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THERMAL STABILITY OF ORGANOPALLADIUM COMPOUNDS: NON-RADICAL METHYL ELIMINATION FROM $[PdXMe(PEt_3)_2]$

A. MORVILLO and A. TURCO

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

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Summary

The thermolysis of the palladium complexes $[PdX(Me)\{P(C_2H_5)_3\}_2]$ (X = Br, I, CN; Me = CH_3, CD_3) in decalin or toluene under argon, in the temperature range 120–160°C, produces methane, ethane and ethylene, in ratios which vary with the temperature. Deuterium labelling shows that the methane is mainly formed through intramolecular abstraction of hydrogen from the phosphine ligands by the coordinated methyl group and not through homolytic fission of the Pd–Me bond. The thermal stability and the decomposition mechanisms of the organopalladium complexes are compared with those of the platinum analogues, which are remarkably more stable. At the higher temperatures, the thermal decomposition involves cleavage of the P–Et bonds in the phosphine ligands, and this leads to the formation of ethane and ethylene. The rate of generation of methane from the Pd–Me moieties is increased by a factor of 10 by the presence of an excess of dioxygen. Deuterium isotopic labelling shows that the rate increase is accompanied by a change from an intramolecular to a radical mechanism involving the abstraction of hydrogen by the methyl groups.

Introduction

As part of our studies of the factors which influence the stability of the M–C bonds in transition metal organometallic compounds, we recently reported that the thermolysis of the $[PtI(CD_3)(PR_3)_2]$ complexes (R = CH_3, C_2H_5, C_6H_5, cyclohexyl) in deuterated or non-deuterated hydrocarbons at 120°C involves mainly homolytic fission of the platinum–methyl bond. The CD_3 radicals then form methane by the abstraction of hydrogen (or deuterium) from the R groups of the phosphines (or from the solvent). A second, less important, decomposition route involves abstraction of deuterium from the coordinated CD_3 groups (the "self-reaction") [1].

Here we report on a similar investigation of the thermolysis of the palladium complexes $[PdX(Me)(PEt_3)_2]$ (X = Br, I, CN; Me = CH_3, CD_3) in decalin or toluene between 120 and 160°C. The complexes decompose in the hydrocarbons mainly with the liberation of methane, but substantial amounts of ethylene and

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TABLE 1

ISOTOPIC COMPOSITION OF THE HYDROCARBONS (METHANE, ETHANE, ETHYLENE) PRODUCED IN THE THERMOLYSIS OF *trans*-[PdX(CD_3)(PEt_3)$_2$] COMPLEXES UNDER ARGON

X	T (°C)	Solvent									
		Decalin-d_0	Decalin-d_{18}			Toluene-d_0			Toluene-d_8		
		CD_4/CD_3H	CD_4/CD_3H	Ethane	Ethylene	CD_4/CD_3H	Ethane	Ethylene	CD_4/CD_3H	Ethane	Ethylene
I	120	0.25									
	140	0.05	0.38			0.11 0.12 [a]	C_2H_6	C_2H_4	0.26 2.9 [a]	C_2H_6	C_2H_4
	160	0.04	0.21	C_2H_6	C_2H_4						
CN	140		0.25			< 0.01			0.13 3.6 [a]		
	160	0.05	0.11	C_2D_6/C_2H_6 = 0.21	C_2H_4						

[a] Reaction under an excess of O_2.

ethane are also formed at the higher temperatures. Under similar conditions the corresponding platinum complexes decompose with the exclusive liberation of methane, although minor amounts of ethane and ethylene are formed at 200°C. The main decomposition route at 120°C is the homolytic fission of the $Pt-CH_3$ bond, accompanied at higher temperatures (170–200°C) by the intramolecular transfer of hydrogen from the phosphine ligands to the coordinated methyl group [1,2]. For the nickel analogues, it is known that $[NiI(CH_3)(PR_3)_2]$, formed by the oxidative addition of CH_3I to $Ni(PR_3)_2$ (R = cyclohexyl), decomposes mainly with the formation of ethane, while the decomposition of the corresponding cyanide complex gives only methane [3]. Thus, nickel and platinum complexes of the type $[MX(CH_3)(PR_3)_2]$ exhibit a variety of decomposition routes which appear to be characteristic of the individual compounds. These decomposition routes are all reasonable for complexes of the type $[MX(CH_3)(PEt_3)_2]$ although, of course, one or more of them may occasionally not be evident for kinetic reasons.

