Decomposition of π-Allylpalladium(II)chloride Dimer by Trisubstituted Group IVB Monohydrides of the Type R3MH (R = Cl, CH3; M = Si, Ge, Sn)

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Palladium and platinum are known to form several π-allyl complexes of the general formula (π-allyl MX)$_2$, (M = Pd, Pt; X = halogen or pseudohalogen); the dimers contain two halogen or pseudohalogen bridges. Of the two metals palladium forms the wider and more stable range of such dimeric complexes, and most of them are stable to thermolysis up to 473 K and are only slowly hydrolysed at 298 K [1–3].

Some of the chemical reactions of these complexes have also been investigated in some depth. These include (i) cleavage of the halogen or pseudo-halogen bridges [4, 5], (ii) cleavage of the π-allyl ligand to metal bond [6], (iii) insertion into the metal–allyl bond [7, 8], (iv) substitution in the allyl ligand [1], and (v) σ to π isomerisation [9]. We have studied the reactions between some π-allyl palladium(II) dimeric complexes and the tri-substituted main group IVB monohydrides of the type R$_3$MH (R = Cl or CH$_3$; M = Si, Ge and Sn). The initial aim of this study was to synthesise palladium–group IVB metallic bonds stabilised by the π-allyl ligands. The results so far obtained with one of the dimers, (π-C$_3$H$_5$PdCl)$_2$, have indicated that the expected reaction does not occur, instead the dimer undergoes decomposition yielding a complex mixture of products.

Experimental

The dimer, (π-C$_3$H$_5$PdCl)$_2$, was prepared in analytically pure form by the method of Powell and Shaw [10]. The hydrides (CH$_3$)$_3$SiH, (CH$_3$)$_3$GeH and (CH$_3$)$_3$SnH were prepared by reducing the corresponding chlorides (CH$_3$)$_3$MCl (M = Si, Ge, Sn) with lithium aluminium hydride and purified by trap-to-

trap high vacuum distillation. Contact with air was excluded by sealing the pure hydrides in evacuated break-seal tubes. Cl$_3$SiH was commercially available (Aldrich Chemicals) and was used without further purification.

The reactions between the palladium dimer and the hydrides were carried out in evacuated break-seal tubes by condensing the hydride onto the dimer at 77 K. The tubes were warmed slowly to room temperature. When the reactions were considered complete (usually after one hr) the tubes were opened to the vacuum line and the volatile products separated by trap-to-trap fractional distillation using slush baths at 298 K, 253 K, 153 K and 77 K respectively. In most cases complete separation of the products was impossible to achieve.

The fractions collected at each temperature were dissolved in dry ether and the solutions passed through a gas chromatograph fitted with a silicone gum rubber (E310) column and coupled to a MS30 mass spectrometer. The gas phase infrared spectra of the various fractions of volatile products obtained from each reaction were also recorded on a Perkin-Elmer 577 spectrophotometer. The involatile fractions left as solid residues were solvent extracted several times with dry benzene and chemically analysed. The totally insoluble residues, which were mainly in the form of mirrors, were analysed by emission spectroscopy.

Results and Discussion

The products isolated from each reaction are listed in Table I and the chromatograms of volatile products of each reaction are reproduced in Fig. 1.

The products isolated from each of the reactions studied are varied and complex. However, it has been observed that certain products were common to all. At the same time a degree of specificity with regard to certain products has also been noted, as can be infered from the chromatograms. In most of the cases it was possible to identify most of the products from each reaction by means of mass and infrared spectrometry, and emission spectroscopy in the case of non-volatile solid products, and by matching the spectra of the products with those of the authentic compounds.

At room temperature or slightly below it, reactions rapidly deposited a metallic mirror on the walls of the break-seal tubes, and were complete within a few seconds of warming to room temperature.

Methane was a product common to all reactions except one involving trichlorosilane as reactant. Its identity was established from its infrared spectrum

