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Preliminary communication

THE PLATINUM–CARBON BOND STRENGTH IN $Pt(PPh_3)_2(Cl)(CPh{=}CHPh)$

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Summary

The enthalpies of the reactions 1 and 2 have been determined as ΔH =

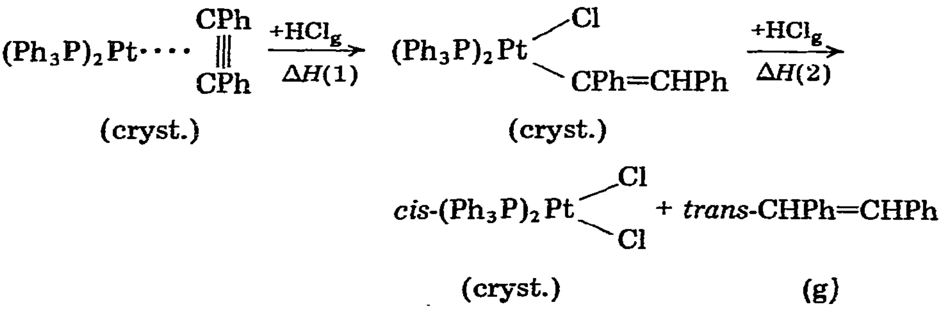
$$Pt(PPh_3)_2(CPh{\equiv}CPh)_{cryst.} + HCl_g \rightarrow Pt(PPh_3)_2(Cl)(CPh{=}CHPh)_{cryst.} \qquad (1)$$

$$Pt(PPh_3)_2(CPh{\equiv}CPh)_{cryst.} + 2HCl_g \rightarrow cis\text{-}Pt(PPh_3)_2Cl_{2\ cryst.} + trans\text{-}CHPh{=}CHPh_g \qquad (2)$$

-90.2 ± 6 and $\Delta H = -139.0 \pm 16$ kJ mol^{-1}, respectively; dissociation energies of bonds involving platinum are expressed by the relationship:

$$41 \text{ kJ mol}^{-1} + D(\text{Pt-tolane}) = 2D(\text{Pt—CPh=CHPh})$$
$$= \{D_1(\text{Pt—Cl}) + D_2(\text{Pt—Cl})\} - 350 \text{ kJ mol}^{-1}$$

In chloroform solution, $Pt(PPh_3)_2(C_2Ph_2)$ reacts with gaseous HCl in a two-stage process [1, 2]. From measurements, at 298 K, of the enthalpies of these two stages and of the relevant enthalpies of solution we have obtained the values $\Delta H(1) = -90.2 \pm 6$ kJ mol^{-1} and $[\Delta H(1) + \Delta H(2)] = -139.0 \pm 16$ kJ mol^{-1} for the following reaction:



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The gas-phase enthalpies of these reactions can provide information about the strengths of the Pt—Cl and Pt—CPh=CHPh bonds, relative to that of the Pt—tolane π-bond. It has not been possible to measure the enthalpies of sublimation of the compounds $Pt(PPh_3)_2(C_2Ph_2)$, $Pt(PPh_3)_2(Cl)(CPh{=}CHPh)$ and *cis*-$Pt(PPh_3)_2Cl_2$, but we make the assumption that these enthalpies are the same (± 10 kJ mol^{-1}) and that our values of $\Delta H(1)$ and $\Delta H(2)$ can be taken to apply to the gas-phase process without the introduction of unacceptable errors.

In terms of bond dissociation energies for the overall reaction we write

$$\Delta H(1) + \Delta H(2) = D(\text{Pt—tolane}) - \{D_1(\text{Pt—Cl}) + D_2(\text{Pt—Cl})\} - \{D_1(\text{C—H}) + D_2(\text{C—H})\} + 2D(\text{H—Cl}),$$

where $D_1(\text{Pt—Cl})$ and $D_2(\text{Pt—Cl})$ are the first and second bond dissociation energies in $Pt(PPh_3)_2Cl_2$, and $\{D_1(\text{C—H}) + D_2(\text{C—H})\}$ is the sum of the first and second C—H bond dissociation energies in *trans*-CHPh=CHPh, given by $D_1(\text{C—H}) + D_2(\text{C—H}) = \Delta H_f^0(\text{CPh}{\equiv}\text{CPh}_g) - \Delta H_f^0(\textit{trans}\text{-CHPh}{=}\text{CHPh}_g) + 2\Delta H_f^0(\text{H}_g)$. We use the values $\Delta H_f^0(\text{H}_g) = +217.97 \pm 0.01$ kJ mol^{-1} [3], $\Delta H_f^0(\textit{trans}\text{-CHPh}{=}\text{CHPh}_{\text{cryst.}}) = +136.9 \pm 1.0$ kJ mol^{-1} [4], $\Delta H_f^0(\text{CPh}{\equiv}\text{CPh}_{\text{cryst.}}) = +312.4 \pm 1.2$ kJ mol^{-1} [4], and estimated enthalpies of sublimation of these two compounds of 100 ± 5 kJ mol^{-1}, to calculate $\{D_1(\text{C—H}) + D_2(\text{C—H})\} = 611.4 \pm 12.2$ kJ mol^{-1}. Combination of the value $D(\text{H—Cl}) = 431.57 \pm 0.01$ kJ mol^{-1} [5] gives $\{D_1(\text{Pt—Cl}) + D_2(\text{Pt—Cl})\} - D(\text{Pt—tolane}) = 391 \pm 17$ kJ mol^{-1}.

