

# Synthesis and Dynamic Stereochemistry of the Complexes [Pt{CH<sub>3</sub>C(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>}(SR)(H)] (R = H or Ph) \*

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The *cis* square-planar hydrido mercapto derivatives [Pt(triphos)(SH)(H)] and [Pt(triphos)(SPh)(H)] [triphos = CH<sub>3</sub>C(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>] have been prepared by reaction of [Pt(triphos)(PPh<sub>3</sub>)] with H<sub>2</sub>S or HSPH. Analysis of the <sup>1</sup>H and <sup>31</sup>P NMR data for the two complexes over a temperature range encompassing slow- and fast-exchange limits characterizes these molecules as stereochemically non-rigid on the NMR time-scale. The fluxional behaviour can be explained on the basis of intramolecular exchange of the unco-ordinated phosphorus atom of triphos with the phosphorus atom co-ordinated in *cis* position to the hydride ligand. At higher temperature, a complete scrambling of the three phosphorus atoms occurs, and at the fast-exchange limit the spin correlation between the phosphorus atoms and platinum metal is retained. The related complexes [Pt(dppp)(SH)(H)] (dppp = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), [Pt(triphos)Cl<sub>2</sub>] and [Pt(triphos)(SH)<sub>2</sub>] have been prepared in order to clarify the mechanism of the fluxionality for [Pt(triphos)(SR)(H)] (R = H or Ph).

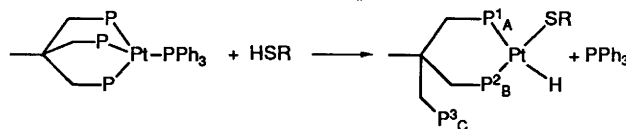
The reactions of H<sub>2</sub>S with organometallic species have been used frequently, in recent years, to prepare compounds such as mercapto-<sup>1</sup> and thio-complexes<sup>2</sup> and metal sulphur clusters,<sup>3</sup> which are relevant to important biological and/or catalytic processes.<sup>4</sup> Further interest in these reactions stems from the possible conversion of H<sub>2</sub>S, a product of hydrodesulphurization reactions, to usable products such as organosulphur compounds and hydrogen.<sup>5</sup>

The previously reported reactions of H<sub>2</sub>S or HSR with platinum(0) species, as far as we know, lead to *trans* square-planar hydrido mercapto derivatives.<sup>6</sup> We now report on the syntheses and <sup>1</sup>H and <sup>31</sup>P NMR characterization of the *cis* square-planar complexes [Pt(triphos)(SR)(H)] (R = H or Ph), where triphos is the potentially tridentate, tripod-like phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane, CH<sub>3</sub>C(CH<sub>2</sub>-PPh<sub>2</sub>)<sub>3</sub>. These molecules show a fluxional behaviour which contrasts with the stereochemical rigidity found previously for [Pt(triphos)(CH<sub>3</sub>)<sub>2</sub>].<sup>7</sup>

## Results and Discussion

The platinum(0) complex [Pt(triphos)(PPh<sub>3</sub>)] undergoes oxidative addition reactions by HSR (R = H or Ph), at room temperature in benzene solution, to give the derivatives [Pt(triphos)(SR)(H)] (R = H, 1 or Ph, 2).

The complexes have been isolated as off-white powders, which decompose slowly in air. The room-temperature <sup>31</sup>P-<sup>1</sup>H NMR spectra of 1 and 2 are quite analogous, showing a broad singlet (δ ca. 4 ppm) with <sup>195</sup>Pt satellites, and a very broad signal in the range δ -26 to -28 ppm. These spectra suggest a dynamic behaviour involving exchange of co-ordinated and unco-ordinated phosphorus atoms or triphos. The low-temperature <sup>31</sup>P-<sup>1</sup>H and <sup>1</sup>H NMR spectra (Tables 1 and 2) are in agreement with a *cis* square-planar geometry, with triphos acting as a bidentate ligand (Scheme 1). The <sup>31</sup>P proton-coupled spectra show that the chemical shift of the phosphorus



Scheme 1 P<sup>1</sup>, P<sup>2</sup> and P<sup>3</sup> represent the spin labels of the phosphorus atoms; A, B and C indicate their chemical shifts. R = H or Ph

in *trans* position to the hydride ligand, P<sub>A</sub>, is *downfield* in comparison with that of P<sub>B</sub>. This finding agrees well with the values of the <sup>1</sup>J(PtP<sub>A</sub>) coupling constants (ca. 1800 Hz) which are considerably smaller than <sup>1</sup>J(PtP<sub>B</sub>) (ca. 3000 Hz) because of the strong *trans* influence of the hydride ligand.<sup>8</sup>

The variable-temperature <sup>1</sup>H and <sup>31</sup>P NMR spectra of 1 and 2 have been recorded in different solvents such as CD<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> or (CD<sub>3</sub>)<sub>2</sub>SO. Apart from small shifts of the signals, the spectra are independent of the solvent. The spectra of 2 recorded in the temperature range of -40 to +107 °C in toluene solution are shown in Fig. 1, together with the fast-exchange limit spectrum [170 °C, (CD<sub>3</sub>)<sub>2</sub>SO]. Compounds 1 and 2 are more soluble in CD<sub>2</sub>Cl<sub>2</sub> and a more detailed measurement of the <sup>31</sup>P-<sup>1</sup>H NMR spectra of 1 in the temperature range -80 to +22 °C in CD<sub>2</sub>Cl<sub>2</sub> is reported in Fig. 2.

