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RELATIVE OLEFIN–METAL BOND STRENGTHS IN SOME PLATINUM (0) COMPOUNDS

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ABSTRACT

Measurements are reported for the enthalpy of the reaction

$$L_2Pt(c) + nCS_2(l) \rightarrow L_2PtCS_2(soln) + (n-1)\ CS_2(l)$$

and for the reactions

$$L_2Pt \cdot olefin(c) + nCS_2(l) \rightarrow L_2PtCS_2(soln) + olefin(soln) + (n-1)\ CS_2(l)$$

where L is triphenylphosphine, and the olefins used were ethylene, phenylethylene, and *cis*- and *trans*-1,2-diphenylethylene. These enthalpies, when combined with other data, lead to the conclusion that the relative strenghts of the platinum–olefin bonds decrease in the order: *trans*-1,2-diphenylethylene > *cis*-1,2-bisphenylethylene > phenylethylene > ethylene.

The difference between the *cis* and *trans* compounds is relatively small. The above order is in agreement with qualitative observations on the relative stabilities of these compounds.

INTRODUTION

Recently Mason et al.[1] have made electron emission spectroscopic studies on some compounds of the type $L_2Pt \cdot$olefin and concluded that the Lewis basicity of the bis(triphenylphosphine) platinum (0) part is so strong that the substituent groups on the olefin play only a minor role in determining the extent to which charge transfer from platinum to olefin anti-bonding orbitals takes place. If this is so, it might perhaps be expected that the energy needed to break the platinum–olefin bond would not vary from one olefin to another. However, it has been found that ethylene in $L_2PtC_2H_4$ can be displaced by *cis*-butene[2], phenylethylene[3], various *meta* and *para* substituted phenylethylenes, and dodecene[4]. Although these reactions will be favoured by the release and escape of gaseous ethylene, it nevertheless seemed possible that different platinum–olefin bond strengths might be involved. Accordingly, calorimetric measurements, as described below, were made on reactions in which the olefins were displaced by carbon disulphide. This allows, within certain limits, conclusions to be drawn about the relative bond strengths.

Recently, Evans and Mortimer[5] have reported that the replacement of ethylene by tetracyanoethylene in complexes of this type has $\Delta H = -156$ kJ mol^{-1}, indicating fairly different bond strengths in that case.

EXPERIMENTAL

The enthalpies of reaction and solution were determined in a single vessel submarine calorimeter of conventional design[6,7]. The temperature was measured by a 2000 Ω thermistor (Fenwal GB 32P28), with a temperature coefficient of −3.2% per degree at 25 °C. This was contained in a Wheatstone bridge circuit with 2000 Ω resistors in each arm, any off-balance voltage being detected by a Model 895A (John Fluke Manufacturing Company) D.C. differential voltmeter. This voltmeter can be read reliably to 1 μV, which corresponded to 2×10^{-4} degree. In general between 1 and 4×10^{-4} mole of compound was used in each run, and this reacted with a considerable excess of carbon disulphide (108 ml was used).

Materials and procedures

Bis(triphenylphosphine) platinum(0) was prepared by the method of Cook and Wan[8] in which the dioxygen adduct, L_2PtO_2, was reduced with sodium borohydride in ethanol. The reaction with carbon disulphide was carried out in an atmosphere of nitrogen.

Bis(triphenylphosphine) phenylethylene platinum(0), $L_2PtH_2C{:}CHC_6H_5$, was prepared as described by Jones and Cook (ref. 3, p. 94).

Bis(triphenylphosphine)-1,2-diphenylethylene. The *cis* and *trans* isomers of this compound, $L_2PtC_6H_5CH{:}CHC_6H_5$, were prepared from bis(triphenylphosphine) platinum(II) carbonate by the general method for the preparation of L_2Pt olefin compounds described by Blake and Mersecchi[9]. The preparation of these particular complexes by this method has not been reported previously. The reaction with *trans*-1,2-diphenylethylene took approximately one day, and gave 75% yield; the reaction with the *cis* compound took three days, and gave 20% yield.

The melting points of all compounds agreed with the values given by Cook and coworkers[3,10].

Carbon disulphide. Reagent grade carbon disulphide, supplied by Allied Chemical Company, was used.