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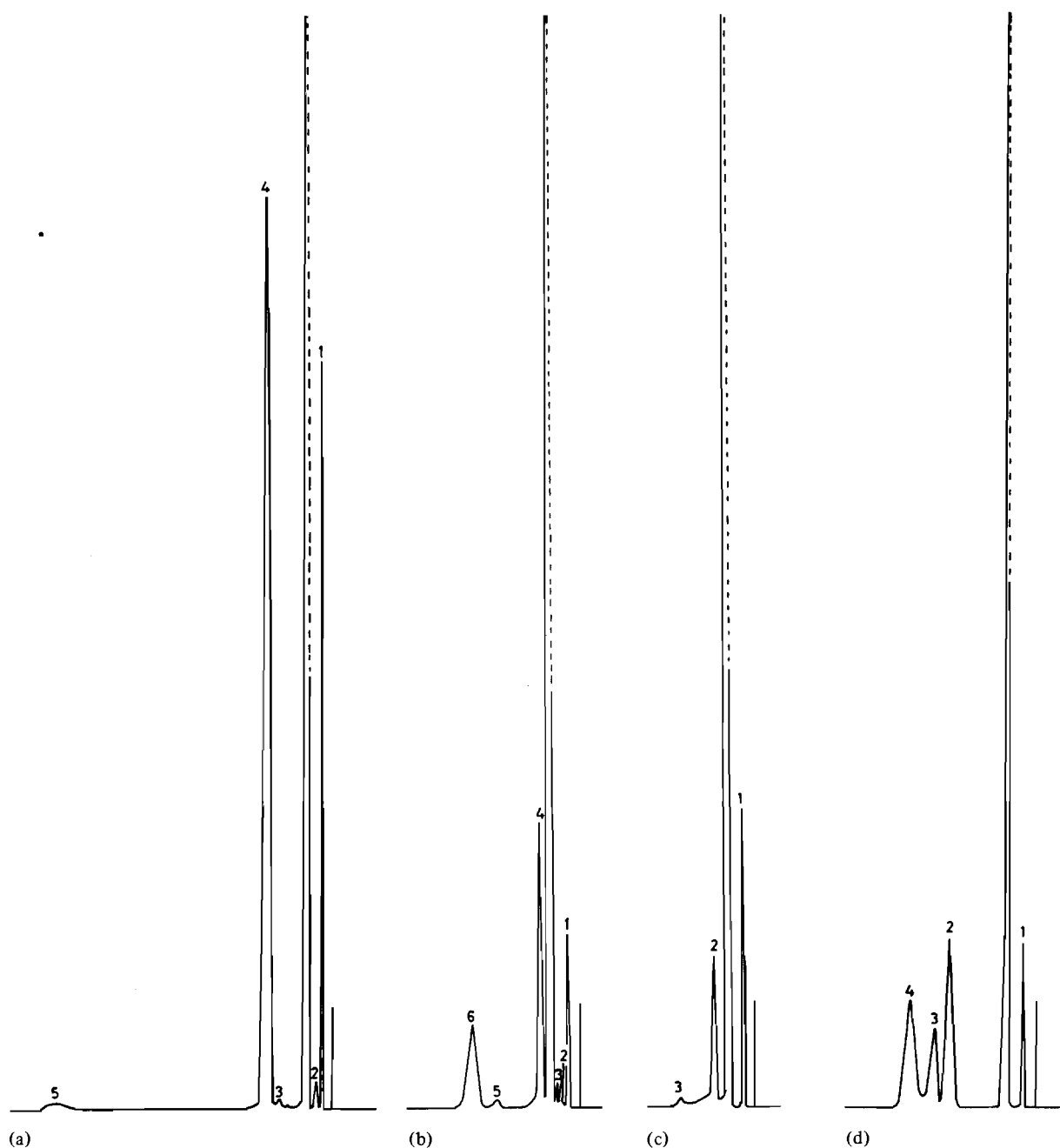
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Fig. 1. (a) Chromatogram of the volatile products of $(\pi\text{-}C_3H_5PdCl)_2$ and $(CH_3)_3SnH$ excluding methane. (1. propene; 2. butene; 3. hexene; 4. tetramethylstannane; 5. trimethyltinchloride.) (b) Chromatogram of the volatile products of $(\pi\text{-}C_3H_5PdCl)_2$ and $(CH_3)_3SiH$ excluding methane. (1. propene; 2. pentene; 3. trimethylsilane; 4. trimethylchlorosilane; 5. trichloromethylsilane.) (c) Chromatogram of the volatile products of $(\pi\text{-}C_3H_5PdCl)_2$ and Cl_3SiH. (1. propene; 2. tetrachlorosilane; 3. unidentified product.) (d) Chromatogram of the volatile products of $(\pi\text{-}C_2H_5PdCl)_2$ and $(CH_3)_3GeH$ excluding methane.

in the vapour phase and from its mass spectrum. The gas was always found in the fraction collected at 77 K. Propene is another product common to all reactions so far studied. Its identity was infered from its mass spectrum (molecular ion at 42 and 41) and from its infrared spectrum (C=C) at 1665 and 1640 cm⁻¹. It was always found in the fractions collected at 253 K and 153 K respectively. Apart from these two products, the reactions appear to give different products. No higher hydrocarbons have been detected, except in the reaction involving trimethyl stannane. This reaction yields two other hydra-

TABLE I. The Products isolated from the Reaction Mixture.

Reactant	Ratio of dimer to reactant	Products of reaction
Trichlorosilane	1:4	Propene, tetrachlorosilane, red solid[a] and palladium mirror
Trimethylsilane	1:4	Methane, propene, pentene, trimethylsilane, trichloromethyl-silane and palladium mirror
Trimethylgermane	1:4	Methane, propene, trimethylgermanium chloride, $(CH_2=CH-CH_2)GeH_2(CH_3)$[b], $(CH_3CH_2CH_2)GeH(CH_3)_2$[c], palladium mirror and a black residue containing free Ge and Pd
Trimethylstannane	1:4	Methane, propene, butene hexene, tetramethyl-stannane, trimethyl chlorostannane, a yellow solid[d], palladium mirror and a black residue containing mainly Pd and Ge

[a]The composition of this solid has not been fully established. [b,c]The formula of these products have been infered from their mass spectra which give molecular ions at m/e of 132 and 148 respectively. [d]The yellow solid contains a chloride and appears to be unreacted dimer.

carbons, namely butene (molecular ion at 56) and hexene (molecular ion at 84); both compounds give a relatively strong absorption peak at around 1640 cm^{-1} in their infrared spectra, which can be assigned to $\nu(C=C)$. Both were present in the fraction collected at 153 K.