As the temperature is raised from -40 °C (Fig. 1), the resonances of P<sub>B</sub> and the dangling P<sub>C</sub> broaden and the P<sub>A</sub>-P<sub>B</sub> coupling disappears. At room temperature the P<sub>A</sub> resonance broadens and, as the temperature is increased further to 60 °C, all signals collapse into the baseline. At 107 °C a new broad singlet, with <sup>195</sup>Pt satellites, appears in the averaged position (δ -5.7 ppm) of P<sub>A</sub>, P<sub>B</sub> and P<sub>C</sub>. This signal sharpens on raising the temperature further [170 °C, (CD<sub>3</sub>)<sub>2</sub>SO]. The platinum-phosphorus coupling at high temperature [<sup>1</sup>J(PtP) = 1610 Hz] is the average of the three platinum-phosphorus coupling constants observed at low temperature [<sup>1</sup>J(PtP<sub>A</sub>) = 1837, <sup>1</sup>J(PtP<sub>B</sub>) = 2998 Hz; J(PtP<sub>C</sub>) = 0], indicating that all three phosphorus atoms are undergoing rapid intramolecular exchange and that the coupling constants with P<sub>A</sub> and P<sub>B</sub> have

\* Non-SI unit employed: cal = 4.184 J.

**Table 1**  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectral data for complexes 1–3 in the slow-exchange limit<sup>a</sup>

Complex	$\delta$ (ppm)			$J$ /Hz		
	$\text{P}_A$	$\text{P}_B$	$\text{P}_C$	$\text{P}_A\text{--P}_B$	$\text{Pt--P}_A$	$\text{Pt--P}_B$
[Pt(triphos)(SH)(H)] <sup>b</sup>	4.4 (d, 1 P)	2.6 (d, 1 P)	–30.7 (s, 1 P)	19.4	1800	3096
[Pt(triphos)(SPh)(H)] <sup>b</sup>	2.6 (d, 1 P)	1.3 (d, 1 P)	–30.8 (s, 1 P)	22.0	1837	2998
[Pt(dppp)(SH)(H)] <sup>c</sup>	4.0 (d, 1 P)	1.1 (d, 1 P)		23.0	1746	3066

<sup>a</sup> Chemical shifts are relative to 85%  $\text{H}_3\text{PO}_4$ ; positive shifts are downfield. The labelling scheme for the phosphorus atoms is indicated in Scheme 1.

<sup>b</sup> In  $\text{CD}_2\text{Cl}_2$  solution,  $-80^\circ\text{C}$ . <sup>c</sup> In  $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ .

**Table 2** Upfield  $^1\text{H}$  NMR spectral data for complexes 1–3 in the slow-exchange limit<sup>a</sup>

Complex	$\delta$		$J$ /Hz						
	SH	H	$\text{P}_A\text{--H(SH)}$	$\text{P}_A\text{--H}$	$\text{P}_B\text{--H(SH)}$	$\text{P}_B\text{--H}$	$\text{H(SH)--H}$	$\text{Pt--H(SH)}$	$\text{Pt--H}$
[Pt(triphos)(SH)(H)] <sup>b</sup>	–0.50 (dt, 1 H)	–3.5 (ddd, 1 H)	4.5	188	20.0	10.0	4.0	64	930
[Pt(triphos)(SPh)(H)] <sup>b</sup>		–3.5 (dd, 1 H)		180		10.0			965
[Pt(dppp)(SH)(H)] <sup>c</sup>	–0.3 (ddd, 1 H)	–4.1 (ddm, <sup>d</sup> 1 H)	5.3	194	21.0	11.4	4.2	63	942

<sup>a</sup> Chemical shifts are relative to  $\text{SiMe}_4$ ; positive shifts are downfield. The labelling scheme for the atoms is indicated in Scheme 1. <sup>b</sup> In  $\text{CD}_2\text{Cl}_2$  solution,  $-80^\circ\text{C}$ . <sup>c</sup> In  $\text{CD}_2\text{Cl}_2$  solution,  $20^\circ\text{C}$ . <sup>d</sup> There is an additional coupling (*ca.* 2 Hz) with the hydrogen atoms of the  $\text{CH}_2\text{P}$  group in *trans* position.

the same sign. Therefore, notwithstanding that such a process involves Pt–P bond breaking and forming (the complex is ultimately square planar), the Pt–P spin correlation is retained. This finding has been considered possible in fluxional metal-chelating phosphine systems<sup>9</sup> and has been observed previously.<sup>7</sup> Re-cooling the solution results in a spectrum indistinguishable from the initial spectrum apart from the signals of some minor decomposition products which are formed at high temperature (*i.e.* above  $100^\circ\text{C}$ ).

