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MECHANISM OF THERMOLYSIS OF MONOALKYLPLATINUM(II) COMPLEXES WITH TERTIARY PHOSPHINE LIGANDS. METHYL RADICAL ELIMINATION FROM *trans*-$Pt(I)(CD_3)[P(CH_3)_2]_2$

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Summary

Thermolysis of the complexes *trans*-$Pt(I)(Me)(PR_3)_2$ ($R = CH_3$, CD_3, C_2H_5, C_6H_5, C_6H_{11}, $Me = CD_3$) in deuterated or non-deuterated hydrocarbons at 120°C produces MeH and/or MeD. Appropriate isotopic labeling has revealed the existence of two decomposition pathways. The main route involves homolytic splitting of the platinum–methyl bond to give methyl radicals, which then form methane by abstraction of hydrogen from the R groups of the phosphines or from the solvent. The second, less important, route has a molecular mechanism involving coordinate methyl groups.

Introduction

The mechanism by which alkylmetal complexes decompose are of interest for an understanding of the factors controlling the stability and reactivity of carbon–metal bonds [1]. In a previous study we showed that the reaction of $Ni(PEt_3)_4$ with CH_3I in toluene at 0°C produces $Ni(I)(CH_3)(PEt_3)_2$, which on thermal decomposition yields a 95/5 mixture of ethane and methane [2]. In contrast, the thermolysis of $Pt(X)(CH_3)(PEt_3)_2$ (X = Cl, Br, I, CN) in decalin at 170°C gives only methane [3]. Similar behaviour was observed for the dimethyl complex $Pt(CH_3)_2(PEt_3)_2$ upon thermolysis in PEt_3 at 250°C [4]. In the present study we focus attention on the mechanism of the thermal decomposition of complexes of the type *trans*-$Pt(I)(CD_3)(PR_3)_2$ ($R = CH_3$, CD_3, C_2H_5, C_6H_5, C_6H_{11}) in a variety of deuterated and non-deuterated hydrocarbons at 120°C.

The formation of alkane in the decomposition of alkylmetal substrates may involve alkyl radicals generated from the homolytic scission of the metal–alkyl bond. Hydrogen abstraction by the radical, either from the substrate itself or from the solvent, then produces the observed alkane. In addition to homolytic cleavage, other transformations of the starting alkylmetal (for example, α-elimination, reductive coupling, and hydrogen transfer [5,6]) can also produce the alkane. Because of the

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superficial resemblance between radical reaction and concerted processes it is often difficult to distinguish homolytic from molecular mechanisms.

In the present case the formation of methane may occur by radical mechanism involving generation of methyl radicals by homolytic cleavage of carbon–platinum bonds, followed by abstraction of hydrogen (or deuterium) from the reaction cage (PR_3 groups, solvent). Alternative non-radical mechanisms for the elimination of methane are: (i) Rearrangement of the initial complex $Pt(I)(CD_3)L_2$ to a 1/1 mixture of $Pt(I)_2L_2$ and $Pt(CD_3)_2L_2$, followed by elimination of CD_4 from the dimethyl complex. The elimination of methane from two methyl ligands coordinated to the same metal ion is a well established process [4]. It may involve α-elimination of hydrogen and the formation of a labile methylene carbene complex [7]. Decomposition to methane does not necessarily require a preliminary rearrangement of the monomethyl complexes to the dimethyl derivatives. Methane could be produced in a bimolecular reaction, by α-hydrogen transfer between two monomethyl complexes, leaving a bridging methylene compound; this type of decomposition has been suggested for methylruthenium complexes [8].

$$2\,M(CH_3)L_x \rightarrow L_xM(\mu\text{-}CH_2)ML_x + CH_4$$

(ii) Transfer of hydrogen from the phosphine to the metal, followed by reductive elimination of CD_3H, leaving in the case of $P(CD_3)_3$ ligands a three-membered metallocycle $\overline{Pt{-}P{-}C}H(CH_3)_2$ [9]. (iii) Reductive elimination of CD_3H by direct transfer of hydrogen from the phosphine. (iv) Cleavage of C–H(D) bonds of the solvent by oxidative addition to the platinum atom, followed by reductive elimination of CD_3H (or CD_4). The radical pathway can be investigated by using isotopically labeled reagents and establishing whether the isotopic composition of the observed methane requires the intermediacy of methyl radicals. This may be done by determining either the selectivity of the methyl radical in abstracting hydrogen from different solvents (solvent selectivity) or the isotopic selectivity k_H/k_D in the presence of non-deuterated and deuterated substrates competing for the radical as hydrogen or deuterium donors.

