu\text{-}X)_2Cl_2]$ (L = PR_3 or AsR_3 and X = Cl or SCN), generally exist exclusively in the *trans* form [1–5]; however, when L = PPh_3 and X = Cl, Hartley and Searle were able to synthesize both *cis* and *trans* isomers [6]. The *cis* configuration becomes more common when Y is an alkyl, aryl, acyl or aroyl group; thus the methyl complex, $[(PMe_2Ph)_2Pt_2Me_2Cl_2]$, adopts the *cis* geometry [7] while the aryl or aroyl complexes isomerize in solution into a mixture of *cis* and *trans* isomers [8–10]. The geometry in mercapto-bridged (X = SR′) complexes is largely governed by the R′ group on sulfur, the alkyl complexes preferring the *cis* geometry while the analogous aryl derivatives exist in the *trans* form [11–13]. *Syn* and *anti* isomerism

* Dedicated to Prof. Jack Halpern on the occasion of his 60th birthday.

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has also been observed in trifluoromethyl mercapto-bridged complexes, the formation of such geometrical isomers depending on the nature of the phosphine and on the preparative method [14].

Recently, we have investigated the catalytic activities of mono- and di-nuclear platinum(II) complexes [15–17] in the presence of $SnCl_2 \cdot 2H_2O$, for olefin hydrogenation and hydroformylation. We found that mixed ligand complexes containing one strong ligand (e.g. phosphine) and a weak ligand (e.g. amine or sulfide) are generally more active catalysts than the corresponding *cis*-$PtCl_2L_2/SnCl_2 \cdot 2H_2O$ (L = phosphine, amine or sulfide) compounds [15].

It was hence considered worthwhile to study the catalytic activity of mercapto-bridged complexes in the homogeneous hydrogenation and hydroformylation of olefins. We have synthesized a series of complexes of the types $[(PR_3)Pt(\mu\text{-}SR')X]_2$ and $[(P\text{–}C)Pt(\mu\text{-}SR')]_2$ and studied the homogeneous hydrogenation and hydroformylation of styrene as a reference system by the $[(PEt_3)PtCl(\mu\text{-}SEt)]_2/SnCl_2 \cdot 2H_2O$ system.

Results and discussion

Halogen-bridged dinuclear platinum(II) complexes of the type $[(PR_3)PtCl(\mu\text{-}Cl)]_2$ ($PR_3 = PEt_3$, PPr^n_3, PBu^n_3 or PMe_2Ph) react with alkylmercaptans (EtSH or Pr^iSH) in acetone at room temperature over a period of 10–15 h, to yield [11–13] mercapto-bridged dinuclear platinum(II) complexes, $[(PR_3)PtCl(\mu\text{-}SR')]_2$ (R′ = Et or Pr^i). The similar reaction of $[(P\text{–}C)Pt(\mu\text{-}Cl)]_2$, I, (P–C = metalated tri-t-butylphosphine) with ethylmercaptan yields $[(PBu^t_3)PtCl(\mu\text{-}SEt)]_2$, II, instead of $[(P\text{–}C)Pt(\mu\text{-}SEt)]_2$; the reaction appears to proceed as shown in eq. 1.

$$\underset{(I)}{[(P\text{–}C)Pt(\mu\text{-}Cl)]_2} + EtSH \xrightarrow{\text{acetone}} [(P\text{–}C)Pt(\mu\text{-}SEt)] + HCl \xrightarrow{\text{fast}} \underset{(II)}{[(PBu^t_3)PtCl(\mu\text{-}SEt)]_2} \quad (1)$$

(where $P\text{–}C = Bu^t_2PCMe_2CH_2$)

The mercapto-bridged dinuclear platinum(II) complexes containing metalated tri-t-butylphosphine can be obtained by the reactions of I with sodium mercaptides, or with pyridine followed by treatment with alkylmercaptan at 60°C in benzene (eq. 2).

$$\begin{array}{l} 2[(P\text{–}C)PtCl(Py)] \xleftarrow{py} I \xrightarrow{NaSR'} [(P\text{–}C)Pt(\mu\text{-}SR')]_2 + NaCl \\ \quad \downarrow R'SH \\ [(P\text{–}C)Pt(\mu\text{-}SR')]_2 + 2py \cdot HCl \end{array} \quad (2)$$

Since the platinum–carbon bond in metalated tri-t-butylphosphine complexes can be cleaved by HCl, the complex $[(P\text{–}C)Pt(\mu\text{-}SEt)]_2$ not surprisingly reacts instantaneously with dry HCl in ether to give complex II. Remetalation of PBu^t_3 in complex II could not be achieved in ethanol at room temperature over a period of 15 h. Unlike the chloro-bridged complexes which can be cleaved by various donor ligands [18,19], the mercapto-bridge is stable towards such ligands, as demonstrated by the fact that the complex $[(P\text{–}C)Pt(\mu\text{-}SEt)]_2$ did not react with triphenylphosphine in chloroform solution.