The  $^1\text{H}$  upfield NMR spectra of the two complexes, recorded in the same temperature range, are fully consistent with the above results. The  $^1\text{H}$  NMR hydride spectra of **2** as a function of temperature are shown in Fig. 3 [from  $-60$  to  $+21^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ ; from  $20$ – $150^\circ\text{C}$  in  $(\text{CD}_3)_2\text{SO}$ ]. The slow-exchange limit spectrum consists of a doublet of doublets with  $^{195}\text{Pt}$  satellites, at  $\delta -3.50$  ( $\text{CD}_2\text{Cl}_2$ ), arising from coupling of the hydridic hydrogen with  $\text{P}_A$  and  $\text{P}_B$ . At high temperature ( $170^\circ\text{C}$ ) the signal consists of a quartet at  $\delta -4.1$  [ $(\text{CD}_3)_2\text{SO}$ ], with  $^2J(\text{PH}) = 55$  Hz, the average of the  $^2J(\text{PH})$  coupling constants at low temperature [ $^2J(\text{P}_A\text{H})$ ,  $^2J(\text{P}_B\text{H})$ ] (Table 2) and  $J(\text{P}_C\text{H}) = 0$ ], assuming that the first two have opposite sign. The corresponding  $^1\text{H}$  NMR spectra of **1**, as far as the hydride signal is concerned, are analogous apart from the additional coupling with the SH hydrogen. The  $^1\text{H}$  resonance of this latter group appears as a doublet of triplets (with  $^{195}\text{Pt}$  satellites) at low temperature as a result of coupling with the *trans* phosphorus atom ( $\text{P}_A$ ) and the nearly equal couplings with the *cis* phosphorus atom ( $\text{P}_B$ ) and the hydride hydrogen. At high temperature the SH resonance appears as a quintet [ $\delta -0.52$ ,  $J = 4.7$  Hz,  $(\text{CD}_3)_2\text{SO}$ ] due to the comparable couplings to the three averaged phosphorus atoms and the hydridic hydrogen. Considering the absolute values of  $^3J(\text{PH})$  reported in Table 2, one has to assume that  $^3J(\text{P}_A\text{H})$  and  $^3J(\text{P}_B\text{H})$  must also be of opposite sign. The fast-exchange limit of this latter signal is already reached at  $125^\circ\text{C}$  in accordance with the lower size of  $^3J(\text{PH})$  in comparison with the corresponding  $^2J(\text{PH})$ . In the  $^1\text{H}$  NMR high-field spectra of **1** the  $\text{H(PtH)--H(SH)}$  spin correlation is retained throughout the temperature range investigated. The  $^1\text{H}$  NMR signal of the hydridic hydrogen of complexes **1** and **2** in the temperature range  $-30$  to  $20^\circ\text{C}$  shows a line shape characteristic of mutual exchange. Since only the

outer lines of the doublets collapse, whilst the inner lines remain sharp,  $^2J(\text{P}_A\text{H})$  and  $^2J(\text{P}_B\text{H})$  are of opposite sign,<sup>10</sup> confirming the above assumption.

Examination of the variable-temperature  $^{31}\text{P}$  NMR spectra of our complexes indicates that in the temperature range  $-60$  to  $-20^\circ\text{C}$  the exchange of  $\text{P}_B$  with the dangling  $\text{P}_C$  is the only exchange process operating, whereas at temperatures higher than  $20^\circ\text{C}$  total scrambling of all three phosphorus atoms occurs.

The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of **1**, calculated in the temperature range  $-60$  to  $0^\circ\text{C}$  as a function of the exchange rate according to the permutation  $123 \rightleftharpoons 132$ , are reported in Fig. 2. The agreement with the experimental spectra is excellent. Calculations have also shown that the absolute low-temperature limit has not yet been reached at  $-80^\circ\text{C}$ , but reliable experimental measurements at lower temperatures are precluded by the sparing solubility of the complexes under such conditions. The values of the exchange-rate constants are presented in Fig. 4 as an Eyring plot. A good straight line is obtained (linear correlation coefficient  $r = 0.99$ ), from which values of  $\Delta H^\ddagger = 7.1 \pm 0.2$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -21 \pm 1$  cal K<sup>-1</sup> mol<sup>-1</sup> are calculated, assuming  $\kappa$ , the transmission coefficient, is equal to 1. The large negative value of the entropy of activation is consistent with an exchange mechanism involving the association of the dangling phosphorus atom as the rate-limiting step. A scheme analogous to that proposed previously by Meek and co-workers<sup>7</sup> for the dimethyl platinum(II) complexes of various tridentate phosphine ligands appears to be acceptable (Scheme 2). However it is interesting to observe that only the [Pt(triphos)(CH<sub>3</sub>)<sub>2</sub>] complex was found to be stereochemically rigid up to  $100^\circ\text{C}$  and this unexpected result was justified by assuming that the step square pyramid  $\rightleftharpoons$  trigonal bipyramid in Scheme 2 would be prevented by the rigidity of triphos. In the attempt to clarify this different behaviour, we have prepared other platinum(II) triphos derivatives, namely [Pt(triphos)Cl<sub>2</sub>] **3** and [Pt(triphos)(SPh)<sub>2</sub>] **4**.<sup>\*</sup> The  $^{31}\text{P}$  NMR spectra of these compounds (see Experimental section), which are consistent with a *cis* square planar geometry, do not indicate any fluxionality up to  $80^\circ\text{C}$ .