It was already known that carbon disulphide reacts non-oxidatively with bis(triphenylphosphine) platinum(0) and its olefin complexes to give L_2PtCS_2[11,12]. The reactivity of the compounds used in the present work with CS_2 was checked. It was found that the starting material, L_2PtCO_3, did not react with, nor appreciably dissolve in, carbon disulphide. The product produced from the olefinic complexes melted at 165–196 °C; compare the previously reported melting point of L_2PtCS_2 of 165–172 °C (ref. 11). It was found that the infrared spectrum of the product showed a strong absorption maximum at 1145 cm^{-1} (compare 1147 cm^{-1} reported in ref. 11); and no shoulder at 818 cm^{-1}, which indicates the absence of L_2PtO_2.

For the reaction of the ethylene complex, a difficulty arises in that the ethylene produced may or may not stay in solution. In our experiments, the carbon disulphide was first saturated with ethylene, and it was assumed therefore that the ethylene produced came out of solution and appeared as gas. This implies that no appreciable degree of supersaturation was present at the end, a situation which would be promoted by the fairly rapid stirring of the solution. It was also checked that this dissolved ethylene did not prevent the reaction going virtually to completion. This was done by following the rate of the reaction with a Durrum stopped-flow spectrophotometer. In these experiments a solution of $L_2PtC_2H_4$ in benzene, reacted with 8% carbon disulphide in benzene, both solutions being saturated with ethylene, and it was found that reaction was virtually complete in less than two minutes. The 8% solution of CS_2 was used, because if pure CS_2 was mixed with the benzene solution, the resulting absorbance of the mixture was irregular at first, presumably owing to the different densities and refractive indices of the two liquids.

RESULTS

The reactions examined are listed below. The relative numbers of moles of compound and CS_2 are somewhat approximate: for instance, 10000 CS_2 varied between 8000 and 15000 CS_2 in different experiments. It was assumed that the enthalpy of dilution (or the reverse) of the actual solution to reach a solution of composition $L_2PtCS_2 \cdot 10000\,CS_2$ was negligible. In all cases the reactions were carried out at 298 K. The reactions were:

	Reaction
$L_2Pt(c) + CS_2(l) \rightarrow [L_2PtCS_2,\ 10000\ CS_2]$	A
$L_2PtC_2H_4(c) + CS_2(l) \rightarrow [L_2PtCD_2,\ 10000\ CS_2] + C_2H_4(g)$	B
$L_2Pt \cdot H_2C{:}CHC_6H_5(c) + CS_2(l) \rightarrow [L_2PtCS_2,\ 10000\ CS_2,\ H_2C{:}CHC_6H_5]$	C
$L_2Pt \cdot cis\text{-}C_6H_5CH{:}CHC_6H_5(c) + CS_2(l) \rightarrow [L_2PtCS_2,\ 10000\ CS_2,\ C_6H_5CH{:}CHC_6H_5]$	D
$L_2Pt \cdot trans\text{-}C_6H_5CH{:}CHC_6H_5(c) + CS_2(l) \rightarrow [L_2PtCS_2,\ 10000\ CS_2,\ C_6H_5CH{:}CHC_6H_5]$	E
In addition the following enthalpies of solution were measured:	
$H_2C{:}CHC_6H_5(l) + CS_2(l) \rightarrow [H_2C{:}CHC_6H_5 \cdot 2000\ CS_2]$	F
$cis\text{-}C_6H_5CH{:}CHC_6H_5(l) + CS_2(l) \rightarrow [C_6H_5CH{:}CHC_6H_5,\ 2000\ CS_2]$	G
$trans\text{-}C_6H_5CH{:}CHC_6H_5(c) + CS_2(l) \rightarrow [C_6H_5CH{:}CHC_6H_5,\ 2000\ CS_2]$	H

The results are given in Table 1. Each result is the average from three experiments, with the average deviation given after the result. Auxiliary data on enthalpies of fusion or vaporisation were needed to enable a better comparison of the bond strengths to be made. The data used were as follows: enthalpies of vaporisation: $C_6H_5CH{:}CH_2$, 43.4; *cis*-$C_6H_5CH{:}CHC_6H_5$, 66.1; *trans*-$C_6H_5CH{:}CHC_6H_5$, 60.6; enthalpy of fusion: *trans*-$C_6H_5CH{:}CHC_6H_5$, 32.2; all in kJ mol^{-1}. The enthalpy of vaporisation for *cis*-$C_6H_5CH{:}CHC_6H_5$ is taken from ref. 13, and the others are calculated from data on vapour pressures. The enthalpy of fusion is taken from ref. 14.