Results

Our previous work has shown that the thermal decomposition of *trans*-$Pt(I)(CD_3)[P(C_2H_5)_3]_2$ in decalin-d_{18} produces a mixture of CD_4 and CD_3H. This indicates that some methane is formed by abstraction of hydrogen from the phosphines. If the formation of CD_4 and CD_3H is assumed to require CD_3 radicals as the common intermediate, one can expect the CD_4/CD_3H ratio to depend on the ability of the deuterated solvent to act as a deuterium donor (solvent selectivity). If the rate-determining step in the formation of methane is the homolytic cleavage of the platinum–methyl bonds, the rate of abstraction of hydrogen from the phosphine should decrease as the rate of abstraction of deuterium from the solvent increases. These considerations are helpful in evaluating the values of the CD_4/CD_3H ratio observed in the thermolysis of some complexes of the type *trans*-$Pt(I)(CD_3)(PR_3)_2$ ($PR_3 = PMe_3$, PEt_3, PPh_3, PCy_3) in deuterated and non-deuterated solvents (Table 1). Table 1 (column 4) also shows that the thermolysis of $Pt(I)(CD_3)[P(CH_3)_3]_2$ produces some CD_4 even in non-deuterated solvents. This indicates that there is an alternative pathway for the elimination of methane (a self-reaction) which does not

TABLE 1

ISOTOPIC COMPOSITION (CD_4/CD_3H) OF METHANE PRODUCED BY THERMOLYSIS OF *trans*-$Pt(I)(CD_3)(PR_3)_2$ COMPLEXES IN SOLUTION [a]

	Solvent	Solvent selectivity	PR_3				
			$P(CH_3)_3$	$P(CD_3)_3$	$P(C_2H_5)_3$	$P(C_6H_5)_3$	$P(C_6H_{11})_3$
1	C_6H_6		0.25				
2	C_6D_6		0.25		0.25		
3	$C_6H_5CH_3$	1	0.24				
4	$C_6D_5CD_3$		0.28		0.33	0.70	0.07
5	$C_6H_5C_2H_5$	4.6	0.25 [b]	0.25			
6			0.27 [c]				
7			0.24 [d]				
8	$C_6D_5C_2D_5$		1.75		0.50	0.83	0.16
9	C_6H_5-s-Bu-d_0	9.7	0.3				
10	C_6D_5-s-Bu-d_9		2.0		0.57	0.90	
11	Decalin-d_0		0.33				
12	Decalin-d_{18}		2.0		1.25	1.05	1.85

[a] Thermolysis temperature 120°C. Estimated error ±10%. Complex concentration: [b] 0.08 *M*, [c] 0.17 *M*, [d] 0.21 *M*.

involve radical attack on the phosphines or the solvent. We shall first comment upon the radical decomposition pathway.