An ethereal solution of methyllithium reacts with $[(PEt_3)PtCl(\mu\text{-}SEt)]_2$ to yield $[(PEt_3)PtMe(\mu\text{-}SEt)]_2$. Analogous phenyl and benzoyl complexes can be prepared by the reaction of $[(PR_3)PtCl(Py)R']$ (R = Et or Ph; R′ = Ph or COPh) with ethyl mercaptan. The complexes $[(PR_3)PtCl(\mu\text{-}SR')]_2$ ($PR_3 = PBu_3$, R′ = Pr^i; $PR_3 = PEt_3$, R′ = Et) react with excess $SnCl_2 \cdot 2H_2O$ in chloroform or dichloromethane to yield the corresponding trichlorostannate complexes.

cis isomer (A) *trans* isomer (B)

For complexes of the type $[(P\text{–}C)Pt(\mu\text{-}SR')]_2$ or $[(PR_3)PtX(\mu\text{-}SR')]_2$, the ^1H NMR spectra showed [13,16] two sets of SR′ resonances for the *cis* isomer (**A**) but only one for the *trans* isomer (**B**). The ^1H NMR spectra of $[(P\text{–}C)Pt(\mu\text{-}SR')]_2$ complexes (Table 1), except $[(P\text{–}C)Pt(\mu\text{-}SPr^i)]_2$, displayed three sets of resonances for the SR′ group in $CDCl_3$ at room temperature. Two are of essentially the same intensity and are assigned to the *cis* isomer, while the third set is assigned to the *trans* isomer. Similarly, in the ^{31}P NMR spectra, except for $[(P\text{–}C)Pt(\mu\text{-}SPr^i)]_2$, two resonances with platinum satellites are observed. Generally, the *cis* isomer predominated (~ 90%) in freshly prepared solutions. The complex $[(P\text{–}C)Pt(\mu\text{-}SPr^i)]_2$ existed exclusively as the *cis* form, showing only two sets of resonances for the SPr^i group in the ^1H NMR spectrum and only one signal with platinum satellites in the ^{31}P NMR spectrum. A freshly prepared sample of $[(P\text{–}C)Pt(\mu\text{-}SEt)]_2$ displayed two resonances of nearly the same intensity in the ^{31}P NMR spectrum but after three recrystallizations, appeared to be converted largely to the *cis* isomer (~ 85%). In general, separation of the two isomers was difficult, since their solubilities were very similar.

Similarly, the complexes $[(PR_3)PtCl(\mu\text{-}SR')]_2$ exist in both *cis* and *trans* forms. Some could be isolated exclusively as the *cis* ($PR_3 = PPr^n_3$, PBu^t_3, PMe_2Ph; R′ = Et) or the *trans* ($PR_3 = PEt_3$, R′ = Et or Pr^i; $PR_3 = PBu^n_3$, R′ = Et) isomer while others ($PR_3 = PPr^n_3$, PBu^n_3; R′ = Pr^i) gave a mixture of the two isomers on first recrystallization. Conversion of *trans*-$[(PEt_3)PtCl(\mu\text{-}SPr^i)]_2$ or a mixture of *cis*- and *trans*-$[(PPr^n_3)PtCl(\mu\text{-}SPr^i)]_2$ into the *cis* isomer occurs in the presence of traces of the corresponding phosphine in benzene solution at room temperature. The *trans* isomer of $[(PPr^n_3)PtCl(\mu\text{-}SPr^i)]_2$ is obtained from the mother liquor on cooling to −70°C. Surprisingly, the complex $[(PBu^t_3)PtCl(\mu\text{-}SEt)]_2$ in spite of the intramolecular crowding due to the bulky t-butyl groups exclusively exists in the *cis* form. It has been shown previously [12] that these *cis* isomers have a non-planar bridge, apparently because of intramolecular crowding between the alkyl groups on the two phosphines. In this PBu^t_3 species, such crowding should be that much greater, leading to either a greater deviation from a planar bridge, or to greater relative stability for the *trans* isomer. As for $[(P\text{–}C)Pt(\mu\text{-}SR')]_2$, two sets of resonances for the *cis* isomer and only one for the *trans* isomer were observed in the ^1H NMR spectra (Table 1) for this class of complex. The ^{31}P NMR spectra show the following interesting features:
(a) The ^{31}P NMR chemical shift for the *trans* isomer is deshielded compared to that of the corresponding *cis* isomer.