The present report describes the different routes observed in the thermal decomposition of $[PdX(Me)(PEt_3)_2]$ complexes.

Results and discussion

Table 1 shows the values of the ratio CD_4/CD_3H ρ observed for the methane released in the thermolysis of complexes of the type *trans*-$[PdX(CD_3)(PEt_3)_2]$ (X = I, CN) in deuterated or non-deuterated decalin or toluene. In these experiments the formation of the fully deuterated CD_4 is expected to occur exclusively by two possible mechanisms. One, the so called "self-reaction", involves only the coordinated CD_3 group; the other involves the abstraction of deuterium from the deuterated solvent by CD_3 radicals [1,2]. The amount of CD_4 formed by the "self-reaction" can be evaluated from the thermolysis data for non-deuterated solvents. The results in Table 1 show that the contribution of the "self-reaction" to the formation of CD_4 is very small, the value of ρ being as low as 0.05 in decalin-d_0 and about 0.1 in toluene-d_0. Thus most of the CD_4 formed in the deuterated solvents must result from the abstraction of deuterium from the solvent. The value of ρ observed in the thermolysis of $[PdI(CD_3)(PEt_3)_2]$ is 0.38 at 140°C and 0.21 at 160°C in decalin-d_{18}. With the cyanide complex even smaller values of ρ (0.25 and 0.11, respectively) are obtained. Thermolysis of the platinum analogue, $[PtI(CD_3)(PEt_3)_2]$, at 120°C is known to produce ethane with $\rho = 0.33$ in toluene-d_8 and $\rho = 1.25$ in decalin-d_{18} [1]. The decrease in the value of ρ on going from the organoplatinum compound (which decomposes chiefly through the production of CD_3 radicals) to the palladium analogues suggests that homolytic fission of the $M-CD_3$ bond is much less important in the thermolysis of the palladium complexes. In fact, generation of CD_3 radicals in a deuterated solvent is expected to be followed mainly by the formation of CD_4, and hence of a high value of ρ. Interpretation of the results in terms of a non-radical decomposition is also supported by the effect observed upon changing the deuterated solvent. We reported recently that the dependence of ρ on the deuterium donor power of the solvent may be used as a criterion of the intermediacy of the R radicals. In the presence of ligands containing hydrogen atoms (e.g., alkylphosphines), a competitive hydrogen-deuterium abstraction from the ligand and solvent takes place. Under these conditions the relative rate of abstraction of deuterium will increase on increasing the deuterium donor power of the solvent and the consequent increase of ρ will provide evidence about the radical nature of the

process. Application of this criterion of radical intermediacy to the decomposition of the palladium complexes at 140°C confirms that the formation of methane occurs mainly by an intramolecular mechanism, as shown by the modest increase of ρ on changing from toluene-d_8 ($\rho = 0.26$) to decalin-d_{18} ($\rho = 0.38$). By comparison, an increase from 0.33 to 1.25 is observed in the thermolysis of the platinum complex at 120°C.

The inorganic products isolated from the solutions of the $[PdI(CD_3)(PEt_3)_2]$ complex after the reaction were palladium metal and the complex $[PdI_2(PEt_3)_2]$, in an approximately 1 : 1 mol ratio. The ^{31}P NMR spectra of the solutions contained only two signals of equal intensity, one is attributed to the coordinated phosphine and the other to the phosphine set free in the solution by the decomposition of the organometallic complex. These NMR spectra show that triethylphosphine is the sole phosphorus compound present in the system, and so it must be concluded that the triethylphosphine moieties, initially dehydrogenated in the reaction with CD_3 groups, must have been reformed by hydrogen abstracted from the solvent. As shown in Table 1 the decomposition of $[PdI(CD_3)(PEt_3)_2]$ in decalin-d_0 at 140°C yields methane with $\rho = 0.05$, and as shown in Table 2 the product of the thermolysis is nearly pure methane. These results are thus accomodated in the following decomposition scheme:

$$2\,[PdI(CD_3)(PEt_3)_2] \xrightarrow{\text{decalin}} Pd + [PdI_2(PEt_3)_2] + 2\,\{CD_4 + CD_3H\} + 2\,P(C_2H_5)_3 \qquad (1)$$

where CD_4 and CD_3H are in a mol ratio of 0.05 : 1.