The CD_4/CD_3H ratios observed in the thermolysis of the PMe_3 complexes in C_6H_6 and C_6D_6 are identical; furthermore, the ratios are almost identical for C_6D_6 and $C_6D_5CD_3$, even though $^{\cdot}CD_3$ should abstract D much more easily from the side-chain of $C_6D_5CD_3$ than from C_6D_6. A simple explanation of this apparently anomalous behaviour can be offered. The CD_4/CD_3H value of 0.25 obtained for the thermolysis in C_6H_6 refers only from the CD_4 produced by the self-reaction, since there can be no deuterium contribution from the solvent. If the additional CD_4 formed by the reaction of $^{\cdot}CD_3$ with C_6D_6 is negligible owing to the very low reactivity of C_6D_6, the ratio will remain almost unchanged in this solvent; and the $^{\cdot}CD_3$ radicals will react almost totally with $P(CH_3)_3$ to give CD_3H. Accordingly, the increase in the rate of deuterium abstraction in going from C_6D_6 to $C_6D_5CD_3$ is not sufficient to alter the ratio CD_4/CD_3H resulting from self-reaction, and the value is the same in the two solvents. It is only with $C_6D_6C_2D_5$ that the increased deuterium donor tendency of the solvent begins to contribute substantially to the formation of CD_4, so that the CD_4/CD_3H ratio increases on going from $C_6D_5CD_3$ to $C_6D_5C_2D_5$. Starting with $C_6D_5CD_3$, therefore, the value of CD_4/CD_3H increases as the ability of the solvents to act as a deuterium donor increases and the thermolysis of $P(CH_3)_3$ complexes in C_6D_5-s-Bu-d_9 produces CD_4 and CD_3H in a ratio approximately seven times greater than in $C_6D_5CD_3$. This difference is in good agreement with the expected selectivity of the methyl radical toward primary, secondary, and tertiary benzylic hydrogens. The selectivity values for hydrogen-donor solvents [10] are given in Table 1, column 3. These values can be taken as meaningful also for the deuterated solvents because the deuterium isotope effects should be identical for chain and ring abstraction [11].

It is difficult to interpret the results discussed above on the basis of a non-radical reaction. For example, if the formation of CD_3H via the phosphine occurred not by a mechanism involving $^{\cdot}CD_3$ radicals but rather by reductive elimination of coordinated CD_3 (vide infra), the CD_4/CD_3H ratio would remain constant upon changing the solvent. Similarly, the amount of CD_4 produced during fixed time intervals by reaction of the $^{\cdot}CD_3$ radicals with various deuterated solvents (fast step) would also remain constant; thus reductive elimination cannot satisfactorily explain the data obtained. Likewise, the formation of CD_4 cannot be explained in terms of a preliminary oxidative addition of the deuterated solvent to the metal, with cleavage of C–D bonds, followed by reductive elimination of CD_4, such a mechanism would require the addition of the bulky C_6D_5-s-Bu-d_9 to be faster than that of the less hindered $C_6D_5CD_3$.

The results in Table 1 do not reveal any apparent relation between the value of the CD_4/CD_3H ratio and nature of the phosphine (Table 1, horizontal rows). In effect, the rates of abstraction in the reaction cage are influenced by several factors, which can operate independently: steric bulk (e.g. cone angles) of the phosphines [12], chemical nature of R, structural and bonding properties of the solvent. The first factor is important in determining the ability of the phosphine to trap the radical before it escapes from the cage of the complex. The chemical nature of R (e.g. availability of primary, secondary, tertiary hydrogens) is of major importance in determining the tendency of the phosphine to undergo hydrogen abstraction. Finally, the molecular structure of the solvent will influence its orientation toward the complex (e.g. side chain or ring in alkylbenzenes) and consequently its reactivity towards the incoming radical. All these factors, along with the selectivity of the solvent, will determine the relative rates of abstraction phosphine/solvent, thus the lack of simple correlations within the horizontal rows of Table 1 is not at all surprising. On the other hand, it is noteworthy that the order of solvent selectivity observed for the $P(CH_3)_3$ complexes also applies to the other complexes in Table 1: the CD_4/CD_3H ratio increases along the series $C_6D_5CD_3$, $C_6D_5C_2D_5$, $C_{10}D_{18}$ independent of the nature of the coordinated phosphine (Table 1, columns 5, 6, 7).

