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RELATIVE ALKYNE–METAL BOND STRENGTHS IN SOME PLATINUM(O) COMPOUNDS

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ABSTRACT

Measurements are reported for the enthalpies of the reaction

$$L_2Pt\cdot\text{alkyne(c)} + n\,CS_2\text{(l)} \rightarrow L_2PtCS_2\text{(sol.)} + \text{alkyne(sol or g)} + (n-1)\,CS_2 \quad (1)$$

where L is triphenylphosphine and the alkynes used were ethyne, 1-butyne, 2-butyne, phenylethyne and diphenylethyne. These enthalpies when combined with other data lead to the conclusion that the relative strengths of the platinum–alkyne bonds increase in the order ethyne < 1-butyne < 2-butyne < phenylethyne < diphenylethyne.

The above order is in agreement with qualitative observations on the relative stabilities of the compounds[1].

INTRODUCTION

In a recent paper[2] Evans and Mortimer have reported the enthalpy for the reaction between crystalline bis(triphenylphosphine)etheneplatinum(O) and gaseous diphenylethyne to produce solid bis(triphenylphosphine)diphenylethyneplatinum(O) and gaseous ethene. They concluded that the platinum–diphenylethyne bond is stronger than the platinum–ethene bond which is in agreement with the observed greater relative increase in the length of the carbon–carbon bond on complexation of diphenylethyne (0.013 nm for diphenylethyne compared to 0.009 nm for ethene)[2].

More recently Davies and Payne[3] have reported their findings on the crystal and molecular structure of bis(triphenylphosphine) (1-phenylpropyne)platinum(O). They have also tabulated data for a number of other $L_2Pt\cdot$alkyne complexes and with these data (8 complexes) have demonstrated that a wide range of Pt–P and Pt–C (alkyne) distances and P–Pt–P angles exist in these complexes. It was concluded that at this time it does not seem possible to correlate any trends in Pt–P and Pt–C distances or P–Pt–P angles with electron-withdrawing or -releasing behaviour of the substituents on the alkyne and that the value of interpreting small changes in Pt–P or Pt–C distances in terms of bonding can only be justified if the values differ markedly from the "mean" values for these parameters. It was suggested that either the mode of bonding in these complexes is relatively insensitive to the nature of the substituent on the alkyne or that such differences in the bonding in these complexes are too small to be detected by X-ray diffraction studies.

It is also apparent from the data that they list that the probable steric effects of the substituents do not show any markedly unusual behaviour.

In the light of these considerations we would like to present some data on calorimetric studies of a series of complexes of the type $L_2Pt\cdot RC\vdots CR'$ where $R=R'=H$; $R=R'=CH_3$; $R=R'=C_6H_5$; $R=C_2H_5$, $R'=H$ and $R=C_6H_5$ and $R'=H$.

EXPERIMENTAL

The enthalpies of reaction and solution were carried out with techniques and equipment that have been described in previous papers[4-6].

Materials and procedures

The compounds were all prepared by known methods either from the bis(triphenylphosphine)oxygenplatinum(II)[7] complex or from carbonatobis(triphenylphosphine)platinum(II)[8]. The products were all analyzed correctly and had melting points corresponding to the literature values.

RESULTS

The reactions examined are listed below. The relative number of moles of compound and CS_2 are somewhat approximate: for instance 10 000 CS_2 varied between 8 000 and 15 000 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 $L_2PtCS_2\cdot 10\,000\ CS_2$ was negligible. In all cases the reactions were carried out at 298 K.

The reactions were:

$$L_2PtC_2H_2(c)+CS_2(l) \rightarrow (L_2PtCS_2\cdot 10\,000\ CS_2)+C_2H_2(g) \tag{A}$$

$$L_2PtC_2H_5C\vdots CH(c)+CS_2(l) \rightarrow (L_2PtCS_2\cdot 10\,000\ CS_2)+C_2H_5C\vdots CH(g) \tag{B}$$

$$L_2PtCH_3C\vdots CCH_3(c)+CS_2(l) \rightarrow (L_2PtCS_2\cdot 10\,000\ CS_2\cdot CH_3C\vdots CCH_3) \tag{C}$$

$$L_2PtC_6H_5C\vdots CH(c)+CS_2(l) \rightarrow (L_2PtCS_2\cdot 10\,000\ CS_2\cdot C_6H_5C\vdots CH) \tag{D}$$

$$L_2PtC_6H_5C\vdots CC_6H_5(c)+CS_2(l) \rightarrow (L_2PtCS_2\cdot 10\,000\ CS_2\cdot C_6H_5C\vdots CC_6H_5) \tag{E}$$

In addition the following enthalpies of solution were measured:

$$CH_3C\vdots CCH_3(l)+CS_2(l) \rightarrow (CH_3C\vdots CCH_3\cdot 2\,000\ CS_2) \tag{F}$$

$$C_6H_5C\vdots CH(l)+CS_2(l) \rightarrow (C_6H_5C\vdots CH\cdot 2\,000\ CS_2) \tag{G}$$

$$C_6H_5C\vdots CC_6H_5(c)+CS_2(l) \rightarrow (C_6H_5C\vdots CC_6H_5\cdot 2\,000\ CS_2) \tag{H}$$

The results are given in Table 1. Each result is the average of three experiments with the average deviation given after the result.

