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INTRAMOLECULAR REARRANGEMENT OF PLATINUM AND PALLADIUM CARBENOIDS

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Summary

Compounds of the general formula (diphos)M(R)(R'), where diphos represents 1,2-bis(diphenylphosphino)ethane, M is Pd or Pt, R is an alkyl group, and R' is a dichloro- or trichloromethyl group which serves as the carbene precursor, exhibit an intramolecular rearrangement whereby the carbene moiety is inserted into the platinum—carbon or palladium—carbon bond. When R' = $CHCl_2$ the product is an α-chloroalkylmetal chloride (M = Pd, Pt), and when R' = CCl_3 the initially formed α,α-dichloroalkylplatinum chloride ((diphos)$PtClCCl_2R$) eliminates hydrogen chloride to give α-chlorovinylplatinum chloride, (diphos)PtCl-(CCl=CHR''), as the final product.

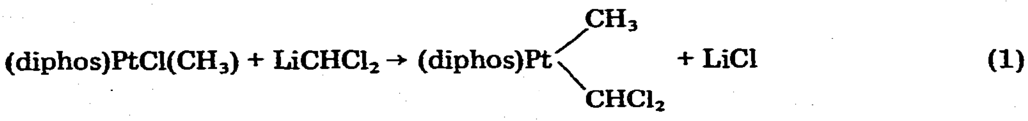
Introduction

Chloromethyl derivatives are known for several metals, e.g. Hg, Sn, Zn, Li and Cd [1a—e]. Some of these derivatives, such as those of Li and Hg, can be successfully used as carbene precursors. Metal carbenoids are often assumed to be intermediates in the metal-catalysed carbene transfer reaction [1a,d]. To our knowledge the literature contains no formation of such compounds of platinum and palladium.

In a previous paper [2] it was reported that during photolysis of dimethylplatinum and -palladium in chloroform with UV light of 220—350 nm, NMR spectroscopy revealed the formation of α-chloroethyl moieties resulting from an intramolecular insertion of carbene into the metal—carbon bond. It was stated that this insertion reaction does not proceed via radical species. This paper deals with the synthesis of di- and tri-chloromethylplatinum and -palladium compounds and their thermal rearrangements.

Results and discussion

A general procedure for the synthesis of platinum alkyls, viz. the reaction of a chloroplatinum complex with a lithium alkyl, was used for the preparation of chloromethylplatinum complexes (eq. 1).

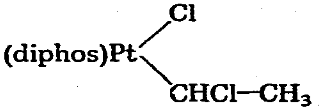


$$(\mathrm{diphos})\mathrm{PtCl}(\mathrm{CH_3}) + \mathrm{LiCHCl_2} \rightarrow (\mathrm{diphos})\mathrm{Pt}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CHCl_2}\end{matrix} + \mathrm{LiCl} \qquad (1)$$

(I)

In view of the instability of $\mathrm{LiCHCl_2}$ the reactions were carried out at temperatures of —100 to —120°C. Thus, reaction of $(\mathrm{diphos})\mathrm{PtCl}(\mathrm{CH_3})$ with $\mathrm{LiCHCl_2}$ yielded a product which, after work-up and isolation, proved to have the empirical formula $(\mathrm{diphos})\mathrm{PtC_2H_4Cl_2}$, which is consistent with that of compound I. However, further identification indicated the product not to have the structure of compound I: (a) decomposition of the product with hydrogen chloride yielded ethyl chloride, and (b) the NMR spectrum featured four overlapping quartets at δ 4.23 ppm with intensity 1 and a triplet at δ 1.62 ppm with intensity 3, which are in accordance with a $\mathrm{CHCl{-}CH_3}$ moiety.

The compound isolated must therefore be formulated as II.



$$(\mathrm{diphos})\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\ \mathrm{CHCl{-}CH_3}\end{matrix}$$

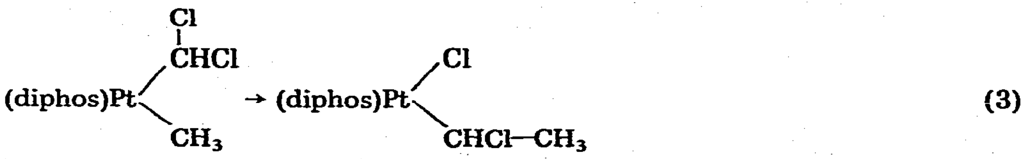
(II)

In order to show that the formation of II is not due to a direct insertion of “CHCl“ into the platinum—carbon bond according to eq. 2 we treated $\mathrm{L_2Pt(CH_3)_2}$