On these basis, the observed dependence of the CD_4/CD_3H ratio on the selectivity of the solvent indicates that the $^{\cdot}CD_3$ radicals must be common reaction intermediates. Further support for this interpretation is provided by the following observations: (1) The thermolysis of $Pt(I)(CD_3)[P(CD_3)_3]_2$ in $C_6H_5C_2H_5$ produces CD_4 and CD_3H in a 1/4 ratio, identical with that observed for $Pt(I)(CD_3)[P(CH_3)_3]_2$ (Table 1). Thus the deuterated phosphines do not yield any of CD_4 in addition to that released by the self-reaction. This result does not rule out a rate-limiting intramolecular transfer of hydrogen (deuterium) from the phosphine to the coordinate CD_3 group. However, the dramatic decrease in abstraction from the phosphines upon deuterium substitution is most readily explained in terms of an isotope effect involving radical attack. (2) The thermal decomposition of $Pt(I)(CD_3)[P(CH_3)_3]_2$ in mixtures of $C_6D_5C_2D_5$ (SD) and $C_6H_5C_2H_5$ (SH) affords the CD_4/CD_3H ratios reported in Table 2. In these experiments deuterated and non-deuterated solvent compete for a CD_3 intermediate at relative rates governed by the isotopic selectivity k_H/k_D of the solvents. Table 2 shows that the CD_4/CD_3H ratio increases with increasing SD/SH ratio in the solvent. The observed trend is satisfactorily explained only in terms of a pathway involving. $^{\cdot}CD_3$ radicals (see also Fig. 1). (3) Finally, the formation of substantial amounts of bibenzyl when the thermolysis is carried out in toluene further confirms that radical intermediates must abstract deuterium from the solvent.

TABLE 2

RATIO CD_4/CD_3H OF THE METHANE PRODUCED IN THE THERMOLYSIS OF $Pt(I)(CD_3)[P(CH_3)_3]_2$ IN MIXTURES OF $C_6H_5C_2H_5$ (SH) AND $C_6D_5C_2D_5$ (SD)

CD_4/CD_3H	[SD] [a]	[SH] [a]
0.25	0	8.20
0.27	1.95	6.25
0.32	3.20	5.00
0.37	4.60	3.60
0.44	5.40	2.80
0.56	6.25	1.95
0.80	6.90	1.30
0.98	7.22	0.98
1.02	7.37	0.83
1.27	7.55	0.65
1.43	7.70	0.50
1.75	8.20	0

[a] Molar concentration.

The CD_4/CD_3H ratios obtained from the thermal decomposition of $Pt(I)(CD_3)[P(CH_3)_3]_2$ in non-deuterated solvents (Table 1), lead to some important additional considerations. Within the limits of the experimental error the CD_4/CD_3H ratios are equal in all the solvents; this indicates that a constant amount of CD_4 is formed even in the absence of deuterated solvent. The formation of this fixed amount of CD_4 cannot involve interaction of $^{\cdot}CD_3$ radicals with coordinate CD_3 groups. The assumption that a free $^{\cdot}CD_3$ radical may encounter a molecule of complex and react with its coordinate CD_3 groups without first reacting with the interposed solvent barrier can reasonably be rejected on the basis of the relative concentrations and reactivities of all the reagents involved, and also on the relatively

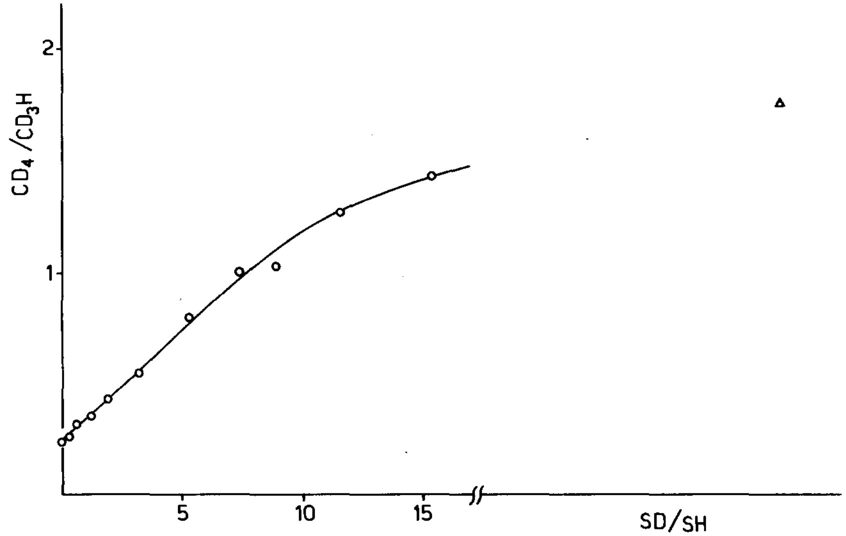

Fig. 1. The variation of CD_4/CD_3H with SD/SH for the thermolysis of $Pt(I)(CD_3)[P(CH_3)_3]_2$ in $C_6D_5C_2D_5$ (SD)/$C_6H_5C_2H_5$ (SH) mixtures at 120°C; CD_4/CD_3H in pure SD, Δ.