Concerning the high-temperature range ( $>20^\circ\text{C}$ ), the  $^{31}\text{P}\{-^1\text{H}\}$  and  $^1\text{H}$  NMR spectra of **1** and **2** show that the three phosphorus atoms of triphos become chemically and magnetically equivalent at the high-temperature exchange limit. Thus a rigorous calculation of the exchanging spectra would involve six configurations ( $123 \rightleftharpoons 231 \rightleftharpoons 312 \rightleftharpoons 321 \rightleftharpoons 213 \rightleftharpoons 132$ ). As such a calculation exceeds the

\* Our attempts to prepare [Pt(triphos)H<sub>2</sub>] by a method analogous to those reported for the synthesis of [Pt(diphosphine)H<sub>2</sub>]<sup>11</sup> were unsuccessful.

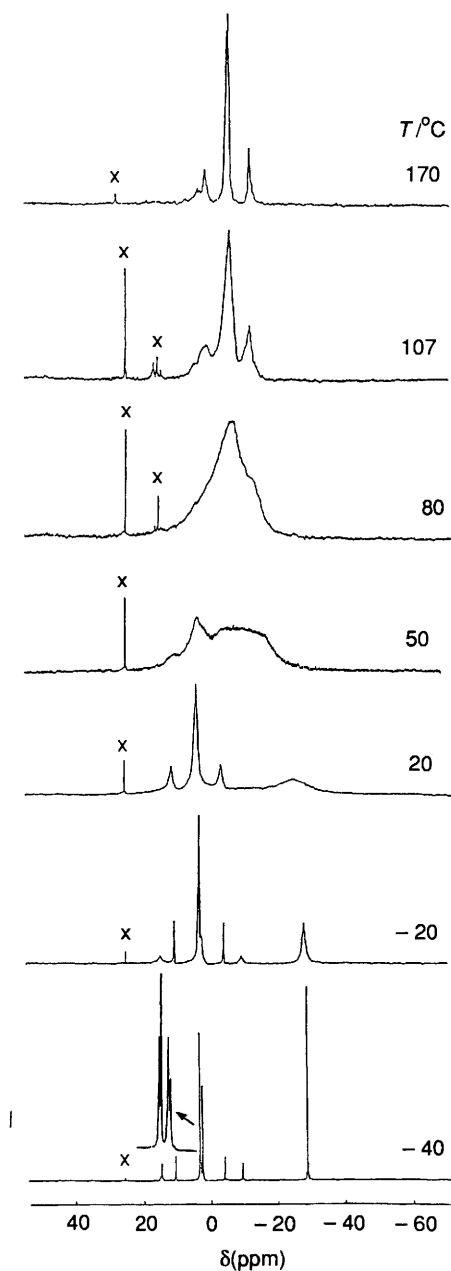


Fig. 1 The variable-temperature  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of  $[\text{Pt}(\text{triphos})(\text{SPh})(\text{H})]$  [ $-40$  to  $107^\circ\text{C}$  in  $\text{C}_6\text{D}_5\text{CD}_3$ , and at  $170^\circ\text{C}$  in  $(\text{CD}_3)_2\text{SO}$ ]. The signals marked by x are due to impurities

capability of our version of the program DNMR3 (see below), which would require major modifications for this purpose, no simulation has been performed.\*

A dissociative mechanism involving a three-co-ordinate intermediate, with triphos acting as unidentate ligand, and a rotation about the only remaining Pt–P bond would lead to the equivalence of the three phosphorus atoms. However (i) it is hard to believe that the strong chelating ligand triphos might act as a monodentate ligand; (ii) a three-co-ordinated platinum(II) compound, even if hypothesized previously as an intermediate species,<sup>12</sup> appears rather unlikely and (iii) such a dissociative mechanism contrasts the results of the line-shape analysis performed on the  $^{31}\text{P}\{-^1\text{H}\}$  low-temperature NMR spectra of **1**.

On the other hand, a simple associative mechanism, which involves a five-co-ordinate intermediate, lacking of three-fold symmetry, cannot lead to equivalence of the three phosphorus atoms, unless the positional ligand exchange  $\text{SH} \rightleftharpoons \text{H}$  also occurs. Indeed the line shape of the hydridic hydrogen in the

variable-temperature  $^1\text{H}$  NMR spectra of **1** and **2**, which is characteristic of mutual exchange, is similar to that previously found in the variable-temperature  $^1\text{H}$  NMR spectra of some *cis* square-planar platinum(II) complexes of formula  $[\text{PtL}_2(\text{Z})(\text{H})]$  ( $\text{Z} = \text{H}, \text{SiR}_3$  or  $\text{SnR}_3$ ;  $\text{L} = \text{phosphine}$ ).<sup>10,13</sup> In these instances the fluxional behaviour has been ascribed to intramolecular exchange of the Z and H groups *via* the formation of an intermediate Pt(HZ) species. To enable comparisons to be made we have prepared the complex  $[\text{Pt}(\text{dppp})(\text{SH})(\text{H})]$  **5**, in which the ligand dppp [bis(1,3-diphenylphosphino)propane] forms a six-membered chelate ring analogous to that present in **1** and **2**. The room-temperature  $^{31}\text{P}$  and  $^1\text{H}$  (upfield) NMR spectral parameters of **5** (Tables 1 and 2) are fully consistent with the corresponding parameters for complex **1**. However the spectra do not show any evidence of chemical exchange up to  $90^\circ\text{C}$ . This result appears to indicate that the fluxional behaviour of **1** and **2** is determined only by the scrambling of the ligand phosphorus atoms.

