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THE PLATINUM—CARBON BOND STRENGTH IN $Pt(PPh_3)_2(CPh{\equiv}CPh)$

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Summary

The enthalpy of the reaction:

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

has been determined as $\Delta H_{298} = -82 \pm 12$ kJ mol^{-1}, from solution calorimetry. The conclusion, that the platinum—tolane bond is stronger than the platinum—ethylene bond, is in agreement with available structural data.

Previously [1], we reported measurement of the enthalpy of reaction 1, from which we concluded that the platinum—olefin bond in $Pt(PPh_3)_2[C(CN)_2{=}C(CN)_2]$ is some 156 kJ mol^{-1} stronger than in $Pt(PPh_3)_2(CH_2{=}CH_2)$. We now report determination of the enthalpy at 298 K, $\Delta H(2)$, of reaction 2.

$$Pt(PPh_3)_2(C_2H_4)(cryst.) + C_2(CN)_4(g) \rightarrow Pt(PPh_3)_2[C_2(CN)_4](cryst.) + C_2H_4(g) \qquad (1)$$

$$Pt(PPh_3)_2(C_2H_4)(cryst.) + C_2Ph_2(g) \rightarrow Pt(PPh_3)_2(C_2Ph_2)(cryst.) + C_2H_4(g) \qquad (2)$$

The enthalpy, $\Delta H(2)$, has been derived from measurements, at 298 K, of the enthalpies, $\Delta H(3)$ — $\Delta H(6)$ of reactions 3-6, where TOL is toluene, together with an estimated value, $\Delta H(7) = 100 \pm 10$ kJ mol^{-1}, for the enthalpy of sublimation of tolane, reaction 7. This estimate is based on the assumption that the enthalpy of sublimation of tolane will be similar to those [2] of the related compounds 1,2-diphenylethane, 84 kJ mol^{-1}, *cis*-1,2-diphenylethene, 90 kJ mol^{-1}, and of other aromatic hydrocarbons of the empirical formula $C_{14}H_{10}$, e.g.

TABLE 1

ENTHALPIES OF REACTIONS 3-6

Reaction 3					
Wt. $Pt(PPh_3)_2(C_2H_4)$(g)	0.069889	0.085820	0.088105	0.084915	0.086343
$\Delta H(3)$ (kJ mol^{-1})	+ 8.42	+ 8.42	+ 7.86	+ 7.96	+ 7.98
	Mean $\Delta H(3) = +8.1 \pm 0.2$ kJ mol^{-1}				
Reaction 4					
Wt. $C_2(C_6H_5)_2$(g)	0.405746	0.403443	0.406046	0.413554	0.410451
$\Delta H(4)$ (kJ mol^{-1})	+16.84	+18.42	+17.23	+18.10	+17.93
	Mean $\Delta H(4) = +17.7 \pm 0.7$ kJ mol^{-1}				
Reaction 5					
Wt. C_2H_4(g)	0.003183	0.003358	0.003185	0.003111	0.003547
$\Delta H(5)$ (kJ mol^{-1})	−10.67	−10.53	−12.33	−10.78	−10.05
	Mean $\Delta H(5) = -10.9 \pm 0.8$ kJ mol^{-1}				
Reaction 6					
Wt. $Pt(PPh_3)_2(C_2Ph_2)$(g)	0.100137	0.103255	0.098430	0.098440	0.096614
$\Delta H(6)$ kJ mol^{-1}	+18.67	+19.91	+18.49	+19.02	+19.60
	Mean $\Delta H(6) = +19.1 \pm 0.5$ kJ mol^{-1}				

anthracene, 105 kJ mol^{-1}, and phenanthrene, 95 kJ mol^{-1}. Values obtained for the enthalpies $\Delta H(3) - \Delta H(6)$ are shown in Table 1, and these together with the estimate for $\Delta H(7)$, lead to the value $\Delta H(2) = -82 \pm 12$ kJ mol^{-1}.

$$\mathrm{Pt(PPh_3)_2(C_2H_4)(cryst.)} + [22\ \mathrm{C_2Ph_2},\ 2000\ \mathrm{TOL}] \rightarrow [\mathrm{Pt(PPh_3)_2(C_2Ph_2)},\ \mathrm{C_2H_4},\ 21\ \mathrm{C_2Ph_2},\ 2000\ \mathrm{TOL}] \qquad (3)$$

$$\mathrm{C_2Ph_2(cryst.)} + [21\ \mathrm{C_2Ph_2},\ 2000\ \mathrm{TOL}] \rightarrow [22\ \mathrm{C_2Ph_2},\ 2000\ \mathrm{TOL}] \qquad (4)$$

$$\mathrm{C_2H_4(g)} + [21\ \mathrm{C_2Ph_2},\ 2000\ \mathrm{TOL}] \rightarrow [\mathrm{C_2H_4},\ 21\ \mathrm{C_2Ph_2},\ 2000\ \mathrm{TOL}] \qquad (5)$$

$$\mathrm{Pt(PPh_3)_2(C_2Ph_2)(cryst.)} + [\mathrm{C_2H_4},\ 21\ \mathrm{C_2Ph_2},\ 2000\ \mathrm{TOL}] \rightarrow [\mathrm{Pt(PPh_3)_2(C_2Ph_2)},\ \mathrm{C_2H_4},\ 21\ \mathrm{C_2Ph_2},\ 2000\ \mathrm{TOL}] \qquad (6)$$

$$\mathrm{C_2Ph_2(cryst.)} \rightarrow \mathrm{C_2Ph_2(g)} \qquad (7)$$

Whilst it would be preferable to know the enthalpy of reaction 2, in which the platinum complexes were in the gas phase, it seems unlikely that the enthalpies of sublimation of the two complexes will be very different, so that the value $\Delta H(2) = -82$ kJ mol^{-1}, will be close to that for the gas-phase reaction. Thus, we obtain a value for the difference between the bond dissociation energies, D(Pt—tolane) — D(Pt—ethylene) = 82 ± 12 kJ mol^{-1}.

The structure [3] of $Pt(PPh_3)_2(C_2Ph_2)$ shows that the central C—C bond length of 0.132 nm is very similar to that [4] in free ethylene, 0.1339 nm, and some 0.013 nm longer than the acetylenic link in free tolane, 0.119 nm [5]. This lengthening is intermediate between that (0.009 nm) [4, 6] when free ethylene bonds to form $Pt(PPh_3)_2(C_2H_4)$ and that (0.017 nm) [7, 8] when free tetracyanoethylene bonds to form $Pt(PPh_3)_2[C_2(CN)_4]$. Thus the structural data and thermochemical data both indicate that the platinum(0)—tolane bond is stronger than the platinum(0)—ethylene bond, but weaker than the platinum(0)—tetracyanoethylene bond. The chemical properties are also consistent with this order of bond strengths since tetracyanoethylene will replace both tolane and ethylene from their respective bis(triphenylphosphine)platinum(0) complexes.

Experimental

$Pt(PPh_3)_2(C_2H_4)$(cryst.) was prepared by the method of Cook and Jauhal [9]; m.p. 122-125° (dec.) (Found: C, 60.7; H, 4.8; calcd. C, 61.0; H, 4.6%.) $Pt(PPh_3)_2(C_2Ph_2)$(cryst.) was recovered from the calorimeter vessel, m.p. 161°. Tolane (Koch Light) was recrystallised (twice) from ethanol. Toluene was dried over sodium. It was saturated with nitrogen (white spot) to prevent the possible formation of $Pt(PPh_3)_2O_2$. 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, by breaking a glass phial of reactant into the solvent. Enthalpies were calculated according to the method described previously [10].

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