high yield of CD_4 produced by this mechanism (approximately one-fifth of the total methane released). Although the results do not provide direct disproof of a radical mechanism, they are most plausibly interpreted in terms of the scheme (i) described in the Introduction, i.e.: (a) α-elimination of CD_4 from a dimethyl platinum complex, (b) bimolecular reaction of two monomethyl complexes leaving a labile (μ-CH_2) complex.

Discussion

The thermolysis of the platinum monoalkyl complexes *trans*-$Pt(I)(CD_3)(PR_3)_2$ in hydrocarbons at 120°C may occur by two pathways.

(A) Self-reaction:

$$2Pt(X)(CD_3)(PR_3)_2 \rightarrow CD_4 + \text{products} \qquad (1)$$

alternatively:

$$2Pt(X)(CD_3)(PR_3)_2 \rightarrow Pt(X)_2(PR_3)_2 + Pt(CD_3)_2(PR_3)_2 \qquad (2)$$

$$Pt(CD_3)_2(PR_3)_2 \rightarrow CD_4 + \text{carbon products} \qquad (3)$$

(B) Radical path:

$$\begin{array}{ll} Pt(X)(CD_3)(PR_3)_2 \rightarrow & {}^{\cdot}CD_3 + Pt^{I}(X)(PR_3)_2 \\ & \qquad\qquad \downarrow \\ & \tfrac{1}{2}Pt(X)_2(PR_3)_2 + \tfrac{1}{2}Pt^0 + PR_3 \end{array} \qquad (4)$$

$${}^{\cdot}CD_3 + Pt^{I}(X)(PR_3)_2 \rightarrow CD_3H + Pt(X)(PR_3)[PR_2(R{-}H)] \qquad (5)$$

$${}^{\cdot}CD_3 \xrightarrow{\text{solvent}} \left[\begin{array}{ll} \xrightarrow[k_H]{SH} CD_3H & (6) \\ \xrightarrow[k_D]{SD} CD_4 & (7) \end{array} \right.$$

The generation of ${}^{\cdot}CD_3$ radicals from the methyl ligands may also take place by an alternative pathway, as suggested by the following considerations. The ratio CD_4/CD_3H is constant for concentrations of $Pt(I)(CD_3)[P(CH_3)_3]_2$ lower than 0.2 *M*, as indicated for experiments 5–7, column 3, Table 1. This indicates that reactions 5–7 must be of the same kinetic order with respect to the methyl radical. Furthermore, the rate-determining step of the self-reaction to produce CD_4 directly (eq. 1) must be of the same kinetic order as the reaction producing ${}^{\cdot}CD_3$ radicals. It is then possible for the ${}^{\cdot}CD_3$ radicals and the directly produced CD_4 to arise from a common dimethyl intermediate in the (rate limiting) process (eq. 8), which replaces eq. 4 and competes with eq. 3.

$$Pt(CD_3)_2L_2 \rightarrow {}^{\cdot}CD_3 + Pt(CD_3)L_2 \text{ etc.} \qquad (8)$$

The mass spectra of solutions of $Pt(I)(CD_3)[P(CH_3)_3]_2$, recorded after 20% of the complex had decomposed, displayed strong peaks arising from the molecular ions $[Pt(I)(CD_3)\{P(CH_3)_3\}_2]^+$ and $[Pt(I)_2\{P(CH_3)_3\}_2]^+$. Peaks arising from other platinum species, including $[Pt(CD_3)_2\{P(CH_3)_3\}_2]$ were not observed. The mass spectrometric data, therefore, provide no evidence for the dimethyl intermediate.