Another plausible explanation of the exchange mechanism at high temperature, which would give rise to the magnetic equivalence of the three phosphorus nuclei, is shown in Scheme 3. The process involves a five-co-ordinate intermediate with the three sulphur and the sulphur atoms arranged in a quasi-tetrahedral geometry and the hydridic hydrogen located on one of the PPS faces. The migration of the hydrogen onto a contiguous face through a PS edge, according to the tetrahedral jump model proposed previously,<sup>14</sup> followed by a molecular rearrangement, can account for the formation of the six different configurations and their presence at the equilibrium in comparable concentrations at high temperature. It is noteworthy that such a mechanism contains the process previously suggested for the low-temperature exchange ( $123 \rightleftharpoons 132$ , first line in Scheme 3). In the subsequent steps the hydrogen jump allows the other four permutations to occur and ultimately it accounts for the equivalence of the three phosphorus atoms.

In conclusion all these results seem to indicate that the presence of the hydride ligand is mandatory for fluxionality of the square-planar platinum(II) triphos complexes. However the dynamic behaviour of **1** and **2** cannot be explained on the basis of the hydride *trans* effect because the phosphorus atom in *trans* position to the hydride appears more rigid than that in *cis* position.† It may be that the peculiarity of complexes **1** and **2** could be attributed to a *cis* effect based essentially on kinetic reasons.<sup>15</sup>

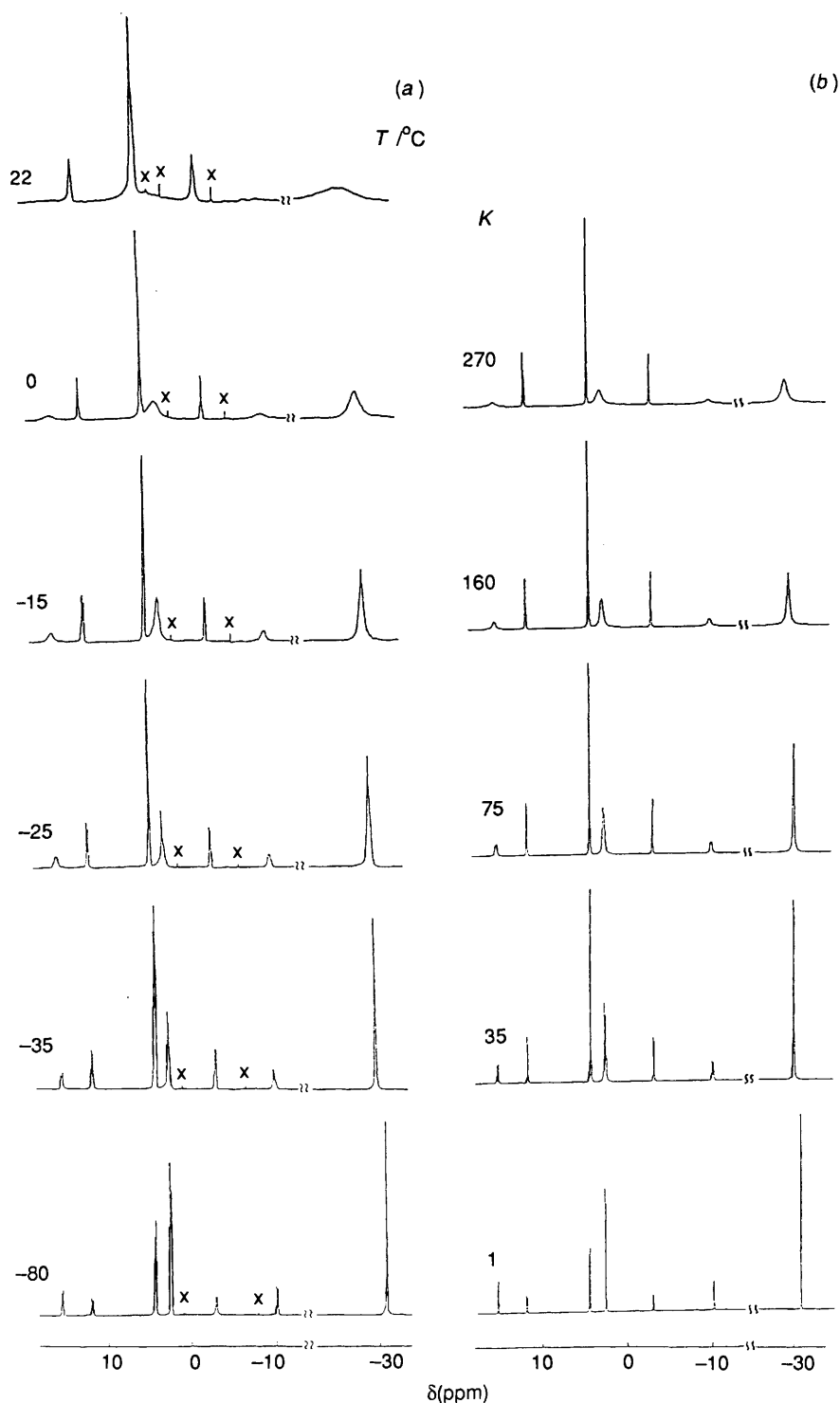
## Experimental

All operations were performed under nitrogen. All reagents were reagent grade and were dried and degassed prior to use. Tris(1,1,1-diphenylphosphinomethyl)ethane (triphos)<sup>16</sup> and the complexes  $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ <sup>17</sup> and  $[\text{Pt}(\text{cod})\text{Cl}_2]$ <sup>18</sup> (cod = cycloocta-1,5-diene) were prepared by the published procedures. Bis(1,3-diphenylphosphino)propane (dppp) was purchased from Strem Chemical Co.