The reaction between the dimer and trichlorosilane was found to yield relatively fewer products than the other substituted hydrides. The absence of the methyl groups could be directly responsible for the range of products observed. However, the reaction gives a red solid which is obtained by extracting the black solid residue several times with hot benzene. The solid crystallizes out of the solvent on cooling to room temperature. Although its elemental analysis seems to be consistent with the formula $(\pi\text{-}C_3H_5PdCl)_2$, its infrared spectrum consists of features which are not characteristic of the dimer of the formula given. For instance, strong sharp bands have been observed at 328 cm^{-1} and 685 cm^{-1} respectively. The former could be attributed to the bridging $\nu(PdCl)$, but in the dimer of the formula given, $\nu(PdCl)$ bridging occurs at 250 cm^{-1}. A high $\nu(PdCl)$ implies terminal rather than bridging chloride.

The band at 685 cm^{-1} disappears when the spectrum is recorded in CsI disc, which is probably the result of halogen exchange. In addition there is a discrepancy between the mass spectrum of the yellow dimer of the formula $(\pi\text{-}C_3H_5PdCl)_2$ and of the red solid. Further work is being undertaken to establish the identity of this product.

The appearance of such a range of products in these reactions is still difficult to rationalise, but we are of the opinion that the reactions involve free radicals which are probably generated on the surface of the freshly deposited palladium mirror. We postulate that the first stage in the reaction

pathway is the formation of a hydride I by oxidative addition to the dimer.

I
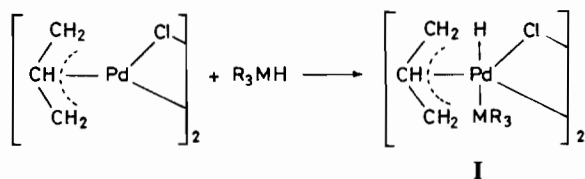
Probably I then undergoes a rapid hydride transfer from palladium to the allyl group to form a π-olefin complex II

II
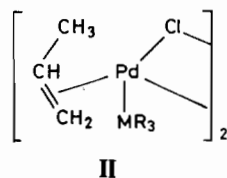
We believe that II undergoes rapid decomposition to produce propene, palladium metal and the radicals $Cl^{\cdot}$ and $R_3M^{\cdot}$.

What follows are radical recombinations.

$R_3M^{\cdot}$ and $Cl^{\cdot}$ can combine to form R_3MCl. This a product which is common to all the reactions.

Subsequently, free radicals are thought to be generated on the surface of the palladium mirror. One of the reactions which can lead to formation of more free radicals by the catalytic action of palladium is the decomposition of the excess R_3MH

$$R_3MH \xrightarrow{Pd} R_3M^{\cdot} + H^{\cdot}$$

$$R_3M^{\cdot} \longrightarrow R^{\cdot} + R_2M$$
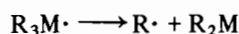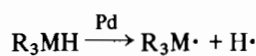
Combination of R· and H· gives RH and where R is CH_3 the product is methane.

Since methane is not produced in the reaction involving trichlorosilane, there is a strong indication that it is derived from the R_3M moiety rather than the allyl group. The other products are also thought to be formed by similar free radical recombination. Further work is planned to study the full mechanism of this decomposition reaction.

Acknowledgement

References

1 M. L. H. Green and P. L. I, *Adv. Organomet. Chem.*, 2, 325 (1964).
2 R. Huttel, J. Rratzer and M. Bechter, *Chem. Ber.*, 94, 766 (1961).
3 R. Huttel, J. Rratzer and M. Bechter, *Angew. Chem.*, 75, 465 (1959).
4 V. N. Sakalov and G. M. Khvostic, *J. Organomet. Chem.*, 29, 313 (1971).
5 D. Walter and G. Wilkie, *Angew. Chem.*, 78, 941 (1966).
6 H. C. Volger and K. Vrieze, *J. Organomet. Chem.*, 13, 495 (1963).
7 J. Tsuji, J. Kiji and M. Marikawa, *Tetrahedron Lett.*, 1811 (1963).
8 W. T. Dent, R. Long and G. H. Whitfield, *J. Chem. Soc.*, 1588 (1964).
9 G. Carturan, A. Scrivanti and U. Belluco, *Inorg. Chim. Acta*, 27, 37 (1978) and refs. therein.
10 J. Powell and B. L. Shaw, *J. Chem. Soc. A:*, 1839 (1967).