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TABLE 1

^1H AND $^{31}P\{^1H\}$ NMR DATA FOR MERCAPTO-BRIDGED DINUCLEAR PLATINUM(II) COMPLEXES AT ROOM TEMPERATURE

Complex	Isomer	$^{31}P\{^1H\}$ NMR		^1H NMR data δ(ppm) [a]
		δ (ppm)	$^1J(^{31}P-^{195}Pt)$ (Hz)	
$[(PEt_3)PtCl(\mu\text{-}SEt)]_2$	*trans*	10.5	3114	δ(S–CH_2) 2.73(m); δ(S–C–CH_3) 1.85(t)
$[(PEt_3)PtCl(\mu\text{-}SPr^i)]_2$	*trans*	9.1	3152	δ(S–CH) 3.34(m); (S–CMe_2) [b]
	cis	6.6	3183	δ(S–CH) 4.37(m), 3.18(m); δ(SC–Me_2) 1.68(d, 7 Hz), 1.42(d, 7Hz)
$[(PPr^n_3)PtCl(\mu\text{-}SEt)]_2$	*cis*	−0.1	3174	δ(SCH_2) 3.20(m), 2.67(q); δ($SCCH_3$) 1.49(t, 7 Hz), 1.31(t, 7 Hz)
$[(PPr^n_3)PtCl(\mu\text{-}SPr^i)]_2$	*trans*	0.7	3130	δ(SCH) 3.31(m); δ(S–CMe_2) [b]
	cis	−1.8	3159	δ(SCH) 4.35(m), 3.18(m); δ($SCMe_2$) 1.68(d, 7 Hz), 1.43 (d, 7 Hz)
$[(PBu^n_3)PtCl(\mu\text{-}SEt)]_2$	*trans*	3.1	3097	δ(SCH_2) 2.73(m); δ($SCCH_3$) [b]
$[(PBu^n_3)PtCl(\mu\text{-}SPr^i)]_2$	*trans*	1.9	3135	δ(SCH) 3.33(m); δ($SCMe_2$) [b]
	cis	−1.0	3159	δ(SCH) 4.37(m), 3 19(m); δ($SCMe_2$) [b]
$[(PBu^t_3)PtCl(\mu\text{-}SEt)]_2$	*cis*	61.0	3157	δ(SCH_2) 3.11(m), 2.91(q); δ($SCCH_3$) 1.66(t), 1.63(t); δ(P–Bu^t_3) 1.60(d, 12 Hz)
$[(PMe_2Ph)PtCl(\mu\text{-}SEt)]_2$	*cis*	−14.4	3230	δ(SCH_2) 3.25(m), 2.25(q); δ($SCCH_3$) 1.50(t), 0.85(t); δ(PMe_2) 1.79(d, 11 Hz), 1.72(d,11 Hz)
$[(PEt_3)Pt(SnCl_3)(\mu\text{-}SEt)]_2$	*trans* [d]	12.9	2860	δ(SCH_2) 3.27(m); δ($SCCH_3$) 1.70(t, 7 Hz)
	cis [e]	10.3	2756	δ(SCH_2) 3.95(m), 3.15(m); δ($SCCH_3$) 1.76(t), 1.55(t)
$[(PBu^n_3)Pt(SnCl_3)(\mu\text{-}SPr^i)]_2$	*trans* [f]	0.7	2873	δ(SCH) 3.93(m); δ($SCMe_2$) 1.60(d, 7 Hz)
$[(PEt_3)PtMe(\mu\text{-}SEt)]_2$	*cis*	8.8	3727	δ(Pt–Me) 0.31 ($J(^{195}Pt-^1H)$ 72 Hz, $J(^{31}P-^1H)$ 4 Hz); δ(SCH_2) 2.78(m), 2.72(q); δ($SCCH_3$) 1.31(t), 1.22(t)