$\mathrm{LiCHCl_2} \rightarrow \mathrm{LiCl} + \bar{\mathrm{C}}\mathrm{HCl}$

$\bar{\mathrm{C}}\mathrm{HCl} + (\mathrm{diphos})\mathrm{PtCl}(\mathrm{CH_3}) \rightarrow \mathrm{II}$ (2)

in a similar manner with $\mathrm{LiCHCl_2}$ and found that the dimethylplatinum compound was recovered unchanged. While this is not complete proof, it seems highly unlikely that compound II is formed via a direct carbene transfer from the lithium carbenoid to platinum. Most probably, the following “carbene” shift occurs at —100°C or during warming to ambient temperature (eq. 3).

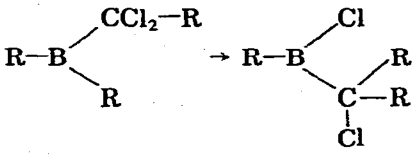


$$(\mathrm{diphos})\mathrm{Pt}\begin{matrix}\overset{\mathrm{Cl}}{\mathrm{CHCl}}\\ \mathrm{CH_3}\end{matrix} \rightarrow (\mathrm{diphos})\mathrm{Pt}\begin{matrix}\mathrm{Cl}\\ \mathrm{CHCl{-}CH_3}\end{matrix} \qquad (3)$$

(I) (II)

Alternatively, this reaction may be regarded as a reaction between an alkyl halide and an alkylmetal, which in general is not very fast (e.g. no reaction takes place between the platinum compounds and the chloroform solvent used). However, an intramolecular process would be expected to accelerate the reaction for entropy reasons. Owing to the symmetry of the diphos ligand we cannot distinguish between an insertion of CHCl into the $\mathrm{Pt{-}CH_3}$ bond and an interchange of the methyl and chloro group, with the CHCl remaining in the same position.

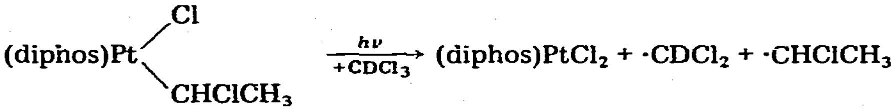
An indication of the type of mechanism operative in such reactions is found in the literature [3]; certain boron alkyls have been reported to exhibit the same carbenoid shift reaction; for instance, compounds of the formula $(RCCl_2)R_2B$, obtained from R_3B and a mercury—dichlorocarbenoid, rearrange according to eq. 4.



(4)

The product readily decomposes into olefin and $RBCl_2$. Such a decomposition reaction was also observed when $L_2PtCl(CHClCH_3)$ was heated at 170°C; ethylene was evolved and L_2PtCl_2 was formed.

Compound II was also identified by its behaviour under photolytic conditions. Upon irradiation (220—350 nm) in a deuteriochloroform solution in a ^1H NMR spectrometer it reacted to give platinum dichloride and the radicals $\cdot CDCl_2$, $\cdot CCl_3$, and $\cdot CHClCH_3$.



$$(\text{diphos})Pt(Cl)(CHClCH_3) \xrightarrow[+CDCl_3]{h\nu} (\text{diphos})PtCl_2 + \cdot CDCl_2 + \cdot CHClCH_3 \quad (5a)$$

(II)

$$.CHClCH_3 + \cdot CDCl_2 \longrightarrow CDCl_2CHClCH_3 \quad (5b)$$

$$\searrow CHClCH_2 + HDCCl_2 \quad (5c)$$

$$\cdot CHClCH_3 + CDCl_3 \longrightarrow DCHClCH_3 + \cdot CCl_3 \quad (5d)$$

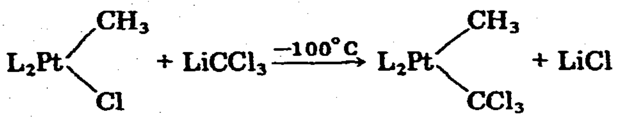
$$\cdot CHClCH_3 + \cdot CCl_3 \longrightarrow CCl_3CHClCH_3 \quad (5e)$$

$$\searrow CHClCH_2 + HCCl_3 \quad (5f)$$

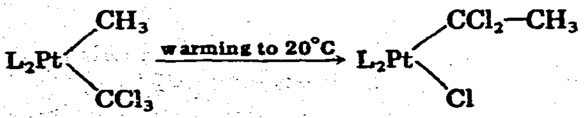
Strong polarizations were observed in the ^1H NMR spectrum for vinyl chloride, ethyl chloride-d_1, 1,1,2-trichloropropane-d_1 and 1,1,1,2-tetrachloropropane, and their signs were in accord with theory.