The values of the first order rate constants, k_{obs}, obtained by measuring the evolution of methane in the thermolysis of the complexes *trans*-$[PdX(CH_3)(PEt_3)_2]$ (X = Br, I, CN) are given in Table 3. These appear to indicate that the methyl group is more labile (by a factor of 10) in the cyanide complex than in the other complexes and one might be tempted to discuss this labilization in terms of an effect induced by the ligand X which is *trans* to the CH_3 group. However, the interpretation of the data is complicated by the simultaneous decomposition to give ethylene and ethane (Table 2), which is especially important for the cyanide complexes. It is difficult to

TABLE 2

PRODUCTS[a] FROM THE THERMAL DECOMPOSITION OF $[PdX(CH_3)(PEt_3)_2]$ COMPLEXES UNDER ARGON

X	T (°C)	Solvent					
		Decalin-d_0			Toluene-d_0		
		CH_4	C_2H_6	C_2H_4	CH_4	C_2H_6	C_2H_4
I	120	97	<1	<1			
	140	98	<1	<1	93	5	5
					96[b]	<1	<1
	160	88	<1	12			
CN	140	85	5	30	90	22	42
					91[b]	23	38
	160	89	24	40			

[a] Given as 100 × mol gas/mol complex. [b] Reaction under O_2.

TABLE 3

APPARENT RATE CONSTANTS k_{obs} FOR THE FORMATION OF METHANE IN THE THERMOLYSIS OF THE *trans*-[PdX(Me)(PEt_3)$_2$] COMPLEXES IN DECALIN-d_0 AT 160°C UNDER ARGON

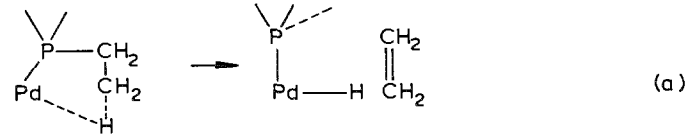
Complex	$10^5\, k_{obsd}\ (s^{-1})$
[PtBr(CH_3)(PEt_3)$_2$]	1.8
[PtI(CH_3)(PEt_3)$_2$]	2.1, 1.3 [a]
[Pt(CN)(CH_3)(PEt_3)$_2$]	18

[a] At 140°C.

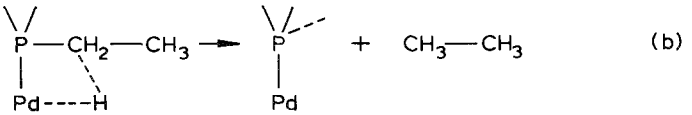
assume that the primary elimination of ethane and ethylene is not followed by secondary cleavage of the metal–methyl bond, with consequent formation of methane. The contribution of this decomposition process to the overall formation of methane is difficult to evaluate separately, and this complicates the interpretation of the increase in rate observed with the cyanide complex.

The isotopic composition of the two hydrocarbons (Table 1) shows that the ethylene is generated exclusively from the ethyl groups of the phosphines, while the ethane can also be derived from the CD_3 groups, as indicated by the results with the cyanide complex at 160°C. The formation of C_2D_6 is best understood in terms of a reductive coupling reaction, because the low value of ρ (0.11) rules out the intermediacy of CD_3 radicals. This suggestion is in keeping with the observation that an even higher production of CD_3 radicals, as observed with the iodide complex which produces methane with a ratio of $\rho = 0.21$, is not sufficient to generate appreciable amounts of C_2D_6. The fact that the ethane released in deuterated solvents does not contain deuterium (Table 1) shows that even the C_2H_6, in addition to the C_2H_4, comes exclusively from the ethyl groups of the phosphines. The formation of the two hydrocarbons at the expense of the tertiary phosphine ligands requires that the phosphorus–ethyl bonds be cleaved independently of the decomposition route leading to methane. Cleavage of the C–P bonds has been observed with some metal complexes of arylphosphines [4] but has rarely been reported for complexes with alkylphosphines [5]. The observed behaviour is not surprising in view of the reported ability of divalent palladium to promote the cleavage of C–P bonds in tertiary phosphines, and the known lability of hydrogen atoms contained in ligands coordinated to palladium. In the present case the ready availability of the phosphine hydrogens is suggested by the observation that the hydrogen utilized in generating the methane comes predominantly from the PEt_3 ligand by an intramolecular mechanism.