For the first stage of the reaction between $Pt(PPh_3)_2(CPh{\equiv}CPh)$ and HCl we write $\Delta H(1) = D(\text{Pt—tolane}) - \{D(\text{Pt—CPh}{=}\text{CHPh}) + D_2(\text{Pt—Cl}) + D_2(\text{C—H})\} + D(\text{H—Cl})$, where $D(\text{Pt—CPh}{=}\text{CHPh})$ and $D_2(\text{Pt—Cl})$ are the enthalpies of the successive gas-phase reactions:

$$Pt(PPh_3)_2(Cl)(CPh{=}CHPh) \rightarrow Pt(PPh_3)_2Cl + CPh{=}CHPh \longrightarrow Pt(Ph_3)_2 + Cl$$

No value for $D_2(\text{C—H})$ is available, so we adopt the approximation $D_2(\text{C—H}) = \frac{1}{2}\{D_1(\text{C—H}) + D_2(\text{C—H})\} = 305.7 \pm 6.1$ kJ mol^{-1}. The following relationship is then derived:

$$D(\text{Pt—CPh}{=}\text{CHPh}) + D_2(\text{Pt—Cl}) - D(\text{Pt—tolane}) = 216.1 \pm 12 \text{ kJ mol}^{-1}$$

Previously [6], we have calculated a value for $\{D_1(\text{Pt—Cl}) + D_2(\text{Pt—Cl})\}$ in $PtCl_2$. Using the more recent [3] enthalpies of formation we obtain $\{D_1(\text{Pt—Cl}) + D_2(\text{Pt—Cl})\} = 780 \pm 6$ kJ mol^{-1}. If the sum of the platinum—chlorine bond dissociation energies has the same value in $Pt(PPh_3)_2Cl_2$ and $D_1(\text{Pt—Cl}) = \frac{1}{2}\{D_1(\text{Pt—Cl}) + D_2(\text{Pt—Cl})\}$ then we derive the bond dissociation energies shown in Table 1.

TABLE 1

BOND DISSOCIATION ENERGIES

Bond	Compound	$D(\text{Pt—L})$ (kJ mol^{-1})
Pt—Cl	$PtCl_2$	390 ± 3
Pt—tolane	$Pt(PPh_3)_2(CPh{=}CPh)$	389 ± 23
Pt—CPh=CHPh	$Pt(PPh_3)_2(Cl)(CPh{=}CHPh)$	215 ± 23
Pt—Ph	$Pt(PEt_3)_2(Cl)Ph$	264 ± 15 [6]

Experimental

$Pt(PPh_3)_2(CPh{\equiv}CPh)$ was prepared [8] by hydrazine reduction of $Pt(PPh_3)_2Cl_2$, followed by addition of $CPh{\equiv}CPh$; m.p. 160 °C, lit. [7] 161-169 °C. $Pt(PPh_3)_2(Cl)(CPh{=}CHPh)$ was prepared by reaction between $Pt(PPh_3)_2$-$(CPh{\equiv}CPh)$ and HCl in either chloroform or diethyl ether; m.p. 180 °C. Recrystallisation of this product (I) from dichloromethane/pentane yielded the same compound, but recrystallisation from methanol yielded II, m.p. 264 °C, lit. [8] 217-218 °C. By use of the Perkin–Elmer Differential Scanning Calorimeter, DSC 1, we have measured enthalpies of the following transformations: $I_{cryst.} \rightarrow I_{liq.}$, $\Delta H_{453} = +15.9 \pm 0.8$ kJ mol^{-1}, and $I_{liq.} \rightarrow II_{cryst.}$, $\Delta H_{491} = -28.0 \pm 0.8$ kJ mol^{-1}. It is assumed that I and II are isomeric about the platinum atom, i.e. *cis*- and *trans*-$Pt(PPh_3)_2(Cl)(CPh{=}CHPh)$, respectively. The enthalpy of isomerisation, $I_{cryst};\rightarrow II_{cryst.}$, -12.1 ± 1.6 kJ mol^{-1}, may be compared with a value of -17.7 ± 1.5 kJ mol^{-1} for the reaction *cis*→*trans*-$Pt(PMe_2Ph)_2(Cl)Me$. $Pt(PPh_3)_2Cl_2$ was prepared [9] by refluxing K_2PtCl_4 and excess PPh_3 in xylene, m.p. 294 °C, lit. 294 °C decomp., [10] and > 300 °C [9].

HCl gas (Air Products) was used directly from the cylinder; $CHCl_3$ (Koch–Light) was distilled, b.p. 58-60 °C/740 mm Hg; *trans*-$CHPh{=}CHPh$ (Fluka, puriss for scintillation) had m.p. 123-125 °C.

Enthalpies of reactions in solutions were measured at 298 K by breaking ampoules of either HCl gas or solid compounds into chloroform solutions saturated with nitrogen, in the LKB 8700 Precision Calorimetry System equipped with the 25 ml reaction vessel. The system was calibrated electrically.

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