Many α-chloroalkylmetal compounds (e.g. those of Li and Hg [1a—d]) can be used as carbene precursors. To find out whether the same applies to $L_2PtCl(CHClCH_3)$ we heated it in cyclohexene for several hours, but no methylnorcarane or derivatives could be detected.

Trichloromethyl derivatives proved to give the same rearrangement:

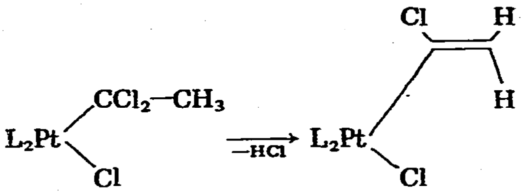


$$L_2Pt(CH_3)(Cl) + LiCCl_3 \xrightarrow{-100^\circ C} L_2Pt(CH_3)(CCl_3) + LiCl \quad (6)$$



$$L_2Pt(CH_3)(CCl_3) \xrightarrow{\text{warming to } 20^\circ C} L_2Pt(CCl_2{-}CH_3)(Cl) \quad (7)$$

The latter complex was not isolated, a vinyl complex being formed by hydrogen

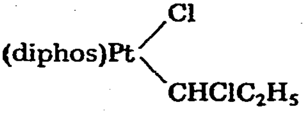


(8)

(III)

chloride elimination (eq. 8). Compound III was identified by its NMR spectrum and by the formation of vinyl chloride upon decomposition with hydrogen chloride. In contrast to most other organoplatinum compounds it is photochemically stable in chloroform (220—350 nm). This is probably due to the stability of the platinum—carbon bond in the vinyl derivative.

In a forthcoming paper [2] we report that ethylplatinum compounds proved to undergo very little if any carbene shift. We also treated $L_2PtCl(C_2H_5)$ with $LiCHCl_2$, and after work-up isolated compound IV.



(IV)

Hence the ethyl compound $(diphos)Pt(CHCl_2)(C_2H_5)$ does show the carbene shift, though a carbene shift reaction was not found during photolysis of $(diphos)Pt(C_2H_5)_2$ in $CHCl_3$ [2]. This indicates, as outlined in ref. 2, that in the photochemical reaction the carbene shift probably occurs in a platinum(III) compound.

Compound IV was identified by its NMR spectrum and the photolysis reaction. Assuming a scheme similar to reactions 5a—5f we tentatively assigned the photo-CIDNP to the following products: $CCl_3CHClCH_2CH_3$, $CDCl_2CHClCH_2CH_3$, $ClHC{=}C(H)CH_3$, $CHCl_3$, C_2H_5D and $CDCl_2CH_2CH_3$. The last two compounds stem from unreacted starting material, $L_2PtCl(C_2H_5)$, in the α-chloropropylplatinum compound.

Again, to make sure that there is no direct transfer of carbene from $LiCHCl_2$ into the platinum—carbon bond, we treated $(diphos)Pt(C_2H_5)_2$ with $LiCHCl_2$ under the same conditions used for the monochloro compound $(diphos)Pt(C_2H_5)$-Cl. The starting material was recovered unchanged.

Two palladium compounds were treated with $LiCHCl_2$, viz. $(diphos)Pd(CH_3)_2$ (V) and $(diphos)PdCl(CH_3)$ (VI). Compound V gave no reaction. Compound VI showed the same carbene shift as the platinum homologue, giving $(diphos)PdCl(CHClCH_3)$. The identification was made by the same methods.

Experimental

Synthesis of (diphos)PtCl(CHClCH$_3$). To a mixture of 6 ml of tetrahydrofuran, 2 ml of diethyl ether, 2 ml of light petroleum (40—60°C), and 17 μl

(0.255 mmol) of carefully purified dichloromethane, 1 ml of n-butyllithium (0.255 *M*) solution in hexane was slowly added [4]. After stirring for 15 min 0.180 g (0.28 mmol) of (diphos)PtCl(CH_3) was added. The mixture was kept at —110°C for 30 min and then allowed to warm to room temperature. The solvent mixture was removed by distillation in vacuo. The residue was extracted with 10 ml of benzene. The crystals recovered from the benzene solution were analysed and shown to be $L_2PtCl(CHClCH_3)$ by ^{1}H NMR and decomposition with HCl. The latter reaction was performed by bubbling HCl gas into the NMR sample in $CDCl_3$ at 0°C. Ethyl chloride was observed by ^{1}H NMR.

