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THE PLATINUM—OLEFIN BOND STRENGTH IN $Pt(PPh_3)_2(\eta$-3-PHENYLCYCLOBUTENE-1,2-DIONE)

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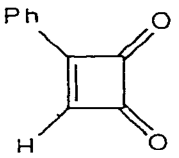
Summary

The enthalpy, $\Delta H = -64.7 \pm 4$ kJ mol^{-1}, for the reaction

$$Pt(PPh_3)_2(\eta\text{-}C_2H_4)(s) + pcbd(g) \rightarrow Pt(PPh_3)_2(\eta\text{-}pcbd)(s) + C_2H_4(g)$$

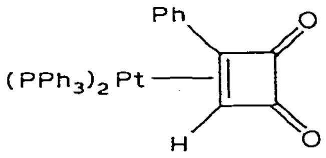
where pcbd is 3-phenylcyclobutene-1,2-dione, $\mathrm{Ph\overline{C{=}CHC(O)C}O}$, has been measured calorimetrically. The Pt—olefin bond in this complex is slightly stronger than that in $Pt(PPh_3)_2(\eta\text{-}PhCH{=}CH_2)$.

Reaction between bis(triphenylphosphine)(ethylene)platinum(0), $Pt(PPh_3)_2(\eta\text{-}C_2H_4)$, and 3-phenylcyclobutene-1,2-dione, pcbd, I, in 1,2-dichloroethane at room temperature is rapid and yields the π-complex $Pt(PPh_3)_2(\eta\text{-}pcbd)$, II, quantitatively. A slow reaction (half life about 10 h) follows in which II is transformed to the platina cyclo compound 1,1-bis(triphenylphosphine)platinaphenylcyclopentenedione, III, $(PPh_3)_2Pt(pcpd)$ [1].



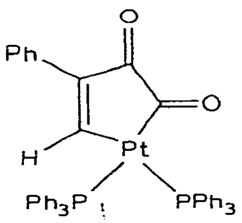
pcbd

(I)



$Pt(PPh_3)_2(\eta$-pcbd)

(II)



$(PPh_3)_2Pt$(pcpd)

(III)

As π-complexes of the type illustrated by II are intermediates in the ring opening, by the $Pt(PPh_3)_2$ group, of a variety of substituted cyclobutenediones and cyclopropenones, it is of interest to gain information about the stability of these intermediates. To this end, we have determined the enthalpy of reaction in which II is formed. The enthalpy, $\Delta H(1) = -64.7 \pm 4$ kJ mol^{-1}, has been derived from measurements of the enthalpies, $\Delta H(2)$ — $\Delta H(4)$, of reactions 2—4 (below), where dce is 10^4 mol 1,2-dichloroethane, a reported [2] enthalpy of sublimation of pcbd, $\Delta H_{\mathrm{sub}} = +54.4 \pm 6.4$ kJ mol^{-1} and a value $\Delta H(5) = +9 \pm 3$ kJ mol^{-1}, for the enthalpy of solution reaction, estimated from values for similar platinum complexes. Because of the slow transformation (II → III) we did not isolate a pure sample of II for measurement of its enthalpy of solution. The values obtained were $\Delta H(2) + 21.9 \pm 0.2$, $\Delta H(3) -13.5 \pm 0.6$, and $\Delta H(4) -10.9 \pm 0.7$ kJ mol^{-1}.

$$\mathrm{Pt(PPh_3)_2(\eta\text{-}C_2H_4)(s) + pcbd(g) \rightarrow Pt(PPh_3)_2(\eta\text{-}pcbd)(s) + C_2H_4(g)} \quad (1)$$

$$\mathrm{pcbd(s) + dce(l) \rightarrow [pcbd, dce](b)} \quad (2)$$

$$\mathrm{Pt(PPh_3)(\eta\text{-}C_2H_4)(s) + [pcbd, dce](l) \rightarrow [Pt(PPh_3)_2(\eta\text{-}pcbd), C_2H_4, dce](l)} \quad (3)$$

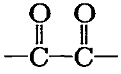
$$\mathrm{C_2H_4(g) + dce(l) \rightarrow [C_2H_4, dce](l)} \quad (4)$$

$$\mathrm{Pt(PPh_3)_2(\eta\text{-}pcbd)(s) + [C_2H_4, dce](l) \rightarrow [Pt(PPh_3)_2(\eta\text{-}pcbd), C_2H_4, dce](l)} \quad (5)$$

Kirkham et al. [3] have measured the enthalpies of reactions 6 and 7 as $\Delta H(6) = -41.3 \pm 2.5$ and $\Delta H(7) = -111.0 \pm 10$ kJ mol^{-1}.

$$\mathrm{Pt(PPh_3)_2(\eta\text{-}C_2H_4)(s) + PhCH{=}CH_2(g) \rightarrow Pt(PPh_3)_2(\eta\text{-}PhCH{=}CH_2)(s) + C_2H_4(g)} \quad (6)$$

$$\mathrm{Pt(PPh_3)_2(\eta\text{-}C_2H_4)(s) + \textit{trans}\text{-}PhCH{=}CHPh(g) \rightarrow Pt(PPh_3)_2(\eta\text{-}\textit{trans}\text{-}PhCH{=}CHPh)(s) + C_2H_4(g)} \quad (7)$$

The value $\Delta H(1) = -64.7 \pm 4$ kJ mol^{-1} for the formation of $\mathrm{Pt(PPh_3)_2(\eta\text{-}pcbd)}$ is 23 kJ mol^{-1} greater than that for the formation of the phenylethylene complex and considerably less than that for the *trans*-stilbene complex. These enthalpies incorporate the effects of intermolecular forces in the three solid complexes which may be dissimilar. It is unfortunate that we have been unable, because of their low vapour pressures, to measure the enthalpies of sublimation of the complexes and take account of these effects. However, it seems probable that the Pt—olefin π bond in II is slightly stronger than that in $\mathrm{Pt(PPh_3)_2(\eta\text{-}PhCH{=}CH_2)}$. Ring formation resulting from replacement of a hydrogen atom on each of the two ethylenic carbon atoms by a  $-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-$ chain causes a small strengthening, of some 23 kJ mol^{-1}, of the Pt—olefin bond.

Experimental

$\mathrm{Pt(PPh_3)_2(\eta\text{-}C_2H_4)}$ [4] and 3-phenylcyclobutene-1,2-dione [2] were prepared as described in the literature. Microanalyses gave satisfactory results. 1,2-Dichloroethane was dried ($\mathrm{MgSO_4}$), purged with nitrogen and distilled, b.p. 82.16—82.23°C, 748.25 torr. Enthalpies were measured by use of an LKB 8700 calorimeter, the vessel of which contained an atmosphere of nitrogen.

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