TABLE 1

ENTHALPIES OF REACTION OR SOLUTION AT 289 K

Reaction	ΔH (*kJ mol*$^{-1}$)	*Mean* ΔH (*kJ mol*$^{-1}$)
A	49.4, 50.4, 49.8	49.9±0.3
B	38.2, 36.4, 40.2	38.3±1.3
C	45.1, 46.9, 45.9	45.8±0.6
D	69.0, 75.2, 72.4	72.2±2.1
E	85.8, 83.3, 75.5	81.5±4.0
F	10.4, 9.7, 9.3, 9.6	9.8±0.4
G	8.2, 11.1, 10.0	9.8±1.0
H	25.2, 28.4, 29.1	27.6±1.6

From these results it is possible to calculate enthalpies for

$$L_2Pt(c) + \text{olefin}(g) \rightarrow L_2Pt\cdot\text{olefin}(c)$$

for each olefin. A better comparison admittedly would be between enthalpies for the reactions in which all compounds are in the gas phase, but the platinum compounds are too unstable to be vaporised, so that the relevant enthalpies of vaporisation are not available. However, the reaction given above gives an indication of the relative bond strengths, provided the enthalpies of sublimation of the various $L_2Pt\cdot$olefins are not very different. The enthalpies calculated for the above reaction are given in Table 2.

TABLE 2

ΔH FOR $L_2Pt(c) + \text{olefin}(g) \rightarrow L_2Pt\cdot\text{olefin}(c)$

Olefin	ΔH (*kJ mol*$^{-1}$)
C_2H_4	11.6
$H_2C{:}CHC_6H_5$	−29.7
cis-$C_6H_5CH{:}CHC_6H_5$	−78.6
trans-$C_6H_5CH{:}CHC_6H_5$	−96.9

It is evident from Table 2 that ΔH for the reaction of a gaseous olefin reacting with solid L_2Pt to give a solid product varies considerably from one olefin to another. As mentioned above a better comparison would be between ΔH for reaction with all substances in the gas phase, but the appropriate enthalpies of vaporisation are not available. If it is assumed that the enthalpy of vaporisation increases with increasing molecular weight, then the differences from one olefin to another would be somewhat reduced; but it seems very unlikely that these differences could be large enough to remove the differences in ΔH altogether. In fact it is unlikely that the differences in enthalpies of sublimation of the complexes are as large as those of the free olefins, and these are not large enough to alter the relative order of ΔH as given in Table 2.

One other number could be included in Table 2. By combining Evans and Mortimer's result[5] of -155.8 kJ for the replacement of ethylene by tetracyanoethylene, we get -144.2 kJ mol^{-1} for the reaction in Table 2 when the olefin is tetracyanoethylene. Their comment about the lack of agreement with the conclusions of Mason et al.[1] from electron emission spectroscopy is supported by the present results. The electron binding energies for $4f_{7/2}$ or $4f_{5/2}$ electrons on platinum vary by 0.4 eV or less between different compounds, and this is appreciably less than the range of ΔH in Table 2.

The relative order of ΔH in Table 2 agrees with the qualitative observations on the stability of these compounds, in terms of the ability of one olefin to replace another, or stability on heating; the ethylene complex is least stable. A simple Hückel molecular orbital treatment of the π-systems of the olefins leads to the conclusion (as might be expected) that the lowest unfilled orbital decreases in energy as more phenyl groups are introduced, and that the electron density of this orbital (if filled) would be about equally concentrated on the two carbon atoms of the olefinic part in the various compounds. Hence, presumably back-bonding from the platinum becomes increasingly important as more phenyl groups are introduced, and this leads to more stable complexes. This would, however, not explain the difference between *cis*- and *trans*-1,2-diphenylethylene, and the explanation of this difference is uncertain.

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