(Diphos)PtCl(CCl=CH$_2$*).* (Diphos)PtCl(CH_3) was added to a solution of $LiCCl_3$, prepared by the same procedure as $LiCHCl_2$ [4] but using $CHCl_3$ instead of CH_2Cl_2. The product obtained was identified as (diphos)PtCl(CCl=CH_2).

(Diphos)PdCl(CHClCH$_3$*)* was prepared in the same way as the platinum homologue.

(Diphos)PdCl(CHCl$_2$*)* was obtained from (diphos)$PdCl_2$ and $LiCHCl_2$ at —110°C.

(Diphos)PdCl(CH$_3$*)* was prepared as described for $L_2PtCl(CH_3)$ [2] from (diphos)$Pd(CH_3)_2$ and acetyl chloride in methanol.

All the compounds were obtained in almost quantitative yield.

^{1}*H NMR spectral data*

(Diphos)PtCl($CHClCH_3$); CH : 4.23 ppm; four overlapping quartets (*J*(H—H) 7 Hz, *J*(P—H) 3 and 10 Hz, *J*(Pt—H) uncertain (30 Hz?); CH_3: 1.62 ppm triplet (*J*(H—H) = *J*(P—H) 7 Hz, *J*(Pt—H) 36 Hz).

(Diphos)PtCl(CCl=CH_2). H *trans* to Pt: 5.75 ppm (*J*(Pt—H) 73.5 Hz, *J*(P—H) 14 Hz); H *cis* to Pt: 4.56 ppm (*J*(Pt—H) 27 Hz, *J*(P—H) 4.5 Hz).

(Diphos)PdCl($CHClCH_3$). CH: 4.17 ppm, four overlapping quartets (*J*(H—H) 7 Hz, *J*(P—H) 2.5 and 15 Hz); CH_3: 1.63 ppm doublet of doublets with two coinciding lines in the centre (*J*(H—H) 7 Hz, *J*(P—H) 3.5 and 10.5 Hz).

(Diphos)PdCl(CH_3). CH_3: 0.76 ppm, double doublet (*J*(P—H) 3.5 and 8 Hz).

(Diphos)PdCl($CHCl_3$); CH: 5.96 ppm (*J*(P—H average) 6 Hz).

(Diphos)PtCl($CHClCH_2CH_3$); CH: 4.05 ppm, multiplet; CH_2 1.50—2.00 ppm multiplet, uncertain; CH_3: 0.65 ppm, triplet (*J*(H—H) 7 Hz).

^{1}*H NMR photo-CIDNP spectral data [2]*

(Diphos)PtCl($CHClCH_3$) in $CDCl_3$. Emissions $CH_3CHCl\underline{CH}Cl_2$, $\underline{CH_2}{=}CHCl$, $CH_3\underline{CH}DCl$, $\underline{CH_3}CHClCDCl_2$, $\underline{CH_3}CHClCCl_3$, CH_3D (trace); enhanced absorptions $CH_2{=}\underline{CH}Cl$, $CH_3\underline{CH}ClCDCl_2$, $\underline{CH_3}CHDCl$.

(Diphos)PdCl($CHClCH_3$) in $CDCl_3$. Emissions $\underline{CH_2}{=}CHCl$, $\underline{CH_3}{-}CHClCDCl_2$, $\underline{CH_3}CHClCCl_3$, CH_3D; absorptions $CH_2{=}\underline{CH}Cl$, $CH_3\underline{CH}ClCCl_3$, $CH_3\underline{CH}ClCDCl_2$, $\underline{CH_3}CHDCl_2$.

References

1 (a) D. Seyferth and C.K. Haas, J. Organometal. Chem., 39 (1972) C41; (b) D. Seyferth and S.B. Andrews, J. Organometal. Chem., 30 (1970) 151; (c) G. Wittig and K. Schwarzenbach, Liebigs Ann. Chem., 650 (1961) 1; (d) G. Köbrich, Angew. Chem., 84 (1972) 557; (e) D.J. Holter and V.I. Sternberg, Chem. Abstr., 60 (1964) 5533.

2 P.W.N.M. van Leeuwen, C.F. Roobeek and R. Huis, J. Organometal. Chem., 142 (1977) 233.

3 D. Seyferth and B. Prokai, J. Amer. Chem. Soc., 88 (1966) 1834.

4 G. Köbrich and H. Trapp, Chem. Ber., 99 (1966) 670.