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THE PLATINUM—CARBON BOND STRENGTH IN $Pt(PPh_3)_2(CH_3)I$

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Summary

The enthalpies of reactions 1—3 have been determined

$Pt(PPh_3)_2(C_2H_4)(s) + I_2(g) \rightarrow$ *trans*-$Pt(PPh_3)_2I_2(s) + C_2H_4(g)$ (1)

$Pt(PPh_3)_2(C_2H_4)(s) + CH_2ICH_2I(g) \rightarrow$ *cis*-$Pt(PPh_3)_2I_2(s) + 2\ C_2H_4(g)$ (2)

$Pt(PPh_3)_2(C_2H_4)(s) + CH_3I(g) \rightarrow$ *cis*-$Pt(PPh_3)_2(CH_3)I(s) + C_2H_4(g)$ (3)

as $\Delta H(1) = -176.6 \pm 5.4$, $\Delta H(2) = -107.8 \pm 6.0$, and $\Delta H(3) = -78.9 \pm 2.0$ kJ mol^{-1}. The bond dissociation energy difference $D_1(Pt—CH_3) - D_1(Pt—I) = +6 \pm 5$ kJ mol^{-1} is calculated, which indicates that the two bonds have very similar strengths.

Bis(triphenylphosphine)(ethylene)platinum(0), $PtP_2(C_2H_4)$, reacts rapidly and quantitatively, at 25°C, with I_2 [1], CH_2ICH_2I, and CH_3I [2] in 1,2-dichloroethane according to eq. 4—6, where dce represents 10^4 mol of solvent.

$PtP_2(C_2H_4)(s) + [I_2, dce](l) \rightarrow [$*trans*-$PtP_2I_2, C_2H_4, dce](l)$ (4)

$PtP_2(C_2H_4)(s) + [10\ C_2H_4I_2, dce](l) \rightarrow [$*cis*-$PtP_2I_2, 2\ C_2H_4, 9\ C_2H_4I_2, dce](l)$ (5)

$PtP_2(C_2H_4)(s) + [100\ CH_3I, dce](l) \rightarrow [$*cis*-$PtP_2(CH_3)I, C_2H_4, 99\ CH_3I, dce](l)$ (6)

Enthalpies of these reactions have been measured calorimetrically. In addition, enthalpies of the solution reactions 7—13 have also been measured.

$I_2(s) + dce(l) \rightarrow [I_2, dce](l)$ (7)

$C_2H_4I_2(s) + [9\ C_2H_4I_2, dce](l) \rightarrow [10\ C_2H_4I_2, dce](l)$ (8)

$CH_3I(l) + [99\ CH_3I, dce](l) \rightarrow [100\ CH_3I, dce](l)$ (9)

$C_2H_4(g) + dce(l) \rightarrow [C_2H_4, dce](l)$ (10)

trans-$PtP_2I_2(s) + dce(l) \rightarrow [$*trans*-$PtP_2I_2, dce](l)$ (11)

cis-$PtP_2I_2(s) + [9\ C_2H_4I_2, dce](l) \rightarrow [$*cis*-$PtP_2I_2, 9\ C_2H_4I_2, dce](l)$ (12)

cis-$PtP_2(CH_3)I(s) + [99\ CH_3I, dce](l) \rightarrow [$*cis*-$PtP_2(CH_3)I, 99\ CH_3I, dce](l)$ (13)

The following values, in kJ mol^{-1}, have been obtained:

$\Delta H(4)$ −138.4 ± 1.4, $\Delta H(5)$ −73.9 ± 1.0, $\Delta H(6)$ −45.9 ± 1.3, $\Delta H(7)$ +22.32 ± 0.52, $\Delta H(8)$ +18.89 ± 0.55, $\Delta H(9)$ +1.21 ± 0.03, $\Delta H(10)$ −10.94 ± 0.74, $\Delta H(11)$ +9.0 ± 1.1, $\Delta H(12)$ +9.0 ± 1.1, $\Delta H(13)$ +17.4 ± 0.48. Incorporating the values $\Delta H(\text{sub})(I_2,s)$ = +62.44 ± 0.02 [3], $\Delta H(\text{sub})$ $(C_2H_4I_2, l)$ = +65.7 ± 4.1, and $\Delta H(\text{vap})(CH_3I, l)$ = +28.03 ± 1.3 kJ mol^{-1} [4] yields the values for $\Delta H(1)$ — $\Delta H(3)$ listed in the abstract.

Using the ΔH_f^0 values [4]: $C_2H_4I_2(g)$ +64.9 ± 1.7, $C_2H_4(g)$ +52.1 ± 0.4 kJ mol^{-1} leads to a value for the enthalpy of isomerization *cis*- → *trans*-$Pt(PPh_3)_2I_2$-(s), −19 ± 5 kJ mol^{-1}. This value is close to the −13.4 kJ mol^{-1} for the isomerization *cis*- → *trans*-$Pt(PEt_3)_2I_2(s)$ obtained by scanning calorimetry [5].

The enthalpies of reactions 1 and 3 and the enthalpy of isomerization may be used to derive the bond dissociation energy relationships

$D(Pt—C_2H_4) + D(I—I) - D_1(Pt—I) - D_2(Pt—I) = -157.4 - W + Y$ (14)

$D(Pt—C_2H_4) + D(CH_3—I) - D_1(Pt—CH_3) - D_2(Pt—I) = -78.9 - W + Z$ (15)

where W, Y and Z are the enthalpies of sublimation of $Pt(PPh_3)_2(C_2H_4)$, *cis*-$Pt(PPh_3)_2I_2$ and *cis*-$Pt(PPh_3)_2(CH_3)I$, respectively. If $W = Y = Z$, and using the values $D(I—I)$ = 151.24 ± 0.01 [3] and $D(CH_3—I)$ = 236 ± 4 kJ mol^{-1} [6], we obtain the relationship

$D_1(Pt—CH_3) - D_1(Pt—I) = +6 \pm 5$ kJ mol^{-1}

which indicates that the platinum—methyl and platinum—iodine bond dissociation energies are virtually the same.

Experimental

$Pt(PPh_3)_2(C_2H_4)(s)$ was prepared by the method of Cook and Jauhal [7]; m.p. 122—125°C (dec.) (Anal.: Found: C, 60.28; H, 4.76. calcd. for $C_{38}H_{34}P_2Pt$: C, 61.04; H, 4.58%). *cis*- and *trans*-$Pt(PPh_3)_2I_2(s)$, and *cis*-$Pt(PPh_3)_2(CH_3)I(s)$ were recovered from the calorimeter vessel, characterised by their infrared spectra [8], and gave satisfactory microanalyses. 1,2-Dichloroethane was dried over magnesium sulphate, purged with nitrogen and distilled, b.p. 82.16—82.23°C/ 748.25 Torr. Enthalpies of reaction were measured by use of the LKB 8700 calorimeter, equipped with a 25 ml reaction vessel.

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