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Preliminary communication

STRENGTH OF THE Pt—CS_2 BOND IN $Pt(PPh_3)_2(CS_2)$

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Summary

The enthalpy of the reaction:

$Pt(PPh_3)_2(CH_2{=}CH_2)(cryst.) + CS_2(g) \rightarrow Pt(PPh_3)_2(CS_2)(cryst.) + CH_2{=}CH_2(g)$

has been determined as $\Delta H = -44.0 \pm 2.2$ kJ mol^{-1} from solution calorimetry, and the bond dissociation energy $D(Pt{-}CS_2)$ shown to be slightly greater than $D(Pt{-}C_2H_4)$.

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

$$Pt(PPh_3)_2(CH_2{=}CH_2)(cryst.) + L(g) \rightarrow Pt(PPh_3)_2L(cryst.) + CH_2{=}CH_2(g) \quad (1)$$

where $L = CS_2$, 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] $\Delta H(6) = 27.7 \pm 0.1$ kJ mol^{-1} for the enthalpy of vaporisation of CS_2. Details of these measurements are shown in Table 1. Uncertainties are twice the standard deviations of mean values.

$$Pt(PPh_3)_2(C_2H_4)(cryst.) + \{80\ CS_2, 3200\ DCE\} \rightarrow \{Pt(PPh_3)_2(CS_2), 79\ CS_2, 3200\ DCE, C_2H_4\} \quad (2)$$

$$CS_2(l) + \{79\ CS_2, 3200\ DCE\} \rightarrow \{80\ CS_2, 3200\ DCE\} \quad (3)$$

$$Pt(PPh_3)_2(CS_2)(cryst.) + \{79\ CS_2, 3200\ DCE\} \rightarrow \{Pt(PPh_3)_2(CS_2), 79\ CS_2, 3200\ DCE\} \quad (4)$$

$$C_2H_4(g) + \{Pt(PPh_3)_2(CS_2), 79\ CS_2, 3200\ DCE\} \rightarrow \{Pt(PPh_3)_2(CS_2), 79\ CS_2, 3200\ DCE, C_2H_4\} \quad (5)$$

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TABLE 1

ENTHALPIES OF REACTIONS 2-5

Reaction 2					
Wt. $Pt(PPh_3)_2(C_2H_4)(g)$	0.08975	0.09480	0.08465	0.10105	0.13105
$\Delta H(2)$ (kJ mol^{-1})	−17.0	−16.1	−14.1	−16.4	−15.3
	Mean $\Delta H(2) = -15.8 \pm 1.0$				
Reaction 3					
Wt. $CS_2(g)$	0.7655	0.7626	0.7339	0.7758	0.7544
$\Delta H(3)$ (kJ mol^{-1})	+3.98	+3.98	+3.96	+3.97	+3.97
	Mean $\Delta H(3) = +3.97 \pm 0.01$ kJ mol^{-1}				
Reaction 4					
Wt. $Pt(PPh_3)_2(CS_2)(g)$	0.05125	0.06145	0.08750	0.07065	0.07045
$\Delta H(4)$ (kJ mol^{-1})	+15.3	+15.1	+14.9	+16.2	+15.3
	Mean $\Delta H(4) = +15.4 \pm 0.4$ kJ mol^{-1}				
Reaction 5					
Wt. $C_2H_4(g)$	0.00097	0.90097	0.00097	0.00097	0.00097
$\Delta H(5)$ (kJ mol^{-1})	−10.3	−10.6	−10.1	−11.9	−11.7
	Mean $\Delta H(5) = -10.9 \pm 0.7$ kJ mol^{-1}				

Assuming that the enthalpies of sublimation of $Pt(PPh_3)(C_2H_4)$ and $Pt(PPh_3)_2(CS_2)$ are the same, we write

$$D(Pt{-}CS_2) - D(Pt{-}C_2H_4) = 44.0 \pm 2.2 \text{ kJ mol}^{-1}$$

Thus, the $Pt\cdots\overset{C}{\underset{S}{\|}}$ bond is slightly stronger than the $Pt\cdots\overset{C}{\underset{C}{\|}}$ 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:

$Pt(PPh_3)_2(C_2H_4)(cryst.) + L(g) \rightarrow Pt(PPh_3)_2L(cryst.) + C_2H_4(g)$

L	ΔH(kJ mol^{-1})	Reference
CS_2	-44.0 ± 2	this work
$CH_2{=}CHC_6H_5$	-41.3 ± 5	2
cis-$C_6H_5CH{=}CHC_6H_5$	-90.2 ± 5	2
trans-$C_6H_5CH{=}CHC_6H_5$	-118.5 ± 5	2
$(CN)_2C{=}C(CN)_2$	-155.8 ± 8	3
$C_6H_5C{\equiv}CC_6H_5$	-82.0 ± 12	4

Experimental

$Pt(PPh_3)_2(C_2H_4)$(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%). $Pt(PPh_3)_2(CS_2)$(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^{-1}, lit. [6] 1141 and 1160 cm^{-1}. 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. Poyntz, 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. Puddephat, 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.