Journal of Organometallic Chemistry, 243 (1983) 111–117
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

BOND ENERGIES AND THERMAL DECOMPOSITION OF $[Pt(X)(CH_3)(P(C_2H_5)_3)_2]$ COMPLEXES

A. MORVILLO, G. FAVERO and A. TURCO

Centro C.N.R. Stabilità e Reattività Composti di Coordinazione, University of Padova (Italy)

(Received August 3rd, 1982)

Summary

The thermal decomposition of the complexes *trans*-$[Pt(X)(CH_3)L_2]$ ($L = P(C_2H_5)_3$; $X = Cl$, Br, I, CN) in decalin at 170 and 200°C affords methane, platinum metal and $[Pt(X)_2L_2]$. The kinetics of the decomposition of the complexes were determined by monitoring the appearance of methane by GLC. The observed first-order rate constant was found to be independent on the nature of the ligand X. The thermal decomposition of the trideuteriomethyl complexes $[Pt(X)(CD_3)L_2]$ ($X = I$, CN) in decalin-d_{18} at 170 and 200°C was studied by GLC/MS. The thermolysis affords CD_3H and CD_4 in ratios which are independent of the nature of X and of the temperature used. The mass spectra of the complexes were also examined. A relative scale of platinum-to-methyl bond dissociation energies has been established by measuring the appearance potential of the fragment ion $[Pt(X)L_2]^+$ and the ionization energies in the series $[Pt(X)(CH_3)L_2]$. Ionization potentials and $Pt-CH_3$ bond energies show a clear dependence on the nature of X which is not reflected in corresponding changes in the decomposition rates.

Introduction

The factors which influence the stabilities of organo transition-metal compounds are not fully understood [1]. The nature of the other coordinated ligands appears to play an importan role in determining the strength of the metal–alkyl bonds. The dissociation energies of the metal–carbon bonds have usually been deduced from kinetic measurements in thermal decompositions proceeding via metal–alkyl bond dissociation [2]. Metal–ligand bond dissociation energies can also be determined mass spectrometrically and provide a relative scale of metal-to-ligand bond strengths when a series of analogous complexes is examined [3]. Generally the bond dissociation energies obtained in this way do not refer to the original complex but to the intermediate positive complex formed by ionization in the mass spectrometer. Nevertheless a complete set of values for a homogeneous series of structurally related complexes can provide valuable information on the relative values of

0022-328X/83/0000–0000/$03.00

metal–ligand bond energies in the parent complexes. We report here on the series of complexes with the general formula $[Pt(X)(CH_3)(PEt_3)_2]$ (X = Cl, Br, I, CN; Et = C_2H_5). We have determined by mass spectrometry the ionization potentials of the compounds, the appearance potentials of $[Pt(X)(PEt_3)_2]^+$ from the ions $[Pt(X)(CH_3)(PEt_3)_2]^+$ and the variations in the Pt–CH_3 bond energies in these ions on changing the nature of the X ligand. In a parallel investigation we have studied the kinetics of the thermal decomposition of the complexes in decalin at 170 and 200°C, involving fission of the Pt–CH_3 bonds. We chose the methyl derivatives because for such compounds decomposition routes other than from homolytic fission are expected to be less important than for the higher alkyl derivatives. It was hoped that ligand exchange reactions leading to dimethyl complexes or internal metallations involving ethyl groups of the phosphine molecules would be absent, since these would complicate the comparison with the mass spectrometric results.

Experimental

Materials

The complexes $[Pt(X)(CH_3)(PEt_3)_2]$ were prepared by literature methods [4]. All reactions were carried out under argon by using standard anaerobic techniques. The solvents and all other compounds were reagent grade and were purified by standard methods.

Product distribution and kinetic study

The kinetics of the decomposition of the complexes (X = Cl, Br, I, CN) were studied in decalin at 170 and 200°C. Under these conditions the complexes were found to decompose to form methane, small amounts of ethane (about 2%) and less than 1% of ethylene. The thermolysis of the complexes was monitored by measuring the amount of CH_4 evolved from 2.5 ml of 5×10^{-2} *M* solutions of the complexes. The determination of the gaseous products (methane) was carried out by GLC according as described previously [5]. The reproducibility and accuracy of the method used was ±5%. The semilogarithmic plots of the difference $x_\infty - x_t$ (x represents the molar amount of liberated methane) were linear for at least three half lives and yielded the values of k_{obsd}, the first-order rate constant of the thermolysis of the complexes. The values of k_{obsd} reported in Table 1 are the average of at least three independent kinetic runs and are subject to an estimated error of ±10%. It was also shown in independent runs that the rate of appearance of methane was the same as that of the disappearance of the complex. To show this, in certain runs the

