

*Journal of Organometallic Chemistry*, 165 (1979) 269–271  
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

## THERMOCHEMISTRY OF ADDITION OF $C_2(CN)_4$ TO $Pt(PMe_2Ph)_2CH_3Cl$ AND $Pt(PPh_3)_2HCl$

C.T. MORTIMER, M.P. WILKINSON,

*Department of Chemistry, University of Keele, Keele, ST5 5BG (Great Britain)*

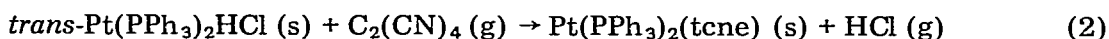
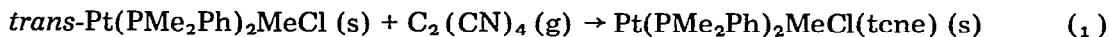
and R.J. PUDDEPHATT

*Department of Chemistry, University of Liverpool, Liverpool, L69 3BX (Great Britain)*

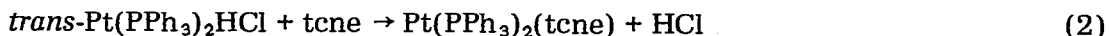
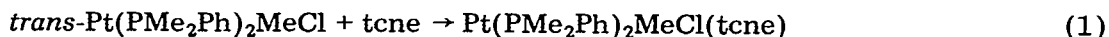
(Received July 14th, 1978)

### Summary

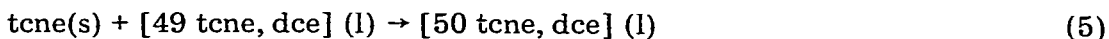
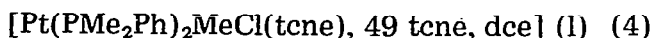
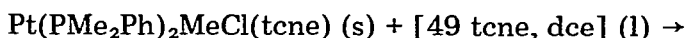
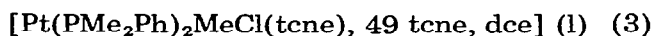
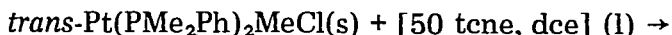
The enthalpies of reactions 1 and 2 have been measured as  $\Delta H(1) = -142 \pm 6$  and  $\Delta H(2) = -112 \pm 6$  kJ mol<sup>-1</sup> to determine whether thermochemical factors are a major influence in the formation of different reaction products (tcne = tetracyanoethylene).

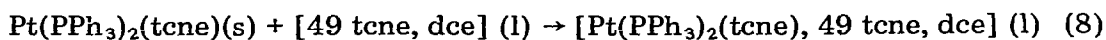
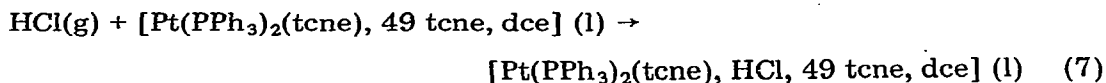
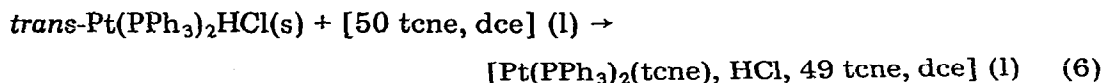


Whereas *trans*-Pt(PMe<sub>2</sub>Ph)<sub>2</sub>MeCl reacts with tetracyanoethylene (tcne) in 1,2-dichloroethane to yield an addition product [1], reaction of *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>HCl leads to elimination of HCl [2].



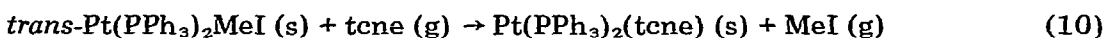
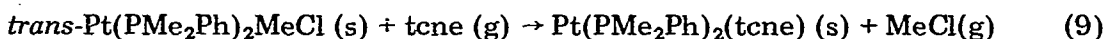
To establish whether or not this difference has a predominantly thermochemical or kinetic cause we have determined the enthalpies of reactions 1 and 2 from calorimetric measurements of the enthalpies of reactions 3–8,





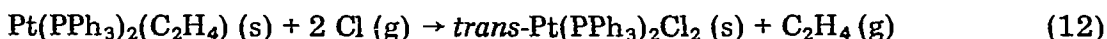
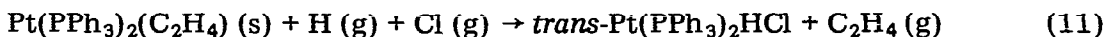
where dce is  $10^4$  mol 1,2-dichloroethane. Values obtained were  $\Delta H(3) - 71.7 \pm 2.2$ ,  $\Delta H(4) + 8.92 \pm 0.36$ ,  $\Delta H(5) + 19.9 \pm 1.1$ ,  $\Delta H(6) - 60.0 \pm 0.6$ ,  $\Delta H(7) - 13.7 \pm 0.2$ ,  $\Delta H(8) + 4.5 \pm 0.7$  kJ mol<sup>-1</sup>. The enthalpy of sublimation of tcne is  $+81.2$  kJ mol<sup>-1</sup> [3].

