

**PLATINUM—OLEFIN BOND STRENGTH IN  $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)$  AND  $\text{Pt}(\text{PPh}_3)_2\{\text{C}(\text{CN})_2=\text{C}(\text{CN})_2\}$**

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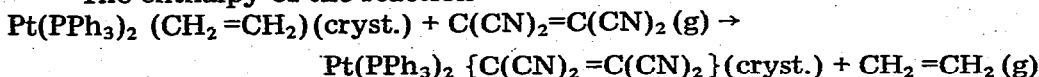
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**Summary**

The enthalpy of the reaction:



has been determined as  $\Delta H_{298} = -155.8 \pm 8.0 \text{ kJ}\cdot\text{mol}^{-1}$ , from solution calorimetry. The interpretation, that the platinum—ethylene bond is much weaker than the platinum—tetracyanoethylene bond, is contrary to conclusions drawn recently from electron emission spectroscopic studies, but in agreement with available structural data.

X-ray structural analyses of the crystalline compounds  $\text{Pt}(\text{PPh}_3)_2(\text{CH}_2=\text{CH}_2)$  [1] and  $\text{Pt}(\text{PPh}_3)_2\{\text{C}(\text{CN})_2=\text{C}(\text{CN})_2\}$  [2] have shown that the structures consist of packed discrete monomeric molecules. The platinum atom is near the centre of a distorted square arrangement of two phosphorus atoms, in *cis* positions, and two carbon atoms of the olefin. The square is not strictly planar and distortion from planarity leads to a dihedral angle,  $\theta$ , between the planes P(1)—Pt—P(2) and C(1)—Pt—C(2). The bond lengths (nm) and dihedral angles are as follows.

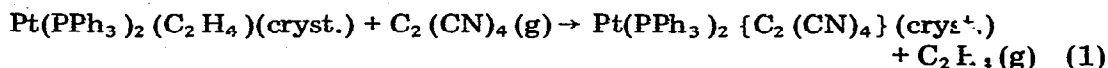
Olefin	C—C	Pt—C	Pt—P	$\theta$
$\text{CH}_2=\text{CH}_2$	0.143 (0.1339)	0.211	0.227	$1.6^\circ$
$(\text{CN})_2\text{C}=\text{C}(\text{CN})_2$	0.139 (0.1317)	0.212, 0.210	0.2291, 0.2288	$8.3^\circ$

Values of C—C bond length refer to the central bond of the olefin and the values in parenthesis are those for the central double bond in the uncoordinated olefin. In changing the olefin from ethylene to tetracyanoethylene, the Pt—C

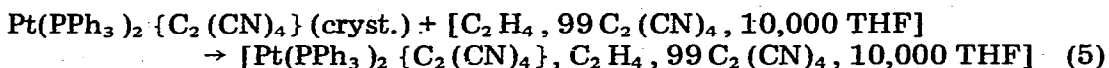
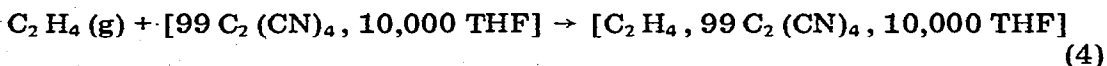
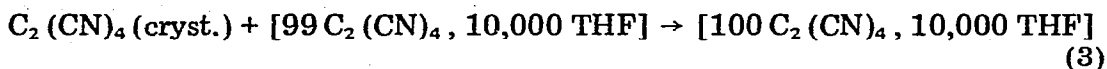
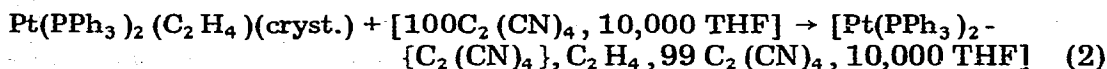
bond length is little affected, although the Pt—P length increases slightly. The major change is in the length of the central C—C bond of the olefin. In the ethylene complex this is 0.143 nm, some 0.009 nm longer than in free ethylene (0.1339 nm) [3], whilst in the tetracyanoethylene complex the bond length is 0.149 nm, some 0.017 nm longer than in the free ligand (0.1317 nm) [4]. The implication of these structural data is that the platinum—olefin bond is stronger in the tetracyanoethylene complex (where there is greater  $d \rightarrow$  olefin  $\pi^*$  electron donation) than in the ethylene complex.

On the other hand, electron emission spectroscopic studies on the compounds  $\text{Pt}(\text{PPh}_3)_2$  (olefin), made by Mason et al. [5] yield values for the binding energies of the Pt  $4f_{5/2}$  and Pt  $4f_{7/2}$  electrons which are independent of the nature of the substituent groups on the olefin. They conclude that the Lewis basicity of the bis(triphenylphosphine)platinum(0) moiety is so strong that the substituent groups on the olefin play but a minor role in determining the extent to which charge transfer from metal to ligand antibonding orbitals takes place.