TABLE 1

ENTHALPIES OF REACTION OR SOLUTION AT 298 K

Reaction	*ΔH° (kJ mol^{-1})*	*Mean ΔH° (kJ mol^{-1})*
A	58.9, 58.8, 61.9	59.9 ±1.4
B	71.4, 67.5, 68.8	69.2 ±1.4
C	73.5, 69.3, 70.5	71.1 ±1.6
D	87.1, 81.1, 84.5	84.2 ±2.1
E	80.3, 75.9, 78.6	78.3 ±1.6
F	0.87, 1.37, 1.35	1.20±0.2
G	10.50, 10.61, 10.40	10.5 ±0.1
H	21.9, 18.5, 20.7	20.4 ±1.2

Auxiliary data were needed in order to enable a better comparison of the bond strengths to be made.

The data used were as follows: reaction of L_2Pt with CS_2, 49.9[5]; enthalpies of vaporization: 2-butyne, 26.6[9], phenylethyne, 40.7; enthalpy of sublimation: diphenylethyne 88, all in kJ mol^{-1}. The enthalpies of vaporization are from vapour pressure data.

The enthalpy of sublimation of diphenylethyne was estimated as 88±5 kJ mol^{-1}, a value somewhat lower than the one used by Mortimer 100±10 kJ mol^{-1})[2]. Our value was derived in two different ways:

(i) By calculating the enthalpy of vaporization of hydrocarbon compounds of similar formula and melting point to diphenylethyne. These values were obtained by subtracting the known heats of fusion[10,11] from the known heats of sublimation[12]. These values were then averaged.

(ii) By estimating the enthalpy of vaporization by Trouton's rule and correcting it to 298 K by using Sidgwick's rule[13].

The values obtained by each of these methods is shown in Table 2. The enthalpy of fusion of diphenylethyne (21.4 kJ mol^{-1})[11] was then added to the mean of these values to yield 88 kJ mol^{-1}. This value is approximately 4 kJ mol^{-1} higher than that for 1,2-diphenylethane[12], a compound whose boiling point and molecular weight are not very different from those of diphenylethyne. This fact coupled with the good

TABLE 2

ENTHALPIES OF VAPORIZATION AT 298 K

Compound	*$\Delta H^{\circ}_{vap.}$ (kJ mol^{-1})*
$C_{14}H_{10}$, phenanthrene	75.0
$C_{14}H_{10}$, anthracene	72.8
$C_{12}H_{18}$, hexamethylbenzene	54.6
$C_{12}H_{10}$, biphenyl	65.0 Avg. 66.9
Trouton's method	67.1

agreement between the values from two independent methods leads us to believe that 88 kJ mol^{-1} is a good estimate of the enthalpy of sublimation of diphenylethyne.

DISCUSSION

From these results it is possible to calculate the enthalpy for the reaction

$$L_2Pt(c)+\text{alkyne}(g) \rightarrow L_2Pt\text{-alkyne}(c) \qquad (1)$$

for each alkyne. A better comparison, admittedly, would be between enthalpies for the reactions in which all of the compounds are in the gas phase, but the platinum compounds are too unstable to be vaporized, so that the relative enthalpies of vaporization are not available. However, the reaction above gives an indication of the relative bond strengths provided that the enthalpies of sublimation of the various platinum complexes are not very different.

The enthalpies calculated for reaction 1 are listed in Table 3.

TABLE 3

$\Delta H°$ for $L_2Pt(c)+\text{alkyne}(g) \rightarrow L_2Pt\text{-alkyne}(c)$

Alkyne	$\Delta H°$ (*kJ mol*$^{-1}$)
C_2H_2	-10.0 ± 2
$C_2H_5C{:}CH$	-19.3 ± 2
$CH_3C{:}CCH_3$	-46.6 ± 3
$C_6H_5C{:}CH$	-64.5 ± 3
$C_6H_5C{:}CC_6H_5$	-96.0 ± 8

The error limits reflect the errors in the experimental enthalpies except in the case of diphenylethyne where they also include the estimated probable error in the enthalpy of sublimation of diphenylethyne.

It is apparent from the data given in Table 3 that the $\Delta H°$ for the reaction of a given gaseous alkyne reacting with solid bis(triphenylphosphine)platinum(O) to give a crystalline product varies from one alkyne to another in a fairly regular fashion. There is a general increase in the exothermicity of reaction (1) with substitution at the acetylenic carbons. The most exothermic reactions occur with alkynes which are the best π-acceptors.

It is also evident that the alkyl substituted alkynes react more exothermically than ethyne. This is probably the result of an increased sigma-donor capability (comparable to that of ethene) coupled with a still favourable π-acceptor capability.

The question of the effect of steric interactions between the substituents on the alkyne and the phenyl hydrogens of the triphenylphosphine on the enthalpies for reaction (1) is open to speculation. It should be pointed out, though, that, barring any unexpected effects (e.g., significantly greater steric interaction for methyl compared to phenyl substituents), the order of increasingly unfavourable steric interaction is also the order of increasing exothermicity for reaction (1). This would indicate that the favourable electronic effects apparently outweigh what should be the increasingly unfavourable steric interactions in these complexes. It would also seem likely; considering the magnitude of the values for reaction (1) with the different alkynes, that X-ray crystallographic determinations are unlikely to yield values in a closely related series of compounds which could be correlated with the electron-donating or -withdrawing nature of the substituents on the alkyne.

Our results for the hypothetical reaction (1) also indicate that there is a possibility for equilibrium mixtures of alkene and alkyne complexes under certain conditions of displacement reactions even with the simple unsaturated hydrocarbons. This has been found to be true in the ethene–ethyne system where bubbling ethyne through a solution of $L_2Pt \cdot$ethene led to a mixture of products and not to the complete displacement of ethene. Further studies are at present underway in order to clarify this situation.

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