

### Preliminary communication

## STRENGTH OF THE Pt–CS<sub>2</sub> BOND IN Pt(PPh<sub>3</sub>)<sub>2</sub>(CS<sub>2</sub>)

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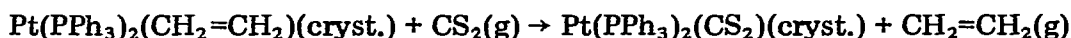
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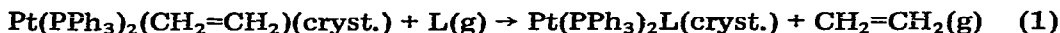
### Summary

The enthalpy of the reaction:



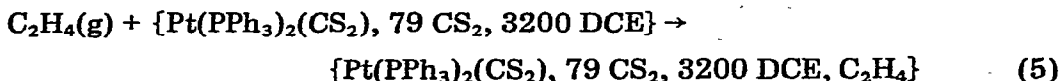
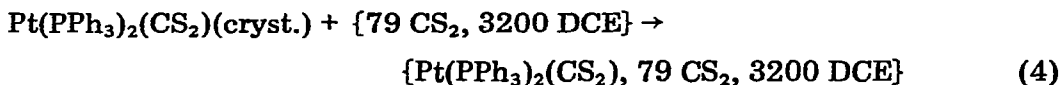
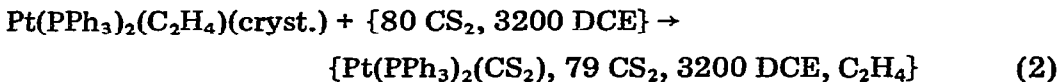
has been determined as  $\Delta H = -44.0 \pm 2.2 \text{ kJ mol}^{-1}$  from solution calorimetry, and the bond dissociation energy  $D(\text{Pt}-\text{CS}_2)$  shown to be slightly greater than  $D(\text{Pt}-\text{C}_2\text{H}_4)$ .

The enthalpy,  $\Delta H(1) = -44.0 \pm 2.2 \text{ kJ mol}^{-1}$ , of reaction 1,



where L = CS<sub>2</sub>, has been derived from measurements, at 298 K, of the enthalpies,  $\Delta H(2) - \Delta H(5)$  of reactions 2-5, where DCE is 1,2-dichloroethane, together with the value [1]  $\Delta H(6) = 27.7 \pm 0.1 \text{ kJ mol}^{-1}$  for the enthalpy of vaporisation of CS<sub>2</sub>. Details of these measurements are shown in Table 1.

Uncertainties are twice the standard deviations of mean values.



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TABLE 1

## ENTHALPIES OF REACTIONS 2-5

<b>Reaction 2</b>					
Wt. Pt(PPh <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> )(g)	0.08975	0.09480	0.08465	0.10105	0.13105
$\Delta H(2)$ (kJ mol <sup>-1</sup> )	-17.0	-16.1	-14.1	-16.4	-15.3
	Mean $\Delta H(2) = -15.8 \pm 1.0$				
<b>Reaction 3</b>					
Wt. CS <sub>2</sub> (g)	0.7655	0.7626	0.7339	0.7758	0.7544
$\Delta H(3)$ (kJ mol <sup>-1</sup> )	+3.98	+3.98	+3.96	+3.97	+3.97
	Mean $\Delta H(3) = +3.97 \pm 0.01$ kJ mol <sup>-1</sup>				
<b>Reaction 4</b>					
Wt. Pt(PPh <sub>3</sub> ) <sub>2</sub> (CS <sub>2</sub> )(g)	0.05125	0.06145	0.08750	0.07065	0.07045
$\Delta H(4)$ (kJ mol <sup>-1</sup> )	+15.3	+15.1	+14.9	+16.2	+15.3
	Mean $\Delta H(4) = +15.4 \pm 0.4$ kJ mol <sup>-1</sup>				
<b>Reaction 5</b>					
Wt. C <sub>2</sub> H <sub>4</sub> (g)	0.00097	0.00097	0.00097	0.00097	0.00097
$\Delta H(5)$ (kJ mol <sup>-1</sup> )	-10.3	-10.6	-10.1	-11.9	-11.7
	Mean $\Delta H(5) = -10.9 \pm 0.7$ kJ mol <sup>-1</sup>				

