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ENTHALPIES OF REACTION OF BIS(TRIPHENYLPHOSPHINE)(*trans*-STILBENE)PLATINUM(0) WITH DIPHENYLCYCLOPROPENONE AND BENZOCYCLOBUTENEDIONE

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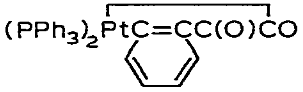
Summary

Enthalpies, $\Delta H(1)$ —94.8 ± 6.0 and $\Delta H(6)$ —57.1 ± 5.1 kJ mol^{-1}, of the following reactions have been measured calorimetrically

$$[\mathrm{Pt}(trans\text{-stilbene})(\mathrm{PPh_3})_2](\mathrm{s}) + \mathrm{dpcp}(\mathrm{g}) \rightarrow (\mathrm{PPh_3})_2\mathrm{Pt}(\mathrm{dpcb})(\mathrm{s}) + trans\text{-stilbene}(\mathrm{g}) \quad (1)$$

$$[\mathrm{Pt}(trans\text{-stilbene})(\mathrm{PPh_3})_2](\mathrm{s}) + \mathrm{bcbd}(\mathrm{g}) \rightarrow (\mathrm{PPh_3})_2\mathrm{Pt}(\mathrm{bcpd})(\mathrm{s}) + trans\text{-stilbene}\ (\mathrm{g}) \quad (6)$$

where dpcp is diphenylcyclopropenone, $(PPh_3)_2Pt(dpcb)$ is (1,1-bistriphenylphosphine)platinadiphenylcyclobutenone, $(PPh_3)_2PtC(Ph)=C(Ph)CO$, bcbd is benzocyclobutene-1,2-dione and $(PPh_3)_2Pt(bcpd)$ is (1,1-bistriphenylphosphine)-platinabenzocyclopentenedione,



$(PPh_3)_2PtC=CC(O)CO$

. It is concluded that the five-membered platinacyclo ring system in $(PPh_3)_2Pt(dpcb)$ is not heavily strained.

Previously, it has been reported that tetrakis(triphenylphosphine)platinum(0) reacts [1] at room temperature with diphenylcyclopropenone, dpcp, (I), in

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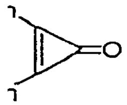
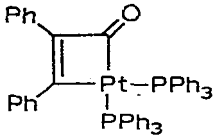
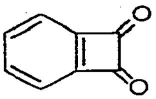
chloromethane to form (1,1-bistriphenylphosphine)platinadiphenylcyclo-ıtenone, $(PPh_3)_2$Pt(dpcb), (II), 60% yield, and with benzocyclobutene-1,2-one, bcbd, (III) in benzene to form (1,1-bistriphenylphosphine)platinabenzo-ɼclopentenedione, $(PPh_3)_2$Pt(bcpd), (IV), 65% yield red form 5% blue form ꜱ]. We find that bis(triphenylphosphine)(*trans*-stilbene)platinum(0) in 1,2-diıloroethane solution also reacts at room temperature to yield II and IV red ›rm.



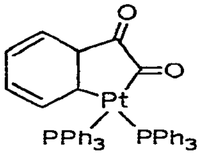
) dpcp



(II)



(III) bcbd



(IV)

ınce the reactions are so rapid and we can find no evidence of the formation f an intermediate π-complex, we assume that the platinacyclo compounds 'e formed quantitatively. Measurements of the enthalpies of reaction of bisriphenylphosphine)(*trans*-stilbene)platinum(0), $Pt(PPh_3)_2$(*trans*-stilbene), ith I and III to yield II and IV red form, respectively, are reported in this ıper.

The enthalpy, $\Delta H(1)$ —94.8 ± 6.0 kJ mol^{-1}, of reaction 1 has been derived 'om measurements of the enthalpies, $\Delta H(2)$ to $\Delta H(5)$ of reactions 2—5, in hich dce refers to 10^4 mole 1,2-dichloroethane, the measured enthalpy of ıblimation of *trans*-stilbene, ΔH(sub) +95.4 ± 3.0 kJ mol^{-1} and the known ıthalpy of sublimation of dpcp [3], ΔH(sub) +141.8 ± 4.2 kJ mol^{-1}. The values btained were: $\Delta H(2)$ +32.6 ± 1.2, $\Delta H(3)$ —53.2 ± 1.1, $\Delta H(4)$ +8.0 ± 6.8 and $H(5)$ +24.0 ± 0.4 kJ mol^{-1}.

t(*t*-stilbene)$(PPh_3)_2$(s) + dpcp(g) → $(PPh_3)_2$Pt(dpcb)(s) + *t*-stilbene(g) (1)

pcp(s) + [dpcp, dce](l) → [2dpcp, dce](l) (2)

'$Ph_3)_2$Pt(*t*-stilbene)(s) + [2dpcp, dce](l) →
[$(PPh_3)_2$Pt(dpcb), *t*-stilbene, dpcp, dce](l) (3)