TABLE 1

RATE CONSTANTS FOR APPEARANCE OF METHANE IN THE THERMOLYSIS OF $[Pt(X)(CH_3)(PEt_3)_2]$ COMPLEXES IN DECALIN AT 200°C

Complex	$10^5 k_{obsd}(s^{-1})$
$[Pt(I)(CH_3)(PEt_3)_2]$	1.5
$[Pt(Br)(CH_3)(PEt_3)_2]$	1.6
$[Pt(Cl)(CH_3)(PEt_3)_2]$	1.2
$[Pt(CN)(CH_3)(PEt_3)_2]$	1.8

TABLE 2

COMPOSITION OF METHANE EVOLVED FROM THE THERMOLYSIS OF $[Pt(X)(CD_3)(PEt_3)_2]$ COMPLEXES IN DECAHYDRONAPHTALENE-d_{18}

Complex	T (°C)	CD_3H/CD_4
$[Pt(CN)(CD_3)(PEt_3)_2]$	170	10.2
	200	10.5
$[Pt(I)(CD_3)(PEt_3)_2]$	170	9.3
	200	9.0

evolution of methane was measured up to times approximately corresponding to the decomposition of one-half of the complex present in solution (as measured by the amount of evolved methane); the reaction was stopped by lowering the temperature, and aqueous HCl was added. The amount of methane evolved by protonolysis of the still undecomposed complex was found to correspond to that expected after allowing for the amount evolved in the thermal decomposition.

Deuterium labelling studies were conducted by thermally decomposing the complexes $[Pt(I)(CD_3)\{P(C_2H_5)_3\}_2]$ and $[Pt(CN)(CD_3)\{P(C_2H_5)_3\}_2]$ in decalin-d_{18} at 170 and 200°C. The solutions were allowed to react for 3 days and the gaseous products were analyzed by GC/MS. The ethane was 100% C_2H_6, the ethylene was 100% C_2H_4, while the methane was a mixture of CD_3H and CD_4 in the ratios shown in Table 2. As shown in the Table, the yields of the two forms of methane are independent of temperature within the limits of accuracy of the mass spectrometric measurements ($\pm 8\%$). When the thermal decomposition of $[Pt(I)(CD_3)(PEt_3)_2]$ was carried out in decalin-d_0 at 200°C, the gaseous products contained CD_3H, C_2H_6 and C_2H_4 but negligible amounts of CD_4.

The inorganic products were isolated at the end of the reaction using the following procedure. Platinum metal (43% yield), formed in the reaction was filtered off and the volume of the solution was reduced under vacuum. The white crystals which separated after addition of light petroleum gave an analysis corresponding to $[Pt(X)_2(PEt_3)_2]$ (yield, 48% based on the starting complex).

Apparatus

The mass spectra were measured at 70 eV with a VG MM 16F mass spectrometer. The samples were introduced directly into the ion source (150°C). No pyrolysis effect was apparent. Ionization and appearance potentials, reported in Table 3, were determined by established procedures [6,7] using xenon as a standard. The appearance potential of each ion was measured at least three times; reproducibility was better than 0.1 eV.

Infrared spectra were recorded with a Perkin–Elmer 599 B spectrophotometer. The platinum–carbon stretching frequencies ν(Pt–C) in the $[Pt(X)(CH_3)(PEt_3)_2]$ complexes in the region 500–600 cm^{-1} have been assigned [8], except for the cyanide complex for which the assignment is complicated by the simultaneous occurrence of the ν(Pt–CN) stretch in the same region. In agreement with the earlier data we find that the spectrum of the complex $[Pt(CN)(CH_3)(PEt_3)_2]$ shows absorptions at 516 and 453 cm^{-1}. The band at 516 cm^{-1} is not present in the spectrum of $[Pt(CN)(CD_3)(PEt_3)_2]$ and consequently can be assigned to the ν(Pt–C) stretching

TABLE 3

ENERGY AND IR DATA FOR THE COMPLEXES $[Pt(X)(CH_3)(PEt_3)_2]$

Complex	I.P. [a]	A.P. [b]	ν(Pt–C) (cm^{-1})	D [c] (eV)
$[Pt(I)(CH_3)(PEt_3)_2]$	7.76	8.29	540 [d]	0.52
$[Pt(Br)(CH_3)(PEt_3)_2]$	7.84	8.45	548 [d]	0.58
$[Pt(Cl)(CH_3)(PEt_3)_2]$	8.02	8.64	551 [d]	0.62
$[Pt(CN)(CH_3)(PEt_3)_2]$	8.34	9.04	516	0.70