$[(PEt_3)PtPh(\mu\text{-}SEt)]_2$	*trans*	9.9	3477	$\delta(SCH_2)$ 2.36(m); $\delta(SCCH_3)$ 1.54(t, 7 Hz)
	cis	6.7	3715	$\delta(SCH_2)$ 2.77(q, 7 Hz), 1.60(t); $\delta(SCCH_3)$ 1.34(t, 7 Hz), 0.25(t, 7 Hz)
$[(PEt_3)Pt(COPh)(\mu\text{-}SEt)]_2$ [g]	*cis*	6.7	3842	$\delta(SCH_2)$ 2.73(br), 2.05 (br); $\delta(SCCH_3)$ 1.34 (t, 7 Hz), 0.56 (t, 7 Hz)
$[(PPh_3)PtPh(\mu\text{-}SEt)]_2$	*trans*	18.9	3857	$\delta(SCH_2)$ 1.71(m); $\delta(SCCH_3)$ 0.44(t)
	cis	14.6	3894	$\delta(SCH_2)$ 2.27(m), 1.71(m); $\delta(SCCH_3)$ 0.58(t), 0.36(t)
$[(P\text{–}C)Pt(\mu\text{-}SEt)]_2$ [h]	*cis*	−7.4	2968	$\delta(PBu^t)$ 1.46(d, 13 Hz); $\delta(PCMe_2)$ 1.46(d, 10 Hz); 1.43(d, 13 Hz);
	trans	−3.5	2910	$(PCCH_2)$ [c]; $\delta(SCH_2)$ 2.77(m), 2.60(m); δ(SCMe) 1.26(t, 7 Hz) (*cis*), 1.19 (t, 7Hz) (*cis*), 1.25(t, 7 Hz) (*trans*)
$[(P\text{–}C)Pt(\mu\text{-}SPr^n)]_2$	*cis*	−6.9	2976	$\delta(PBu^t)$ 1.45(d, 13 Hz); $\delta(PCMe_2)$ 1.46(d, 13 Hz), 1.43(d, 13 Hz); $\delta(PCCH_2)$ 1.17(d, 10 Hz); $\delta(SCH_2)$ 2.70(m), 2.50(m); $\delta(SCCH_2)$
	trans	−2.8	2904	1.58(m); $\delta(SCCCH_3)$ 0.90(t, 7 Hz), 0.88(t, 7 Hz)
$[(P\text{–}C)Pt(\mu\text{-}SPr^i)]_2$	*cis*	−6.3	2928	$\delta(PBu^t)$ 1.47(d, 13 Hz); $\delta(PCMe_2)$ 1.42(d, 13 Hz); $\delta(PCCH_2)$ [c]; δ(SCH) 3.40(m), 3.14(m); $\delta(SCMe_2)$ 1.36(d, 7 Hz), 1.29 (d, 7 Hz)
$[(P\text{–}C)Pt(\mu\text{-}SBu^n)]_2$	*cis*	−7.1	2974	$\delta(PBu^t)$ 1.45(d, 13 Hz); $\delta(PCMe_2)$ 1.46(d, 12 Hz), 1.43(d, 13 Hz); $\delta(P\text{–}CCH_2)$ 1.17(d, 10 Hz); $\delta(SCH_2)$ 2.73(m), 2.55(m);
	trans	−2.8	2901	$\delta(SCCH_2CH_2)$ 1.31(m); $\delta(SCCCH_3)$ 0.85(t), 0.82(t), 0.85(t)
$[(P\text{–}C)Pt(\mu\text{-}SBu^t)]_2$	*cis*	−7.2	2986	$\delta(PBu^t)$ 1.45(d, 13 Hz); $\delta(PCMe_2)$ 1.42(d, 13 Hz), 1.46(d, 14 Hz); $\delta(PCCH_2)$ 1.13(d, 9 Hz); $\delta(SCCMe_2)$ 0.92(d, 7 Hz) 0.91(d, 7 Hz),
	trans	−3.2	2912	0.95(d, 7 Hz)

[a] d = doublet, t = triplet, q = quartet, m = multiplet, br = broad unresolved signal. [b] Merged with phosphine proton resonances. [c] Not observed. [d] $^2J(^{117/119}Sn\text{–}^{31}P)$ 257 Hz. [e] $^2J(^{117/119}Sn\text{–}^{31}P)$ 257 Hz. [f] $^2J(^{117/119}Sn\text{–}^{31}P)$ 234 Hz. [g] ν(C=O) 1600 cm^{-1}; ^{13}C NMR data in $CDCl_3$ = SEt: methylene carbon δ 26.8, 25.1 ppm, methyl carbon δ 20.7, 17.1 ppm; PEt_3: methylene carbon δ 15.5 ppm (d, $^1J(^{31}P\text{–}^{13}C)$ 34 Hz), methyl carbon δ 7.7 ppm; Ph: δ 148.4, 130.7, 129.5, 127.9 ppm; carbonyl carbon: δ 226.0 ppm. [h] P–C = metalated tri-t-butylphosphine.

(b) The magnitude of $^1J(^{31}P-^{195}Pt)$ is greater in the *cis* isomer than the *trans*, although for $[(PR_3)PtR'(\mu\text{-}Cl)]_2$ Eaborn et al. [10] have assigned the higher value of ^1J to the *trans* isomer.

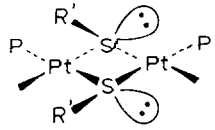
(c) The values of $^3J(^{31}P-^{195}Pt)$ and $^4J(^{31}P-^{31}P)$ for the *trans* isomer (^3J 50 Hz and ^4J 12 Hz) are larger than those of the corresponding *cis* isomer (^3J = 15–20 Hz and ^4J < 2 Hz).