The following reaction scheme can be tentatively envisaged to account for the formation of ethylene and ethane:



(a)



(b)

Step (a) is not necessarily followed by step (b), which alternatively may be replaced by the transfer of hydrogen to a coordinated CD_3 group, leading to CD_3H.

In conclusion, the following decomposition mechanisms appear to be feasible for organopalladium compounds of the type $[PdX(Me)(PEt_3)_2]$, for which decomposition pathways such as β or γ elimination are precluded. At lower temperatures (120°C) the iodide complex yields methane which is almost completely free of ethane and ethylene (Table 2), but which contains a significant proportion of CD_4, derived from the "self-reaction" ($\rho = 0.25$ in decalin-d_0) (Table 1) which becomes less at 140°C (ρ = ca. 0.05 in decalin-d_0). At 140°C the thermolysis of the iodide complex involves only elimination of the CD_3 group, with formation of CD_3H and CD_4. The value of ρ (0.38) indicates that elimination of methane occurs mainly by intramolecular abstraction of hydrogen from the phosphines (to give CD_3H), with a significant homolytic contribution producing CD_4 by the interaction of CD_3 radicals with the deuterated solvent. At 160°C the intramolecular formation of methane increases at the expense of the radical decomposition (the value of ρ decreases to 0.21) but at the same time cleavage of the P–C bonds in the phosphines becomes important and ethylene is generated from the ethyl groups of the ligands (Table 2). For reasons that are not readily understood, the presence of a cyanide group in the complex favors the involvement of the alkyl substituents in the decomposition processes, with consequent formation of ethylene and ethane. Moreover, as shown in Table 2, decomposition of the iodide complex gives only small amounts of ethane, in contrast to the cyanide derivative.

The palladium complexes $[PdX(Me)(PEt_3)_2]$ are less stable than the corresponding platinum derivatives $[PtX(Me)(PEt_3)_2]$ (X = Cl, Br, I, CN). The rate of thermal elimination of methane (described by the first order rate constant k_{obs}) from $[PdI(Me)(PEt_3)_2]$ at 140°C ($k_{obs} = 1.3 \times 10^{-5}$ s^{-1}) is comparable to that of the analogous platinum complex at 200°C (k_{obs} 1.6×10^{-5} s^{-1}) [2]. Also the platinum compounds show a markedly higher stability towards cleavage of the P–C bonds in the coordinated phosphines. In decalin at 200°C the complexes $[PtX(Me)(PEt_3)_2]$ decompose to give 97% methane, 2% ethane and less than 1% ethylene [2], while $[PdI(Me)(PEt_3)_2]$ gives 12% ethylene at 160°C (Table 2).

The values of ρ for the methane evolved in the thermolysis of $[PtI(CD_3)(PEt_3)_2]$ in decalin-d_{18} at various temperatures, are listed in Table 4. Change from a radical (homolytic fission of the Pt–CD_3 bond) to an intramolecular (abstraction of hydrogen from the phosphine ligands) decomposition mechanism is clearly shown by the decrease of ρ which occurs upon increasing the temperature. The data in Table 1 suggest a similar trend in the thermolysis of $[PdI(CD_3)(PEt_3)_2]$. As the temperature

TABLE 4

COMPOSITION OF METHANE EVOLVED IN THE THERMOLYSIS OF $[PtI(CD_3)(PEt_3)_2]$ IN DECALIN-d_{18}

T (°C)	CD_4/CD_3H	Ref.
120	1.25	1
170	0.11	2
200	0.16	2

is raised from 140 to 160°C, a decrease of ρ from 0.38 to 0.21 in decalin-d_{18} and from 0.26 to 0.13 in toluene-d_8 is observed.