**Spectral Characterization.**—Infrared spectra of the solids were measured on a Perkin-Elmer 457 spectrophotometer in the range  $4000\text{--}250\text{ cm}^{-1}$  as Nujol mulls. Proton and  $^{31}\text{P}$  NMR spectra were recorded using a Varian VXR-300 spectrometer operating at 300.00 and 121.421 MHz and were referenced

\* Both the  $^{31}\text{P}\{-^1\text{H}\}$  and the  $^1\text{H}$  NMR spectra (hydridic region) of **2** have been simulated satisfactorily however in the temperature range  $20\text{--}150^\circ\text{C}$  on the basis of the reduced set of permutations  $123 \rightleftharpoons 231 \rightleftharpoons 312$ . Such calculations are based on the 'jump model' and do not give any direct information about the physical mechanism. As these calculated spectra are not related unambiguously to a physical exchange mechanism, it is not possible to obtain meaningful thermodynamic parameters out of them.

† A similar behaviour was observed for the system  $[\text{Pt}(\text{PPh}_3)_2(\text{SiPh}_3)(\text{H})] + \text{PPh}_3$ .<sup>10</sup>



**Fig. 2** The variable-temperature  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra of  $[\text{Pt}(\text{triphos})(\text{SH})(\text{H})]$ ; (a) the experimental spectrum in the temperature range  $-80$  to  $+22$  °C in  $\text{CD}_2\text{Cl}_2$  (the signals marked by x are due to impurities); (b) the corresponding computer simulated spectra for the indicated exchange rates ( $k/\text{s}^{-1}$ );  $T_2 = 0.16$  s

relative to  $\text{SiMe}_4$  (internal standard) and phosphoric acid (external standard) respectively. Positive chemical shifts are to high frequency. The computer simulation of NMR spectra was carried out with a locally developed package containing the programs LAOCN 3<sup>19</sup> and DAVINS,<sup>20</sup> running on a COMPAQ Deskpro 386/25 personal computer. The simulation of the spectra of platinum compounds containing the  $^{195}\text{Pt}$  satellites was performed using the procedure in three steps described by Meek and co-workers.<sup>7</sup> The line-shape analysis of the variable-temperature NMR spectra was accomplished by means of the DNMR3 program<sup>21</sup> adapted for the COMPAQ

computer. Errors in the calculated rate constants were estimated by varying the rate constant around the best-fit value, until an observable difference between simulated and experimental spectra, both displayed on the graphical terminal, could be detected. This error proved to be 10% or less.

*Syntheses of the Complexes.*—The previously reported complexes  $[\text{Pt}(\text{triphos})(\text{PPh}_3)]$ <sup>22</sup> and  $[\text{Pt}(\text{dppp})_2]$ <sup>23</sup> were prepared by the following improved method.

To a solution of  $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$  (0.750 g, 1 mmol) in