The ^1H and ^{31}P NMR spectra (Table 1) of $[(PEt_3)Pt(SnCl_3)(\mu\text{-}SEt)]_2$ and $[(PBu^n_3)Pt(SnCl_3)(\mu\text{-}SPr^i)]_2$ showed that the former complex exists in a mixture of *cis* and *trans* isomers (70% *trans*) while the latter complex exclusively exists in the *trans* form. The ^{119}Sn NMR spectrum of $[(PBu^n_3)Pt(SnCl_3)(\mu\text{-}SPr^i)]_2$ showed a single resonance with ^{195}Pt and ^{31}P coupling ($\delta(^{119}Sn)$ −85.0 ppm, $^1J(^{119}Sn-^{195}Pt)$ 21.681 Hz, $^3J(^{119}Sn-^{195}Pt)$ 2325 Hz and $^2J(^{119}Sn-^{31}P)$ 223 Hz).

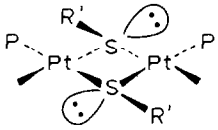
The ^1H NMR spectrum of $[(PEt_3)PtMe(\mu\text{-}SEt)]_2$ displayed a doublet at 0.31 ppm with $^2J(^{195}Pt-^1H)$ 72 Hz and $^3J(^{31}P-^1H)$ 4 Hz for the platinum-methyl group. The spectrum showed two sets of resonances for the S-CH_2CH_3 protons, thus confirming a *cis* geometry in solution. The phenyl analogue, $[(PEt_3)PtPh(\mu\text{-}SEt)]_2$, on the other hand, displayed a single set of resonances for the S-CH_2CH_3 protons in $CDCl_3$ solution, indicating a *trans* configuration for the complex. The *trans* isomer can be converted to the more stable *cis* isomer either by leaving the complex (*trans*) in chloroform solution for a few hours at room temperature, or by passing CO for an hour through such a solution. The ^1H NMR spectrum of the *cis* isomer displayed, as expected, two sets of resonances for the S-CH_2CH_3 protons. Interestingly, one of the methyl groups of the S-CH_2CH_3 moieties shows a greater degree of shielding than for any other *cis* dimers (Table 1). This shielding of the methyl group can be attributed to the ring-current effect of the phenyl groups *cis* to the SEt moiety. Resonances due to the methylene protons of the SEt group (*cis* to phenyl groups) are merged in the CH_2 resonances of the triethylphosphine ligand; this is confirmed by a homonuclear spin-decoupling experiment. Irradiation of the signal at δ 1.63 ppm (due to CH_2 protons) with a second frequency leads to the observation of a doublet for methyls of the PEt_3 ligand and a singlet for the methyl group of SEt. The complex $[(PPh_3)PtPh(\mu\text{-}SEt)]_2$ exists as a mixture of *cis* and *trans* isomers which thus showed three sets of resonances for the SCH_2CH_3 protons in the ^1H NMR spectrum (Table 1). Similarly, in the ^{31}P NMR spectrum, two Pt–P signals with platinum satellites appeared. The *cis* geometry for the benzoyl complex, $[(PEt_3)Pt(COPh)(\mu\text{-}SEt)]_2$, has been observed in $CDCl_3$ solution.

The magnitude of $^1J(^{31}P-^{195}Pt)$ in these mercapto-bridged complexes is reduced considerably (by 654 to 1324 Hz) compared to corresponding chloro-bridged complexes [1,9,10,20] indicating a high *trans* influence for the bridging mercapto group. As illustrated previously, the magnitude of ^1J ($^{195}Pt-^{31}P$) decreased on increasing the *trans* influence of the ligand [21,22].

Both *cis* and *trans* isomers of mercapto-bridged dinuclear platinum(II) complexes may exist in two geometrical forms, *syn* and *anti*, depending on the arrangement of the R′ groups with respect to each other:



cis-syn isomer



cis-anti isomer

The X-ray structural analysis of *cis*-$[PPr^n_3)PtCl(\mu\text{-}SEt)]_2$ has shown that the complex has an *anti* configuration with a non-planar central $\{PtS_2Pt\}$ bridge [12]. Dixon et al. [14] have prepared cationic complexes of the type $[(PR_3)_2Pt(\mu\text{-}SCF_3)]_2^{2+}$ ($PR_3 = PEt_3$, PPh_3) and were the first to provide evidence for the existence of *syn* and *anti* isomers. On the basis of ^{19}F NMR spectral data they concluded that *syn* and *anti* configurations of the complexes depend on the nature of the phosphine (*trans* influence) and on the method of preparation, with some complexes isomerizing into a mixture of *syn* and *anti* forms in solution [14]. A mechanism involving inversion at the sulfur atom(s) has been suggested for such isomerizations and in some cases inversion has been found to be very fast [13,23,24]. The rate of inversion at sulfur in the molecules $[PtX_2\{EtSCH_2CH_2SEt\}]$ increases with increasing *trans* influence of X [23]. It is possible that we do not detect *syn* and *anti* isomers for our complexes by ^1H or ^{31}P NMR spectroscopies, because of the occurrence of such a fast inversion process.