'$Ph_3)_2$Pt(dpcb)(s) + [*t*-stilbene, dpcp, dce](l) →
[$(PPh_3)_2$Pt(dpcb), *t*-stilbene, dpcp, dce](l) (4)

stilbene(s) + [dpcp, dce](l) → [*t*-stilbene, dpcp, dce](l) (5)

The enthalpy $\Delta H(6)$ —57.1 ± 5.1 kJ mol^{-1}, of reaction 6 has been derived 'om measurements of the enthalpies, $\Delta H(7)$ to $\Delta H(10)$, of reactions 7—10 and ıe measured enthalpy of sublimation of bcbd, ΔH(sub) +88.6 ± 1.9 kJ mol^{-1}. he values obtained were: $\Delta H(7)$ + 16.7 ± 0.3, $\Delta H(8)$ —55.5 ± 2.0, $\Delta H(9)$ + 0.8 2.5 and $\Delta H(10)$ +24.4 ± 0.2 kJ mol^{-1}.

t(*t*-stilbene)$(PPh_3)_2$(s) + bcbd(g) → $(PPh_3)_2$Pt(bcpd)(s) + *t*-stilbene(g) (6)

cbd(s) + [9bcbd, dce](l) → [10bcbd, dce](l) (7)

$\mathrm{Pt}(t\text{-stilbene})(\mathrm{PPh_3})_2(\mathrm{s}) + [10\mathrm{bcbd, dce}](\mathrm{l}) \rightarrow$

$$[(\mathrm{PPh_3})_2\mathrm{Pt(bcpd)}, t\text{-stilbene}, 9\mathrm{bcbd, dce}](\mathrm{l}) \quad (8)$$

$(\mathrm{PPh_3})_2\mathrm{Pt(bcpd)}(\mathrm{s}) + [t\text{-stilbene}, 9\mathrm{bcbd, dce}](\mathrm{l}) \rightarrow$

$$[(\mathrm{PPh_3})_2\mathrm{Pt(bcpd)}, t\text{-stilbene}, 9\mathrm{bcbd, dce}](\mathrm{l}) \quad (9)$$

$$t\text{-stilbene}(\mathrm{s}) + [9\mathrm{bcbd, dce}](\mathrm{l}) \rightarrow [t\text{-stilbene}, 9\mathrm{bcbd, dce}](\mathrm{l}) \quad (10)$$

Unfortunately, it has not been possible either to measure the enthalpies of sublimation of $\mathrm{Pt}(t\text{-stilbene})(\mathrm{PPh_3})_2$, $(\mathrm{PPh_3})_2\mathrm{Pt(dpcb)}$ and $(\mathrm{PPh_3})_2\mathrm{Pt(bcpd)}$ because of their low vapour pressures, or to estimate these values reliably, so as to refer reactions 1 and 6 entirely to the gas phase. However, we make the simplifying assumption that the enthalpies of sublimation of these three compounds are the same so that the values of $\Delta H(1)$ and $\Delta H(6)$ may be taken to refer to the gas phase reaction. We then write

$2D(\mathrm{Pt{-}C})$ in $\mathrm{Pt(PPh_3)_2(dpcb)} - D(\mathrm{Pt{-}stilbene}) =$

$$D(\mathrm{C{-}C}) \text{ in dpcp} + (95 \pm 6)\ \mathrm{kJ\ mol^{-1}}$$

An estimate of the magnitude of the bond dissociation energy, $D(\mathrm{C{-}C})$, of the single $\mathrm{C}_{sp^2}{-}\mathrm{C}_{sp^2}$ bond, which is broken in the ring opening of the diphenylcyclopropenone molecule, can be made in the following way. The bond dissociation energy, $D(\mathrm{CH_2{=}CH{-}CH{=}CH_2}) = +(459 \pm 12)\ \mathrm{kJ\ mol^{-1}}$, of the central bond between two C_{sp^2} atoms in 1,3-butadiene, can be calculated from the enthalpy of the reaction

$$\mathrm{CH_2{=}CH{-}CH{=}CH_2(g)} \rightarrow 2\ \mathrm{CH_2{=}CH^{\bullet}(g)}$$

using the values $\Delta H_f^0(\mathrm{CH_2{=}CHCH{=}CH_2, g})$ +$(109.9 \pm 0.8)\ \mathrm{kJ\ mol^{-1}}$ [4], and $\Delta H_f^0(\mathrm{CH_2{=}CH^{\bullet}, g}) = +(284.5 \pm 12)\ \mathrm{kJ\ mol^{-1}}$ [5]. Kerr [6] has recommended a value of 268 $\mathrm{kJ\ mol^{-1}}$ for the enthalpy of formation of the vinyl radical, but, more recently, Golden and Benson [5] have preferred the higher value of at least 284.5 $\mathrm{kJ\ mol^{-1}}$. We adopt this higher value. The bond dissociation energy, $D(\mathrm{C{-}C})$, in the cyclopropenone is likely to be less than in 1,3-butadiene, because of the relief of ring strain on ring opening. Hopkins et al. [3] have measured the enthalpies of combustion and sublimation of diphenylcyclopropenone and, using the Laidler scheme [7], have calculated a strain energy in this molecule of $326 \pm 8\ \mathrm{kJ\ mol^{-1}}$. Consequently, we estimate an approximate value $D(\mathrm{C{-}C}) = 133 \pm 20\ \mathrm{kJ\ mol^{-1}}$ in this molecule. Using this value, the difference between the sum of the two platinum—carbon bond dissociation energies in the platinacyclobutenone II, and the platinum—styrene bond dissociation energy is calculated as