A plot of CD_4/CD_3H as a function of SD/SH (SD = $C_6D_5C_2D_5$, SH = $C_6H_5C_2H_5$) based on the data of Table 2, is shown in Fig. 1. At lower values of SD the curve shows a linear dependence of CD_4/CD_3H on SD/SH. At higher SD values the slope falls steadily, eventually, reaching the limiting value CD_4/CD_3H = 1.75. This behaviour is consistent with the sequence represented by equations 1, 5, 6 and 7, a linear dependence at lower values of SD/SH being expected for a process in which solvent SH and solvent SD compete for a $^{\cdot}CD_3$ radical [13]. On the other hand, at high concentrations of SD the CD_4/CD_3H ratio is expected to approach the limiting value of 1.75 obtained in a pure deuterated solvent.

Conclusions

The present work has established that the thermal decomposition of the complexes $Pt(I)(CH_3)(PR_3)_2$ in hydrocarbons at 120°C involves two pathways both giving methane. The more important route involves the homolytic cleavage of the platinum–methyl bond, followed by abstraction of hydrogen from the phosphine ligands or from the solvent to produce methane; the competition between tertiary phosphine and solvent for the methyl radical is governed by the relative effectiveness of the two substrates to act as hydrogen or deuterium donors in the reaction cage. The second route probably involves molecular elimination of methane from coordinated methyl ligands. Our results show that deuterium labeling experiments may be used to distinguish homolytic from molecular mechanisms in decompositions involving the cleavage of metal–alkyl bonds.

Experimental

Materials. All compound and solvents were reagent grade and were purified by standard methods. All reactions were carried out under argon by standard anaerobic techniques.

Preparation of the complexes trans-$Pt(I)(CD_3)(PR_3)_2$ (R = CH_3, C_2H_5, C_6H_5, C_6H_{11}). These complexes were prepared by the following general procedure. The appropriate $Pt(Cl)_2(PR_3)_2$ complex (4 mmol) was reduced with potassium in THF as described by Schunn [4]. The solid $Pt(PR_3)_4$ complex (1.8 mmol) was dissolved in toluene (30 ml) and CD_3I (5.5 mmol) was added. The solution was stirred at room temperature for 2 h and the solid phosphonium salt was filtered off. The filtrate was evaporated to dryness in vacuo at room temperature; the white solid residue was dissolved in 20 ml of n-hexane and the solution was cooled at −78°C for 3 h. The white crystalline solid which separated was collected at −78°C, washed with cold n-hexane, and dried at 20°C in vacuo. The complex *trans*-$Pt(I)(CD_3)[P(CD_3)_3]_2$ was prepared by the same general procedure, except that $P(CD_3)_3$ was used. The deuterated phosphine was prepared by standard methods [14].

All the complexes gave satisfactory elemental analyses and their purities were confirmed by mass spectrometry. The mass spectra showed only the peaks of the molecular ion $[Pt(I)(CD_3)(PR_3)_2]^+$ and of the ions produced by its fragmentation. A single resonance ^{31}P was observed in the NMR spectra of the compounds in benzene at 25°C, showing them to be the *trans* isomers.

Deuterium labeling experiments. The complexes (0.5 ml of 8×10^{-2} *M* solution) were thermally decomposed by heating in the appropriate solvent (see Table 1) at

120°C for periods of time corresponding to 20% of complete decomposition. This value was selected because isotopic labeling experiments gave reproducible results over the first 20–30% of the reaction. However, since these thermal decomposition reactions are partly heterogeneous, due to the separation of platinum metal, their mechanisms were not examined in detail. The organic products of the thermolysis were analyzed as described earlier [2] by use of a Perkin–Elmer σ 3B chromatograph equipped with a 2 m column packed with 5A molecular sieves. The determination of bibenzyl was carried out using a 2 m column packed with 15% Apiezon L on Chromosorb W. The gas samples were analyzed on a VG MM 16F mass spectrometer equipped with a Dany 3800 F chromatograph by a procedure similar to that used by Gifford et al. [15]. The mass spectral data showed that the gaseous products derived from the coordinated methyls consisted exclusively of CD_4 and/or CD_3H. The molar CD_4/CD_3H ratios were obtained by scanning at least ten times across the 17–21 mass range. The mass ratio 20/19 gave directly the values of CD_4/CD_3H reported in Tables 1 and 2. The reproducibility and accuracy of the method was ±10%.

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