It is possible to estimate the enthalpy of the elimination reaction 9 in the following way. The enthalpy,  $\Delta H(10) - 58 \pm 10$  kJ mol<sup>-1</sup>, of reaction 10 and



the bond dissociation energy difference  $D(\text{Pt}-\text{Cl}) - D(\text{Pt}-\text{I}) = 82 \pm 10$  kJ mol<sup>-1</sup> can be calculated from data published previously [4-6]. If we assume that the enthalpies of sublimation of the platinum complexes are the same then the enthalpy,  $\Delta H(10)$  can be adjusted to account for (i) the dissociation of a Pt-Cl rather than a Pt-I bond and (ii) the formation of a CH<sub>3</sub>-Cl bond rather than a CH<sub>3</sub>-I bond. Using the values  $D(\text{CH}_3-\text{Cl}) 351 \pm 4$  and  $D(\text{CH}_3-\text{I}) 236 \pm 4$  kJ mol<sup>-1</sup> [7] we obtain an estimated value  $\Delta H(9) - 91 \pm 28$  kJ mol<sup>-1</sup>. Whilst the different phosphine ligand will have some influence on the estimate of  $\Delta H(9)$ , it is likely to reduce the magnitude, as found [8] in the case of the adducts Pt(AsMe<sub>2</sub>Ph)<sub>2</sub>MeCl(C<sub>2</sub>F<sub>4</sub>). This estimated value for the enthalpy of the overall reaction 9 is less than that for the formation of Pt(PMe<sub>2</sub>Ph)<sub>2</sub>MeCl(tcne),  $\Delta H(1) - 142 \pm 6$  kJ mol<sup>-1</sup>, so that this adduct is in an enthalpy "valley". However, the entropy change of reaction 1, in which a mol of gaseous tcne becomes incorporated in the adduct, will be negative and of considerable magnitude. On the other hand, the value of  $\Delta S$  for reaction 9 will be small. Consequently, the free energy change,  $\Delta G(1)$ , for the adduct formation reaction could be equal to, or even of lesser magnitude than the value  $\Delta G(9)$  for the overall reaction involving elimination of MeCl. Thermodynamically, the formation of the adduct is not particularly favoured. It seems likely, therefore, that the different course of reaction between tcne and Pt(PMe<sub>2</sub>Ph)<sub>2</sub>MeCl and between tcne and Pt(PPh<sub>3</sub>)<sub>2</sub>HCl results mainly from kinetic than from thermochemical factors.

The thermochemical analysis of reaction 2 may be taken a step further in an examination of whether the elimination of HCl results from inherent weakness of the Pt-H bond. The value of  $\Delta H(2)$ , combined with the enthalpy of replacement [4] of C<sub>2</sub>H<sub>4</sub> in Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>) by C<sub>2</sub>(CN)<sub>4</sub> and the value  $D(\text{H}-\text{Cl}) 431.6$  kJ mol<sup>-1</sup> [9] can be used to yield a value,  $\Delta H(11) - 476 \pm 14$  kJ mol<sup>-1</sup> for the enthalpy of reaction 11. This may be compared with the value  $\Delta H(12) - 488 \pm 27$  kJ mol<sup>-1</sup> obtained from data in ref. 4 and 5, together with an estimated value



of  $\Delta H -15 \pm 2 \text{ kJ mol}^{-1}$  for the isomerization *cis*  $\rightarrow$  *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>. The *trans*-influence in platinum compounds is considerable and clearly the Pt—Cl bonds in *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>Cl will be stronger than the Pt—Cl bond in *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>-HCl, since Cl has a greater *trans*-influence than H. It is difficult to calculate the magnitude of this difference in bond dissociation energies of the Pt—Cl bonds. However, we can conclude that  $D(\text{Pt—H}) \approx D(\text{Pt—Cl})$ . The Pt—Cl bond is strong so that reaction 2, which occurs with elimination of HCl, is encouraged by the formation of a strong H—Cl bond rather than because of the ease of rupture of the Pt—H bond.

## Experimental

Tcne (Emanuel) was recrystallised from dichloromethane, sublimed and stored over solid NaOH. 1,2-Dichloroethane was dried over MgSO<sub>4</sub> and distilled. Enthalpies were measured by use of the LKB 8700 calorimeter.

*Analyses.* *trans*-Pt(PMe<sub>2</sub>Ph)<sub>2</sub>MeCl. Found: C, 39.21; H, 4.97. C<sub>17</sub>H<sub>25</sub>ClP<sub>2</sub>Pt calcd.: C, 39.13; H, 4.83%. *trans*-Pt(PPh<sub>3</sub>)<sub>2</sub>HCl. Found: C, 57.45; H, 4.14. C<sub>36</sub>H<sub>31</sub>ClP<sub>2</sub>Pt calcd.: C, 57.19; H, 4.13%.

## References

- 1 H.C. Clark and R.J. Puddephatt, *Inorg. Chem.*, 10 (1971) 416.
- 2 W.H. Baddley and L.M. Venanzi, *Inorg. Chem.*, 5 (1966) 33.
- 3 R.H. Boyd, *J. Chem. Phys.*, 38 (1963) 2529.
- 4 A. Evans, C.T. Mortimer and R.J. Puddephatt, *J. Organometal. Chem.*, 72 (1974) 295.
- 5 A. Evans, C.T. Mortimer and R.J. Puddephatt, *J. Organometal. Chem.*, 85 (1975) 101; 96 (1975) C58.
- 6 C.T. Mortimer, M.P. Wilkinson and R.J. Puddephatt, *J. Organometal. Chem.*, 165 (1979) 265.
- 7 J.A. Kerr, *Chem. Rev.*, 66 (1966) 465.
- 8 C.T. Mortimer, Janice I. McNaughton and R.J. Puddephatt, *J. Chem. Soc. Dalton*, (1972) 1265.