[a] Ionization potential of the complex. [b] Appearance potential of $[Pt(X)(PEt_3)_2]^+$ [c] Dissociation energy of the $Pt-CH_3$ bond in $[Pt(X)(CH_3)(PEt_3)_2]^+$. [d] See also Ref. 8.

frequency in the methyl derivative. The values of the platinum–carbon stretching frequencies are listed in Table 3.

Discussion

We first discuss the mass spectral data summarized in Table 3. It is generally accepted that ionization potentials in a related series of complexes depend to a large degree on the ratio of the donor strength to acceptor strength of the ligands [9]. Thus the values of the ionization potential of the complexes can provide a measure of the donor/acceptor (or σ-basicity/π-acidity) ratio of the ligands. The increase of the ionization potentials observed along the series I, Br, Cl, CN, (Table 3) provides evidence that the *d*-electron density produced on the platinum atom upon substitution of the ligand ions decreases in the same order. This is in agreement with the known back-bonding description of the cyanide–metal bonds in the transition metal complexes.

By measuring the ionization potential (I.P.) of the complex $[Pt(X)(CH_3)(PEt_3)_2]$ and the appearance potential (A.P.) of the species $[Pt(X)(PEt_3)_2]^+$ the $Pt-CH_3$ bond dissociation energy in the molecular ion $[Pt(X)(CH_3)(PEt_3)_2]^+$ can be obtained:

$$D(Pt-CH_3)^+ = A.P. - I.P.$$

The absolute values of the bond energies thus obtained are subject to the known limitations inherent in the method but provide a relative scale of metal-to-ligand bond dissociation energies. Furthermore several studies have shown that the sequences of bond energies measured for the molecular ions in a series of structurally related complexes are also valid for the parent complex molecules [10]. For this investigation it can be assumed that the small increases in the Pt–C bond strengths observed for the ion $[Pt(X)(CH_3)L_2]^+$ in the series I, Br, Cl, CN, will be reflected in similarly small changes in the corresponding neutral complexes $[Pt(X)(CH_3)L_2]$. With reference to the cyanide group, this finding is rather unexpected. Thus the cyanide group occupies a position far removed from the halides in a number of series, involving a variety of properties; such as electronegativity, *trans*-effect, ligand field splitting, nephelauxetic effect, spectrochemical series, but, Table 3 shows that the difference in the $Pt-CH_3$ bond dissociation energy is only 0.18 eV on replacing iodide by cyanide in the position *trans* to the methyl group. On the other hand the observed differences, although relatively small in terms of bond energy, can dramatically influence the rate of release of the methyl group in a homolytic decomposition involving the platinum–carbon bond. This expectation is based on the assumption that radical recombination, the reverse reaction of homolytic bond fission, occurs with negligible activation energy. Under these circumstances the activation energy for the homolysis coincides with the bond strength. Thus a change of 0.18 eV in the Pt–CH_3 bond energy should result in a change by a factor of about 100 in the rate of decomposition at 200°C, assuming that there is a negligible change in the activation entropy.

Furthermore, it was expected that the influence of the ligand X on the labilization of the platinum–methyl bond is primarily determined by the amount of electron density donated to the metal via the σ-bond [1]. The quantitative assessment of this hypothesis requires rates data which reflect the influence of the *trans* ligand on the thermolysis rates [11]. However, the rates of release of CH_3 (Table 1) are independent of the nature of the *trans* ligand, in spite of the fact that the ionization potentials increase steadily on going from the iodide to the cyanide complex (Table 3). It is pertinent here to discuss the mechanisms which may lead to the formation of methane. That methane can arise by two (or more) simultaneous decomposition reactions is not incompatible with the observed first order kinetics. The nature of the possible reaction mechanisms can be defined on the basis of the isotopic labelling data, summarized in Table 2. The deuterium labelling data were obtained by carrying out the thermolysis of complexes of composition $[Pt(X)(CD_3)(P(C_2H_5)_3)_2]$ in perdeuterated decalin; evolution of CD_3H involves abstraction of hydrogen from ethyl groups of the phosphines, whereas the formation of CD_4 involves abstraction of one deuterium atom from the solvent. In principle, rearrangement of $[Pt(X)(CD_3)(PEt_3)_2]$ to $[Pt(X)_2(PEt_3)_2]$ and $[Pt(CD_3)_2(PEt_3)_2]$ *, followed by thermal decomposition of the dimethyl complex, could also give CD_4. However, it seems very unlikely that the thermolysis of $[Pt(CD_3)_2(PEt_3)_2]$ could occur without a concomitant production of ethane-d_6, and we know (see Experimental) that the small amount of ethane evolved in the reaction has the composition C_2H_6. Moreover, the methane produced by the thermal decomposition of $[Pt(X)(CD_3)(PEt_3)_2]$ in undeuterated decalin is practically pure CD_3H, ruling out an important abstraction of deuterium from coordinated methyls.