The bridge in the complexes $[(PR_3)PtCl(\mu\text{-}Cl)]_2$ is fragile and can be cleaved by weak donor ligands. Thus, the catalytic activity shown by such complexes is not primarily due to the $Pt\langle^{Cl}_{Cl}\rangle Pt$ skeleton, but is probably due to some other species formed in solution by the cleavage of the chloro-bridge.

Although the mercapto bridge is relatively stable towards cleavage by donor ligands under ambient conditions, it might well cleave under catalytic conditions to generate mixed ligand complexes, which we have already shown [15,17] to be generally more active catalysts. In order to assess the catalytic activity of such complexes, we have carried out hydrogenation and hydroformylation of styrene employing $[(PEt_3)PtCl(\mu\text{-}SEt)]_2/SnCl_2 \cdot 2H_2O$ as a homogeneous catalyst. The results of catalytic hydrogenation of styrene to ethylbenzene in dichloromethane are summarized in Table 2. The complex, $[(PEt_3)PtCl(\mu\text{-}SEt)]_2$, in the absence of $SnCl_2 \cdot 2H_2O$ does not show any catalytic activity for the hydrogenation of styrene at 60°C under 800 psi of hydrogen in CH_2Cl_2. In the presence of one equivalent of tin(II) chloride, slight activity is observed which increases upon addition of 2 to 5 equivalents of $SnCl_2 \cdot 2H_2O$. In the presence of a large excess (10 equivalents), a decrease in activity is observed (T.N. 84). The efficiency of a homogeneous catalytic system is also known to be affected by the hydrogen gas pressure [25], and the present system also shows a variation in rate with change in pressure, catalytic activity increasing with pressure (Table 2).

TABLE 2

CATALYTIC HYDROGENATION OF STYRENE TO ETHYLBENZENE USING $[(PEt_3)PtCl(\mu\text{-}SEt)]_2/SnCl_2 \cdot 2H_2O$ AS CATALYST

Pt^{II}/Sn^{II} ratio	Solvent	Temperature (°C)	H_2 pressure (psi)	Turnover number [a]
1/0	CH_2Cl_2	60	800	0
1/1	CH_2Cl_2	60	650	6
1/1	CH_2Cl_2	60	1050	28
1/2	CH_2Cl_2	60	1050	51
1/5	CH_2Cl_2	60	1050	94
1/10	CH_2Cl_2	65	1150	84
1/1	CH_2Cl_2	60	1600	41

[a] Moles of styrene converted to ethylbenzene per mole of platinum (i.e. half a dimeric unit) per hour.

Hydroformylation of styrene was carried out in dichloromethane employing $[(PEt_3)PtCl(\mu\text{-}SEt)]_2/SnCl_2 \cdot 2H_2O$ at 60°C and 600 psi of H_2/CO. Little variation in turnover number was noticed on varying the partial pressure of carbon monoxide (H_2/CO 300/300, 200/400 or 400/200 psi) the best results giving T.N. = 14. Both 2- and 3-phenylpropanal were formed in these reactions. Hydrogenation of styrene is not observed in these reactions.

The species used in these catalytic system studies, namely $[(PEt_3)PtCl(\mu\text{-}SEt)]_2$ exists as the *trans* isomer. Earlier arguments have been made [11] that the *trans* isomers are less stable than the *cis* analogues and are therefore relatively more susceptible to bridge cleavage. It should be noted, however, that even in $[(P\text{–}C)Pt(\mu\text{-}SEt)]_2$ where this ligand is always *trans* to ligands of strong *trans* effect (phosphine and σ-bonded carbon), cleavage with a strong donor such as triphenylphosphine does not proceed easily even though *cis–trans* isomerization in such complexes is reasonably facile. It seems likely therefore that complexes such as *cis*-$[(PEt_3)PtCl(\mu\text{-}SEt)]_2$ or $[(P\text{–}C)Pt(\mu\text{-}SEt)]_2$, even with $SnCl_2$ as co-catalyst, would not provide markedly improved catalyst systems, and that under the conditions employed, the dithio bridge is too stable to provide a source of active catalytic species.