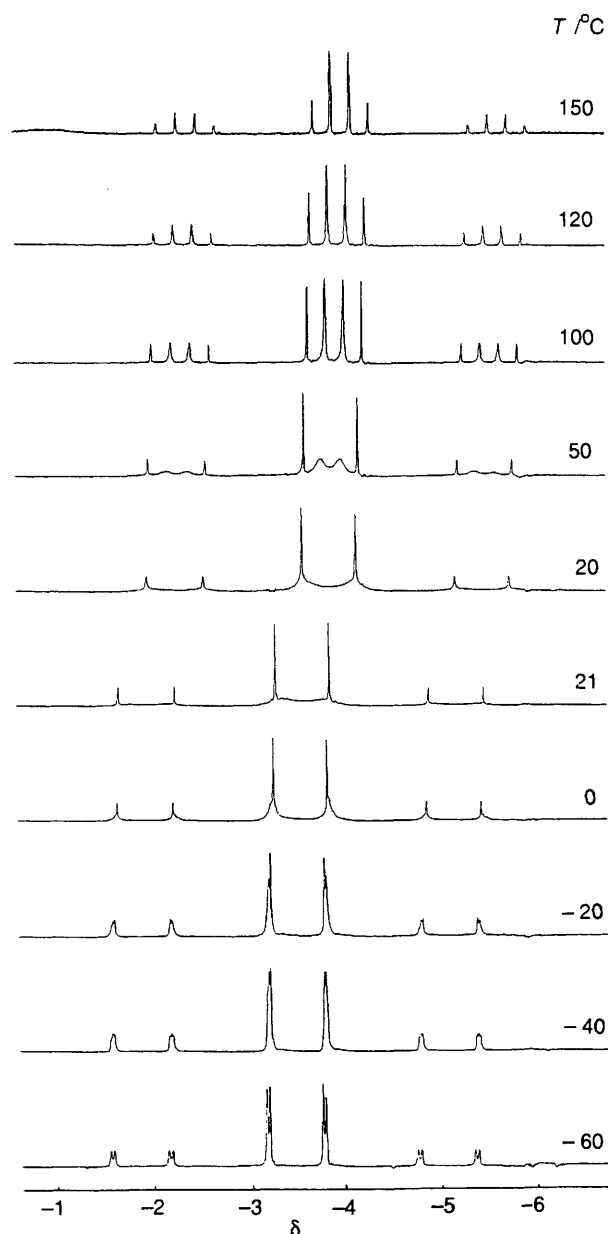


Fig. 3 The variable-temperature  $^1\text{H}$  NMR spectra (hydride region) of  $[\text{Pt}(\text{triphos})(\text{SPh})(\text{H})]$  [ $-60$  to  $+21$   $^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$ ;  $20$ – $150$   $^\circ\text{C}$  in  $(\text{CD}_3)_2\text{SO}$ ]

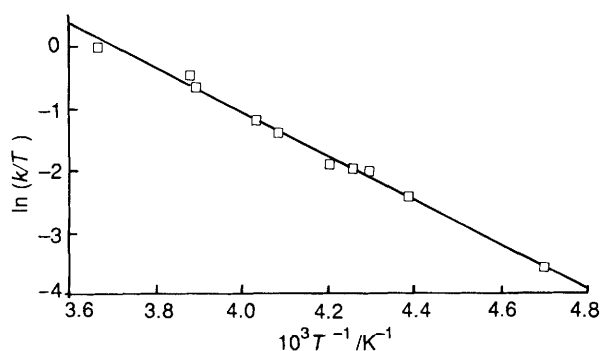
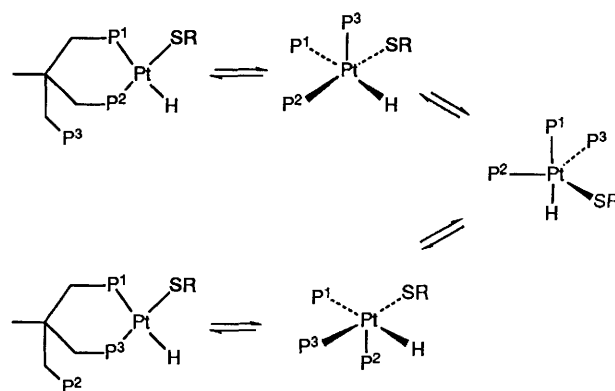


Fig. 4 Eyring plot for the rate constants obtained from  $^{31}\text{P}\{-^1\text{H}\}$  NMR data of  $[\text{Pt}(\text{triphos})(\text{SPh})(\text{H})]$

benzene ( $20\text{ cm}^3$ ) triphos ( $0.625\text{ g}$ ,  $1\text{ mmol}$ ) or dppp ( $0.825\text{ g}$ ,  $2\text{ mmol}$ ) was added at room temperature. The resulting solution was heated at  $40$   $^\circ\text{C}$  for  $10\text{ min}$  and then hexane ( $20\text{ cm}^3$ ) was added portionwise. The solvent was evaporated until yellow



Scheme 2

crystals precipitated. The complexes were collected on a sintered-glass frit, washed with butanol and then with hexane, and dried in a current of nitrogen; yield was almost quantitative. The complexes were identified on the basis of their  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra.

**[Pt(triphos)(SH)(H)] 1.** The complex  $[\text{Pt}(\text{triphos})(\text{PPh}_3)]$  ( $1.081\text{ g}$ ,  $1\text{ mmol}$ ) was dissolved in benzene ( $20\text{ cm}^3$ ) and  $\text{H}_2\text{S}$  was bubbled, at room temperature, through the solution for  $5\text{ min}$ . To the resulting colourless solution  $\text{H}_2\text{S}$ -saturated hexane ( $30\text{ cm}^3$ ) was added and a thick oil separated. The supernatant solution was discarded and the oil was washed with hexane ( $10\text{ cm}^3$ ) until the formation of a colourless solid occurred. The complex was filtered off and dried in a current of nitrogen. Yield  $0.775\text{ g}$  ( $91\%$ ) (Found: C,  $57.95$ ; H,  $4.90$ . Calc. for  $\text{C}_{41}\text{H}_{41}\text{P}_3\text{PtS}$ : C,  $57.70$ ; H,  $4.85\%$ ). IR:  $\nu(\text{Pt-H})$   $2080\text{ cm}^{-1}$ .

**[Pt(triphos)(SPh)(H)] 2.** The complex  $[\text{Pt}(\text{triphos})(\text{PPh}_3)]$  ( $1.081\text{ g}$ ,  $1\text{ mmol}$ ) was dissolved in benzene ( $20\text{ cm}^3$ ) and a slight excess of  $\text{PhSH}$  ( $0.130\text{ g}$ ,  $1.2\text{ mmol}$ ) was added. The yellow solution was heated gently at  $40$   $^\circ\text{C}$  until the formation of a pale yellow colour. Then crystals were precipitated and separated as described for the above compound. Yield  $0.780\text{ g}$  ( $84\%$ ) (Found: C,  $60.90$ ; H,  $4.95$ . Calc. for  $\text{C}_{47}\text{H}_{45}\text{P}_3\text{PtS}$ : C,  $60.70$ ; H,  $4.85\%$ ).