Assuming that the enthalpies of sublimation of Pt(PPh<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>) and Pt(PPh<sub>3</sub>)<sub>2</sub>(CS<sub>2</sub>) are the same, we write

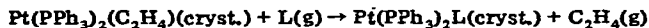
$$D(\text{Pt}-\text{CS}_2) - D(\text{Pt}-\text{C}_2\text{H}_4) = 44.0 \pm 2.2 \text{ kJ mol}^{-1}$$

Thus, the Pt $\cdots\overset{\text{C}}{\parallel}\text{S}$  bond is slightly stronger than the Pt $\cdots\overset{\text{C}}{\parallel}\text{C}$  bond.

Kirkham, Lister and Poyntz [2] have determined the enthalpies of reaction 1, where the ligands L are phenyl-substituted olefins. With these results, and our previous work [3,4] a short list of the enthalpies of reaction 1 with a variety of ligands can be drawn up (Table 2).

TABLE 2

## ENTHALPIES OF THE REACTION:



L	$\Delta H(\text{kJ mol}^{-1})$	Reference
CS <sub>2</sub>	-44.0 ± 2	this work
CH <sub>2</sub> =CHC <sub>6</sub> H <sub>5</sub>	-41.3 ± 5	2
<i>cis</i> -C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	-90.2 ± 5	2
<i>trans</i> -C <sub>6</sub> H <sub>5</sub> CH=CHC <sub>6</sub> H <sub>5</sub>	-118.5 ± 5	2
(CN) <sub>2</sub> C=C(CN) <sub>2</sub>	-155.8 ± 8	3
C <sub>6</sub> H <sub>5</sub> C≡CC <sub>6</sub> H <sub>5</sub>	-82.0 ± 12	4

## Experimental

Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(cryst.) was prepared by the method of Cook and Jauhal [5]; m.p. 122-125°C (dec.) (Found: C, 60.7; H, 4.8; calcd.: C, 61.0; H, 4.6%). Pt(PPh<sub>3</sub>)<sub>2</sub>(CS<sub>2</sub>)(cryst.) was recovered from the calorimeter vessel, m.p. 145°C (dec.) lit. [5] 145°C (dec.). The infrared spectrum (KBr disc) showed absorption at 1142 and 1159 cm<sup>-1</sup>, lit. [6] 1141 and 1160 cm<sup>-1</sup>. Enthalpies of

reaction were measured by use of the LKB 8700 Precision Calorimetry System equipped with a 25 ml reaction vessel. The system was calibrated electrically. Reactions were initiated at 298 K and enthalpies were calculated by the method described previously [7]. The associated uncertainties are twice the standard deviations from mean values.

## References

- 1 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, *Nat. Bur. Stand. Tech. Note* 270-3, 1968.
- 2 W.G. Kirkham, M.W. Lister and R.B. Foyntz, *Thermochim. Acta*, 11 (1975) 89.
- 3 A. Evans, C.T. Mortimer and R.J. Puddephatt, *J. Organometal. Chem.*, 72 (1974) 295.
- 4 A. Evans, C.T. Mortimer and R.J. Puddephatt, *J. Organometal. Chem.*, 85 (1975) 101.
- 5 C.D. Cook and G.S. Jauhal, *Inorg. Nucl. Chem. Lett.*, 3 (1967) 31; *J. Amer. Chem. Soc.*, 90 (1968) 1464.
- 6 M.C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, (1976) 865.
- 7 J.O. Hill, G. Öjelund and I. Wadsö, *J. Chem. Thermodynam.*, 1 (1969) 111.