Experimental

The complexes $[(PR_3)PtCl(\mu\text{-}Cl)]_2$ ($PR_3 = PEt_3$, PPr^n_3, PBu^n_3 or PMe_2Ph) [26,27], $[(P\text{–}C)Pt(\mu\text{-}Cl)]_2$ [19], $[(PR_3)Pt(CH_2{=}CH_2)Cl_2]$ [10] and $[(PR_3)PtPh(\mu\text{-}Cl)]_2$ [10] were prepared by the literature methods. The chloro-bridged benzoyl complex, $[(PEt_3)Pt(COPh)(\mu\text{-}Cl)]_2$ [28], was prepared by the reaction of *cis*-$[(PEt_3)(CO)PtCl_2]$ with Me_3PhSn in dichloromethane. Phosphines were obtained from Strem Chemicals; $SnCl_2 \cdot 2H_2O$, styrene and mercaptans were purchased from Aldrich. Styrene was passed through a florisil column and deoxygenated prior to use. Spectroanalysed solvents were used in all reactions. Infrared spectra were recorded on a Perkin–Elmer 180 spectrophotometer in $CDCl_3$ using KBr cells. ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-400 spectrometer in $CDCl_3$, and chemical shifts were relative to external tetramethylsilane. $^{31}P\{^1H\}$ NMR spectra were obtained on Bruker WP-60 and WH-400 spectrometers operating in Fourier transform mode at 24.3 and 161.98 MHz respectively. Chemical shifts are relative to external 85% H_3PO_4, more positive shifts represent deshielding. $^{119}Sn\{^1H\}$ spectra were recorded on a Bruker WH 400-spectrometer at 149.16 MHz and chemical shifts were relative to external Me_4Sn (50% in C_6D_6). Microanalyses were performed by Guelph Chemical Laboratories. Melting points were determined in a capillary tube and are uncorrected.

Catalytic reactions were carried out at 60°C using a method analogous to that which we have previously reported [16,17]. Gas chromatographic analyses were performed on an Aerograph autoprep 700 chromatograph equipped with a 32 foot × 0.25 inch. (O.D.) Carbowax 4000 (60–80 mesh) column by comparison with known standards. Integration of the ^1H NMR spectra ($\delta(CH{=}CH_2)$ vs. $\delta(CH_2CH_3)$ and $\delta(CH_2CH_2CHO + CH_3\rangle CHCHO)$ vs. $\delta(CH{=}CH_2)$] allowed confirmation and definite identification of the products.

Preparation of $[(PR_3)PtCl(\mu\text{-}SR')]_2$

To an acetone solution of $[(PR_3)PtCl(\mu\text{-}Cl)]_2$ ($PR_3 = PEt_3$, PPr^n_3, PBu^n_3 or PMe_2Ph) or $[(P\text{–}C)Pt(\mu\text{-}Cl)]_2$ alkylmercaptan (R'SH, R' = Et or Pr^i) in excess (ca. 5

fold) was added at room temperature. The colour of the solution immediately changed from orange to pale yellow. The reactants were stirred for 10–15 h and the solvent was then evaporated under reduced pressure. The residue was washed with pentane and the resulting cream coloured solid was recrystallized from hot, ethanol/chloroform mixture in good yields (70–80%). Pertinent data for these complexes are given in Table 3.

Preparation of [(P–C)Pt(μ-SR')]$_2$

(a) Pyridine (0.2 ml) was added to [(P–C)Pt(μ-Cl)]$_2$ (201 mg) in benzene (~ 8 ml).