These observations allow us to conclude that only the following processes need be considered in discussing the thermal decomposition of $[Pt(X)(CD_3)(P(C_2H_5)_3)_2]$ in $C_{10}D_{18}$:

(1) Homolytic cleavage of the Pt–CD_3 bond followed by abstraction of deuterium within the solvent cage of a geminate $[L_2(X)Pt\cdot \cdot CD_3]$ radical pair.

(2) Abstraction of deuterium from the solvent by a free CD_3 radical.

(3) Transfer of deuterium from the solvent to the metal to give a deuterio-complex, followed by transfer of deuterium to the coordinate CD_3 group.

(4) Transfer of one hydrogen atom from an ethyl group of the phosphine to the coordinated methyl; this may occur by simultaneous cyclometallation of one ethyl group of the phosphine. It seems unlikely that mechanism 3 can operate in a solvent like decalin. We are more inclined to think that all of the observed CD_4 is formed

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* This type of rearrangement has been invoked for the analogous complexes of nickel which has shown that the relevant thermolysis gives more than 90% of ethane and only 4% of methane [4].

exclusively by abstraction of deuterium by CD_3 radicals from the deuterated solvent.

As Table 2 shows, intramolecular abstraction is strongly preferred, but this may simply mean that the CD_3 radicals are more reactive towards the ethyl groups of the phosphines than towards the solvent. A change of 30°C in the reaction temperature does not noticeably affect the ratios of the yields, which also appear to be little influenced by the nature of the X ligand. That the thermal decomposition occurs predominantly by homolytic fission of the $Pt-CH_3$ bond is also suggested by nature and yields of the inorganic products. They consist of an equimolar mixture of platinum metal and $[Pt(X)_2(PEt_3)_2]$, which may be formed according to the following scheme:

$$L_2(X)Pt-CH_3 \rightarrow L_2(X)Pt\cdot + \cdot CH_3$$

$$2\,L_2(X)Pt\cdot \rightarrow Pt + 2L + Pt(X)_2L_2$$

Processes 3 and 4 provide a less plausible explanation for the observed products and the yields.

The results favour the conclusion that CD_3H and CD_4 are both products of radical reactions occurring within the solvent cage, but they do not permit a correlation of the $Pt-CH_3$ bond energies with the kinetic data. The results become significant in a more general sense if one considers that for the mechanisms 1–4 the $Pt-CH_3$ bond energy term is expected to make an important contribution to the overall activation enthalpy $\Delta H^\ddagger$ of the thermolysis reaction (making the reasonable simplification that the changes of the activation entropy parameter $\Delta S^\ddagger$ are of negligible importance in the series studied). In fact the rates of thermal decomposition of the $[Pt(X)(CH_3)(PEt_3)_2]$ complexes appear not to be significantly influenced by changes in the $Pt-CH_3$ bond dissociation energies; in other words the decomposition rates appear to be independent of the ground state conditions and are unexpectedly levelled out by predominant transition state effects.

It may be of interest to compare these conclusions with attempts to correlate the *trans*-labilizing abilities of the ligand X in substitution reactions involving the same monoalkyl complexes of platinum [8]. It has been observed that the platinum–carbon stretching frequencies (Table 3) decrease along the series X = Cl, Br, I, CN as the *trans*-effects of the X ligand increase. On this basis the *trans*-effect should reflect the order of $Pt-CH_3$ bond strength in the series, in keeping with the known correlation between high *trans*-effect and weakening of the bonds in *trans* position. The results of the present study, although not strictly related to the lability to nucleophilic substitution, do not support the view that the *trans*-effect can be a ground state effect.

Acknowledgment

We thank Mr. F. Bergamin for laboratory assistence.

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