$$2D(\mathrm{Pt{-}C}) - D(\mathrm{Pt{-}styrene}) = +(228 \pm 26)\ \mathrm{kJ\ mol^{-1}}$$

From data given previously [8,9], it is possible to calculate the bond energy difference in $\mathrm{Pt(PPh_3)_2(CH_3)_2}$ and $\mathrm{Pt(PPh_3)_2}(t\text{-stilbene})$

$$2D(\mathrm{Pt{-}CH_3}) - D(\mathrm{Pt{-}styrene}) = +(209 \pm 20)\ \mathrm{kJ\ mol^{-1}}$$

Thus, the platinum—carbon bonds in the platinacyclobutenone are of similar strength to platinum—methyl bonds. Consequently, we reach the conclusion that the five-membered platinacyclo ring system is not heavily strained. Potential strain may be offset by stabilization of the platinacyclobutenone molecule due to delocalization of electrons between the platinum atom and either of the adjcacent C=C or C=O bonds.

Analysis of the enthalpy of the reaction in which the platinacyclopentenedione forms from benzocyclobutene-1,2-dione must await calculations of the strain energy in this latter molecule. In the meantime, we simply note that the difference, $\Delta H(1) - \Delta H(6) = -38 \pm 11$ kJ mol^{-1}, between the enthalpies of reactions 1 and 6 probably reflects the difference in relief of strain on insertion of the $Pt(PPh_3)_2$ group into the two cyclic alkenones, although it could be due to differences in intermolecular forces between the two platinacyclo products, II and IV, in the solid state.

Experimental

Diphenylcyclopropenone, I, (Aldrich) was recrystallised (hexane) m.p. 121.5°C. Benzocyclobutenedione, III, was prepared from 1,1,2,2-tetrabromobenzocyclobutene by refluxing with silver trifluoroacetate in aqueous acetonitrile in the dark for 12 hours [10]. It was recrystallised from dichloromethane and petroleum spirit and finally sublimed in vacuo. Bis(triphenylphosphine)-(*trans*-stilbene)platinum(0) was prepared as described in the literature [11] and gave satisfactory microanalysis. (1,1-Bistriphenylphosphine)platinabenzocyclopentenedione, IV, red form, was prepared by reaction between [Pt(*trans*-stilbene)$(PPh_3)_2$] and III in 1,2-dichloroethane, m.p. 213°C (dec.) (lit. [2] 205—212°C, dec.); ν(CO) 1640, 1660, 1687 cm^{-1} (Nujol mull) (lit. [2] 1640, 1660, 1686 cm^{-1}). Enthalpies of reaction were measured by use of the LKB 8700 calorimeter, equipped with a 25 ml reaction vessel. Enthalpies of sublimation were determined by measurement of the rate of effusion of a sample contained in an LKB neckless ampoule, sealed with silicone rubber, with a minute hole pierced in the end wall by use of a white-hot tungsten wire. The diameter of this hole was approximately 0.2 mm. The rate of weight loss of the sample was measured by use of the Dupont 950 Thermobalance and 900 Differential Thermal Analyzer. The method gave values for the enthalpies of sublimation of benzoic and salicylic acids close to those in the literature.

References

1 W. Wong, S.J. Singer, S.F. Watkins and W.H. Baddley, J. Chem. Soc. Chem. Commun., (1972) 672.
2 J.A. Evans, G.F. Everitt, R.D.W. Kemmitt and D.R. Russel, J. Chem. Soc. Chem. Commun., (1973) 158.
3 H.P. Hopkins, D. Bostwick and C.J. Alexander, J. Amer. Chem. Soc., 98 (1976) 1355.
4 J.B. Pedley and J. Rylance, N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds, University of Sussex, 1977.
5 D.M. Golden and S.W. Benson, Chem. Rev., 69 (1969) 125.
6 J.A. Kerr, Chem. Rev., 66 (1966) 465.
7 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London, 1970, p. 539.
8 C.T. Mortimer, M.P. Wilkinson and R.J. Puddephatt, J. Organometal. Chem., 165 (1979) 265.
9 W.G. Kirkham, M.W. Lister and R.B. Poyntz, Thermochim. Acta, 11 (1975) 89.
10 M.P. Cava, D.R. Napier and R.J. Pohl, J. Amer. Chem. Soc., 85 (1963) 2076.
11 J. Chatt, B.L. Shaw and A.A. Williams, J. Chem. Soc., 1962, 3269.