TABLE 3

PHYSICAL AND ANALYTICAL DATA FOR MERCAPTO-BRIDGED DINUCLEAR PLATINUM(II) COMPLEXES

Complexes	Colour m.p. (°C)	Recrystallization solvent	Analyses (Found (calcd.)(%))			
			C	H	S	Cl
[(PEt$_3$)PtCl(μ-SEt)]$_2$	off white	Ethanol	23.35	4.89	7.77	
	199–202	Chloroform	(23.44)	(4.92)	(7.82)	
[(PEt$_3$)PtCl(μ-SPr^i)]$_2$	white	EtOH/CH_2Cl_2	25.85	5.18	7.71	
	212–216		(25.50)	(5.23)	(7.56)	
[(PPr$^n_3$)PtCl(μ-SEt)]$_2$	cream	EtOH/$CHCl_3$	29.15	5.85	7.44	
	121–122		(29.24)	(5.80)	(7.10)	
[(PPr$^n_3$)PtCl(μ-SPr^i)]$_2$	off white	Ethanol	30.79	5.93	6.76	
	162–164		(30.93)	(6.06)	(6.88)	
[(PBu$^n_3$)PtCl(μ-SEt)]$_2$	white	Ethanol	34.61	6.56	6.55	
	103–104		(34.04)	(6.53)	(6.49)	
[(PBu$^n_3$)PtCl(μ-SPr^i)]$_2$	white	Ethanol	36.24	6.83	(6.46)	
	125–126		(35.46)	(6.75)	(6.31)	
[(PBu$^t_3$)PtCl(μ-SEt)]$_2$	cream	Benzene/hexane	34.11	6.70	6.42	7.95
	197–198		(34.04)	(6.53)	(6.49)	(7.18)
[(PEt$_3$)Pt(SnCl$_3$)(μ-SEt)]$_2$	yellow	CH_2Cl_2 or	15.87	3.37	6.22	18.01
	165–170 [a]	$CHCl_3$	(16.03)	(3.36)	(5.35)	(17.76)
[(PBu$^n_3$)Pt(SnCl$_3$)(μ-SPr^i)]$_2$	yellow	CH_2Cl_2/hexane	25.76	4.73	4.92	14.95
	200–202		(25.82)	(4.91)	(4.60)	(15.25)
[(PEt$_3$PtMe(μ-SEt)]$_2$	white	Benzene/hexane	27.86	5.89	8.19	
	90		(27.76)	(5.95)	8.23)	
[(PEt$_3$)PtPh(μ-SEt)]$_2$	white	Benzene/hexane	36.61	5.69	7.31	
	175–176		(37.24)	(5.58)	(7.10)	
[(PEt$_3$)Pt(COPh)(μ-SEt)]$_2$	yellow	Benzene/hexane	37.79	5.71	6.88	
	120–122		(37.57)	(5.25)	(6.69)	
[(PPh$_3$)PtPh(μ-SEt)]$_2$	white	Benzene/CH_2Cl_2	53.90	4.42	5.50	
	190–195		(52.43)	(4.23)	(5.38)	
[(P–C)Pt(μ-SEt)]$_2$ [b]	cream	Ethanol	36.72	6.77	7.26	
	215 [a]		(36.75)	(6.83)	(7.01)	
[(P–C)Pt(μ-SPr^n)]$_2$	cream	Ethanol	36.61	7.03	7.02	
	185–188		(38.21)	(7.05)	(6.80)	
[(P–C)Pt(μ-SPr^i)]$_2$	yellow	Ethanol	37.76	7.05	6.95	
	213–215 [a]		(38.21)	(7.05)	(6.80)	
[(P–C)Pt(μ-SBu^n)]$_2$	cream	Ethanol	39.69	7.02	7.52	
	165–166		(39.57)	(7.26)	(6.60)	
[(P–C)Pt(μ-SBu^i)]$_2$	yellow	Ethanol	39.83	7.23	6.76	
	193–195 [a]		(39.57)	(7.26)	(6.60)	

[a] Decompose. [b] P–C = metalated tri-t-butylphosphine.

The reactants were heated at 60°C with stirring for 30 min. To this solution isobutylmercaptan (0.2 ml) was added and the reactants were further stirred for an hour at 60°C. During the course of the reaction, py · HCl was precipitated as a white solid and was filtered off. The filtrate was evaporated under vacuum leaving a yellow residue which was recrystallized from 95% ethanol in 63% yield as a white crystalline solid.

Similarly, other complexes, $[(PR_3)PtPh(\mu\text{-}S)]_2$ and $[(PEt_3)Pt(COPh)(\mu\text{-}SEt)]_2$ were prepared and the pertinent data are given in Table 3.

(b) To the benzene solution (~ 10 ml) of $[(P\text{–}C)Pt(\mu\text{-}Cl)]_2$ (150 mg), a solution of $NaSPr^i$ (400 mg) in methanol was added with stirring, which was continued for 6 h at room temperature. The solvent was stripped off, leaving a pasty mass which was extracted with benzene, and the benzene solution was passed through a florisil column. The benzene was evaporated under vacuum leaving the mercapto-bridged dimer which was recrystallized from hot ethanol (95%) in 61% yield.

Preparation of $[(PEt_3)PtMe(\mu\text{-}SEt)]_2$

To a benzene solution (5 ml) of $[(PEt_3)PtCl(\mu\text{-}SEt)]_2$ (150 mg), an ethereal solution of MeLi in excess (5 ml, 1.6 *M* solution) was added with stirring. After 15 min, the solution was hydrolysed by saturated ammonium chloride solution at 5°C. The organic layer was separated off, and the aqueous layer washed with ether. The product was obtained by evaporation of the dried organic layer to leave a colourless paste. This was crystallized from hexane containing small amounts of benzene to give colourless crystals (56% yield).

Preparation of $[(PR_3)Pt(SnCl_3)(\mu\text{-}SR')]_2$

To the $CDCl_3$ or CH_3Cl_2 solution of $[(PR_3)PtCl(\mu\text{-}SR')]_2$ ($PR_3 = PEt_3$, $R' = Et$; $Pr_3 = PBu^n_3$; $R' = Pr^i$), excess of $SnCl_2 \cdot 2H_2O$ was added and stirred for an hour. Unreacted $SnCl_2 \cdot 2H_2O$ was filtered off. Yellow crystals of the complex can be obtained on slow evaporation of the solution.

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28 White crystalline solid; ν(CO) 1610 cm^{-1}; ^{31}P NMR in $CDCl_3$, δ 11.3 ppm; $^1J(^{31}P-^{195}Pt)$ 5040 Hz. Preparation of this compound employing diphenylmercury is given in ref. 9.