**[Pt(dppp)(SH)(H)] 3.** This complex was prepared by a procedure analogous to that used for **1**, by use of  $[\text{Pt}(\text{dppp})_2]$  in place of  $[\text{Pt}(\text{triphos})(\text{PPh}_3)]$ . Yield  $0.500\text{ g}$  ( $78\%$ ) (Found: C,  $50.30$ ; H,  $4.35$ . Calc. for  $\text{C}_{27}\text{H}_{28}\text{P}_2\text{PtS}$ : C,  $50.55$ ; H,  $4.40\%$ ).

**[Pt(triphos)Cl<sub>2</sub>] 4.** Triphos ( $0.624\text{ g}$ ,  $1\text{ mmol}$ ) was added to a  $\text{CH}_2\text{Cl}_2$  solution ( $30\text{ cm}^3$ ) of  $[\text{Pt}(\text{cod})\text{Cl}_2]$  ( $0.373\text{ g}$ ,  $1\text{ mmol}$ ) at room temperature. Diethyl ether ( $40\text{ cm}^3$ ) was then added and colourless crystals precipitated. These were filtered off, washed with diethyl ether and dried in a current of nitrogen. Yield  $0.835\text{ g}$  ( $94\%$ ) (Found: C,  $55.10$ ; H,  $4.40$ . Calc. for  $\text{C}_{41}\text{H}_{39}\text{Cl}_2\text{P}_3\text{Pt}$ : C,  $55.35$ ; H,  $4.40\%$ ).

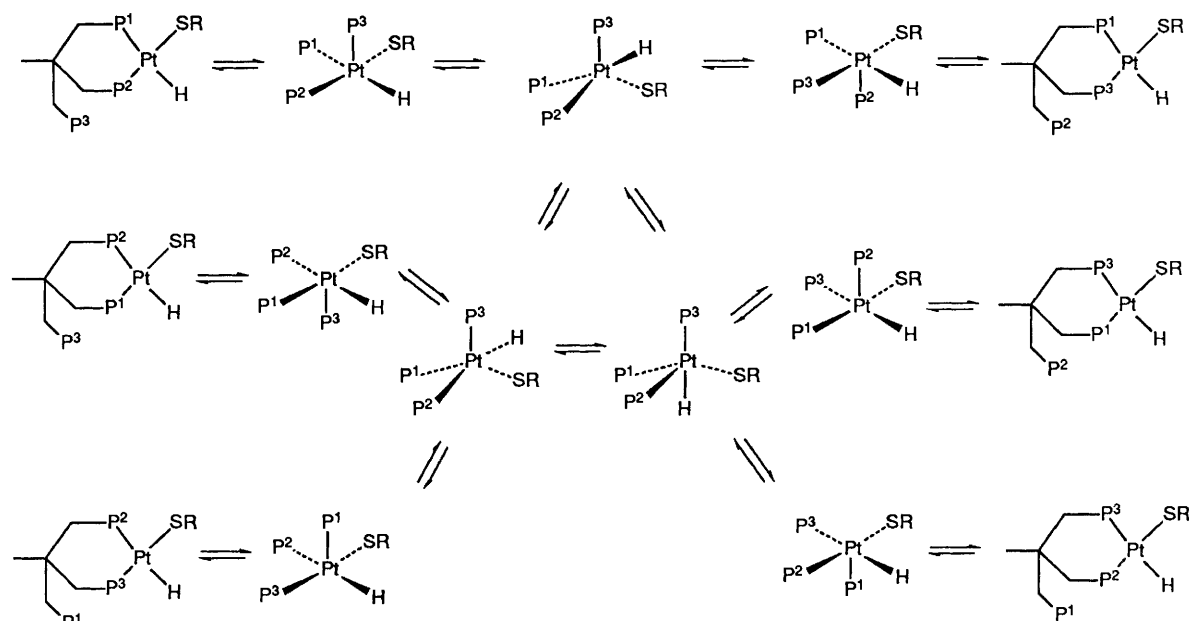
**[Pt(triphos)(SPh)<sub>2</sub>] 5.** A tetrahydrofuran (thf) solution ( $20\text{ cm}^3$ ) of  $\text{NaSPh}$  ( $0.265\text{ g}$ ,  $2\text{ mmol}$ ) was added to  $[\text{Pt}(\text{triphos})\text{Cl}_2]$  ( $0.890\text{ g}$ ,  $1\text{ mmol}$ ) in thf ( $10\text{ cm}^3$ ). After addition of hexane ( $30\text{ cm}^3$ ), pale yellow crystals precipitated. These were filtered off and dried in a current of nitrogen. Yield  $0.850\text{ g}$  ( $82\%$ ) (Found: C,  $60.95$ ; H,  $4.80$ . Calc. for  $\text{C}_{53}\text{H}_{49}\text{P}_3\text{PtS}_2$ : C,  $61.35$ ; H,  $4.75\%$ ).

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Scheme 3

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