In order to provide further information about the comparative strengths of the platinum—ethylene and platinum—tetracyanoethylene bonds, we have determined the enthalpy at 298 K,  $\Delta H(1)$ , of reaction 1.



This datum has been obtained from measurements of enthalpies at 298 K,  $\Delta H(2)$  to  $\Delta H(5)$ , of the following reactions, in which THF is tetrahydrofuran, together with the literature [6] value, at 298 K of  $\Delta H(6) = 81.2 \pm 5.9 \text{ kJ}\cdot\text{mol}^{-1}$  for the enthalpy of reaction (6).



Values obtained for the enthalpies  $\Delta H(2)$  to  $\Delta H(5)$  are shown in Table 1, and from these we obtain the value  $\Delta H(1) = -155.8 \pm 8.0 \text{ kJ}\cdot\text{mol}^{-1}$ . Whilst it would be preferable to know the enthalpy of reaction 1, in which the platinum—olefin 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,  $\Delta H(1) = -155.8 \text{ kJ}\cdot\text{mol}^{-1}$ , will be close to that for the gas-phase reaction.

This enthalpy reflects not only the difference between the energies of the platinum—ethylene and platinum—tetracyanoethylene bonds, but also changes of the strengths of bonds within the olefin molecules themselves. Thus, on dissociation, the C—C bond in the ethylene molecule is shortened and strengthened and this leads to an exothermic contribution to the enthalpy of the reaction.

TABLE 1  
ENTHALPIES OF REACTIONS 2-5

<i>Reaction 2</i>					
Wt. Pt(PPh <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> ) (g)	0.025926	0.019776	0.023179	0.027598	0.020010
$\Delta H(2)$ (kJ·mol <sup>-1</sup> )	-88.7	-82.1	-89.7	-86.2	-77.8
mean $\Delta H(2) = -84.9 \pm 1.8$ kJ·mol <sup>-1</sup>					
<i>Reaction 3</i>					
Wt. C <sub>2</sub> (CN) <sub>4</sub> (g)	0.005554	0.003713	0.003371	0.005067	0.005829
$\Delta H(3)$ (kJ·mol <sup>-1</sup> )	+1.5	+2.7	+1.6	+2.0	+2.3
mean $\Delta H(3) = +2.0 \pm 0.4$ kJ·mol <sup>-1</sup>					
<i>Reaction 4</i>					
Wt. C <sub>2</sub> H <sub>4</sub> (g)	0.000406	0.000765	0.000486	0.000586	0.000641
$\Delta H(4)$ (kJ·mol <sup>-1</sup> )	-13.8	-15.0	-13.5	-13.7	-12.3
mean $\Delta H(4) = -13.7 \pm 0.8$ kJ·mol <sup>-1</sup>					
<i>Reaction 5</i>					
Wt. Pt(PPh <sub>3</sub> ) <sub>2</sub> {C <sub>2</sub> (CN) <sub>4</sub> } (g)	0.023272	0.026258	0.029967	0.027140	0.023560
$\Delta H(5)$ (kJ·mol <sup>-1</sup> )	+5.9	+5.2	+5.2	+4.6	+6.0
mean $\Delta H(5) = +5.4 \pm 0.6$ kJ·mol <sup>-1</sup>					

This effect will be more than offset by the endothermic contribution resulting from the lengthening and weakening of the central C—C bond in the tetracyanoethylene molecule, when it bonds to platinum. We conclude that the platinum—tetracyanoethylene bond is stronger than the platinum—ethylene bond by at least 156 kJ·mol<sup>-1</sup>.

## Experimental

Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)(cryst.) was prepared by the method of Cook and Jauhal [7]; m.p. 122–125° (dec.) (Found: C, 60.7; H, 4.8; calcd.: C, 61.0; H, 4.6%.) Tetracyanoethylene (R.N. Emanuel) was resublimed prior to use. Tetrahydrofuran (THF) (Koch Light) was dried (molecular sieve) and GLC indicated only a trace of impurity (unidentified). It was saturated with nitrogen (white spot) to prevent the possible formation of Pt(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub>. Neither the reactant, Pt(PPh<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>), nor the product Pt(PPh<sub>3</sub>)<sub>2</sub>{C<sub>2</sub>(CN)<sub>4</sub>}, showed an absorption at 818 cm<sup>-1</sup>, which is characteristic of Pt(PPh<sub>3</sub>)<sub>2</sub>O<sub>2</sub>.

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 [8].

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