Effect of dioxygen. The rate of the thermal decomposition of the $[PdX(Me)(PEt_3)_2]$ complexes is greatly increased by the presence of dissolved oxygen gas. The first-order rate constants, k_{obs}, for the evolution of methane in toluene under dioxygen at 140°C is 1.3×10^{-4} s^{-1}, compared with the value 1.3×10^{-5} s^{-1} obtained in the absence of dioxygen (Table 3). Also, the added dioxygen has a profound effect on the decomposition pathway. A dramatic increase in the value of ρ (from 0.26 to 2.9, see Table 1) is observed when the thermolysis in toluene-d_8 is carried out under an excess of dioxygen (mol ratio O_2/complex = 40). Under these conditions homolytic fission of the Pd–CD_3 bond clearly becomes the preferred decomposition pathway. The inorganic products of the thermolysis are palladium metal and $[PdI_2(PEt_3)_2]$, as found in the absence of oxygen, but the phosphine liberated in the decomposition of the complex is all present as the phosphine oxide. The ^{31}P NMR spectra of the reacted solutions show that the coordinated phosphine ligand and the free phosphine oxide are present in a 1 : 1 mol ratio (see Experimental). The products formed by the decomposition are all shown in equation 2, where the observed value of ρ (= 2.9) has been rounded-up to 3.0.

$$2[PdI(CD_3)(PEt_3)_2] \xrightarrow[-0.5\ H]{O_2\ \text{excess}} [PdI_2(PEt_3)_2] + Pd + 2\ OPEt_3 + 1.5\ CD_4 + 0.5\ CD_3H \qquad (2)$$

As with the iodide, the cyanide complex decomposes at 140°C at a higher rate in the presence of dioxygen, yielding methane with the ratio $\rho = 3.6$ (Table 1).

Two mechanisms can account for the results observed in the presence of dioxygen. One involves the direct participation of O_2 in a key step which involves M–O_2 moieties and which leads to the homolytic displacement of CD_3 radicals and, although not necessarily, to the simultaneous oxidation of the phosphine. A second mechanism involves interaction of the metal complex with alkyl hydroperoxides or other peroxidic intermediates. A direct attack on the original complex by the dioxygen molecule cannot be ruled out, although palladium(II) complexes are not known to form stable dioxygen adducts. However, the observed results are more easily understood in terms of an attack of alkylperoxy species on the metal complex, followed by oxidation of the liberated phosphine. The yield of phosphine oxide is not stoichiometrically equivalent to the methane released as CD_4, showing that the formation of phosphine oxide is not necessarily associated with the homolytic cleavage of the Pd–CD_3 bond. In conclusion, it is very difficult to distinguish between processes due to "oxygen activation" and/or "autoxidation", and the mechanism of radical formation of CD_4 (and $OPEt_3$) in the presence of dioxygen remains unresolved.

Experimental

The solvents and reagents were obtained commercially and purified by standard methods. Except where stated, all experiments were carried out under argon.

The complexes *trans*-$[PdI(Me)(PEt_3)_2]$, (Me = CD_3, CH_3; Et = C_2H_5) were prepared according to literature methods [6]. *trans*-$[Pd(CN)(Me)(PEt_3)_2]$ was prepared

by the reaction of *trans*-[PdI(Me)(PEt_3)$_2$] with KCN in a 1 : 1 mol ratio in ethanol. The complexes gave satisfactory analyses. A single ^{31}P resonance in the NMR spectra of the compounds in benzene at 25°C showed them to be the *trans* isomers. The inorganic products were isolated after the reactions by the following procedure. The palladium metal was filtered off and the volume of the solution was reduced under vacuum. The white crystals which separated after the addition of light petroleum were the pure [$PdX_2(PEt_3)_2$] complexes (X = I, CN), mol yield 45%, which were identified by their mass spectra (M^+ ions).

Kinetics

The kinetics of the decomposition of the complexes were studied in toluene. The thermolysis of the complexes was monitored by measuring the amount of methane evolved from 0.50 ml of 5.0×10^{-2} *M* solutions of the complexes. The gaseous products were determined by the use of a Perkin-Elmer Sigma 3B chromatograph as described previously [3]. The semi-logarithmic plots of the difference $x_\infty - x_t$ (x represents, in mmol, the amount of methane liberated) were linear for four half-lives and gave the values of k_{obs}, the first order rate constant of the thermal decomposition producing the methane.

Deuterium labeling studies

The complexes (0.50 ml of 8.0×10^{-2} *M* solutions) were thermally decomposed in the appropriate solvent by heating at 120, 140 and 160°C. The gas samples were analyzed on a VG MM 16F mass spectrometer equipped with a Dany 3800F chromatograph by a procedure similar to that used by Gifford et al. [7].

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