Journal of Organometallic Chemistry, 142 (1977) 233—241

PHOTODECOMPOSITION OF PLATINUM AND PALLADIUM ALKYLS: A CIDNP STUDY

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(Received July 19th, 1977)

Summary

Several alkyl-palladium and -platinum compounds of the general formulae L_2MR_2 and L_2MRX have been subjected to UV irradiation. A reaction occurs in chlorinated solvents such as chloroform to yield a metal chloride and a radical pair consisting of the alkyl stemming from the organometallic compound and a solvent-derived radical. The radical pair reaction is revealed by CIDNP. The decomposition products containing one more carbon atom than expected according to this mechanism can be accounted for by a novel type of rearrangement, viz. an intramolecular carbene migration. In hydrocarbon solvents alkylplatinums undergo very little reaction, but alkylpalladiums decompose homolytically.

Introduction

In recent years the thermal decomposition of alkylmetal compounds has received much attention and a variety of decomposition pathways have been described, such as β-elimination [1], homolytic scission of the carbon—metal bond [2], reductive elimination [3,4], and α-elimination [5]. It is generally claimed that in contrast, to thermal decomposition, photochemical decomposition leads to radical processes via homolysis. There is little evidence that such processes take place with alkyl-transition metal compounds, in spite of the recently marked increase in interest in both radical reactions and photolysis in this area [6]. Photolysis of alkyl-transition metal compounds would be expected to lead to unusual oxidation states and to unusual reactions.

Previously we reported on the photolysis of $(PPh_3)AuCH_3$ [7]. We have now subjected several alkyl-palladium and -platinum compounds to photolysis. In order to gain some insight into the mechanism of possible radical reactions we followed the reactions by proton magnetic resonance, which enabled us to observe chemically induced dynamic nuclear polarization [8] (CIDNP).

Results and discussion

Photolysis of methylplatinum compounds in $CDCl_3$

Irradiation of $(CH_3)_2PtL_2$ ($L_2 = PPh_3$ or diphos) in $CDCl_3$ with UV light (220—350 nm) causes a number of reactions, as is evident from the NMR spectra. The CIDNP polarized ^{1}H NMR spectrum obtained during photolysis is shown in Fig. 1; the enhanced absorptions and emissions together with their assignments are shown in Table 1. Some of the products, namely the main product CH_3D, CH_3CDCl_2 and CH_3CCl_3, and their polarizations have also been found in the photoreaction of CH_3AuPPh_3 in chloroform-*d*. It is known that this CIDNP stems from the radical pairs $\overline{\mathrm{CH_3\cdot + \cdot CDCl_2\ (or\ \cdot CCl_3)}}$ T or F formed according to reactions 1—4 *.

$$\mathrm{(CH_3)_2PtL_2 + CDCl_3 \xrightarrow{h\nu} (CH_3)PtL_2Cl + \overline{CH_3\cdot + \cdot CDCl_2}^{\,T}} \quad (1)$$

$$\mathrm{\widetilde{CH_3}\cdot + CDCl_3 \rightarrow \widetilde{CH_3D} + \cdot CCl_3} \quad (2)$$

$$\mathrm{\overline{\widetilde{CH_3}\cdot + \cdot CDCl_2}^{\,T,F} \rightarrow \widetilde{CH}_3CDCl_2} \quad (3)$$

$$\mathrm{\overline{\widetilde{CH_3}\cdot + \cdot CCl_3}^{\,F} \rightarrow \widetilde{CH}_3CCl_3} \quad (4)$$

The remaining products mentioned in Table 1 (chloroform, methylene chloride, ethyl chloride, vinyl chloride, tri- and tetrachloropropane) must come from a different reaction. The question arises as to how propane derivatives can be formed from methylplatinum and chloroform. The answer can be derived from the following observations:

(a) The formation of propane derivatives and vinyl chloride-d_1 indicates that a $\cdot$CDCl CH_3 radical is one part of the radical pair leading to polarization. According to the sign of the polarization [9] a T or F pair is involved:

$$\mathrm{\overline{\cdot CDCl_2\ (or\ \cdot CCl_3) + \cdot CDClCH_3}^{\,T\ or\ F}}$$

(b) The $\cdot$CDCl CH_3 radical is not generated via an interaction of methyl radicals and the chloroform solvent or from radicals derived from chloroform, since it would then also have been observed in many other reactions in chloroform which produce methyl radicals (such as the (photo) decomposition of acetyl peroxide, CH_3AuPPh_3, $(CH_3)_4Pb$), which is not the case. This suggests that the —$CDClCH_3$ moiety is formed at the platinum metal centre.

(c) We have found that initially two methyl groups must be attached to platinum in order to produce $\cdot$CDCl CH_3 radicals upon irradiation with UV light in $CDCl_3$; the monomethyl compound CH_3PtClL_2 gives no $\cdot CDClCH_3$. This means that in the first part of the reaction sequence one methyl group leaves the reacting complex.

(d) One can envisage that attack of $\cdot CDCl_2$ radicals at the platinum complex might ultimately lead to formation of propane derivatives. The main product,

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* The wavy line denotes polarization (only shown for H-containing species) and the bar denotes a radical pair [8]; T and F indicate the triplet and free encounter origins, respectively. We do not distinguish between F and T pairs because this would require suppresion of F-pair formation by radical scavengers, which would cause side reactions in our systems.

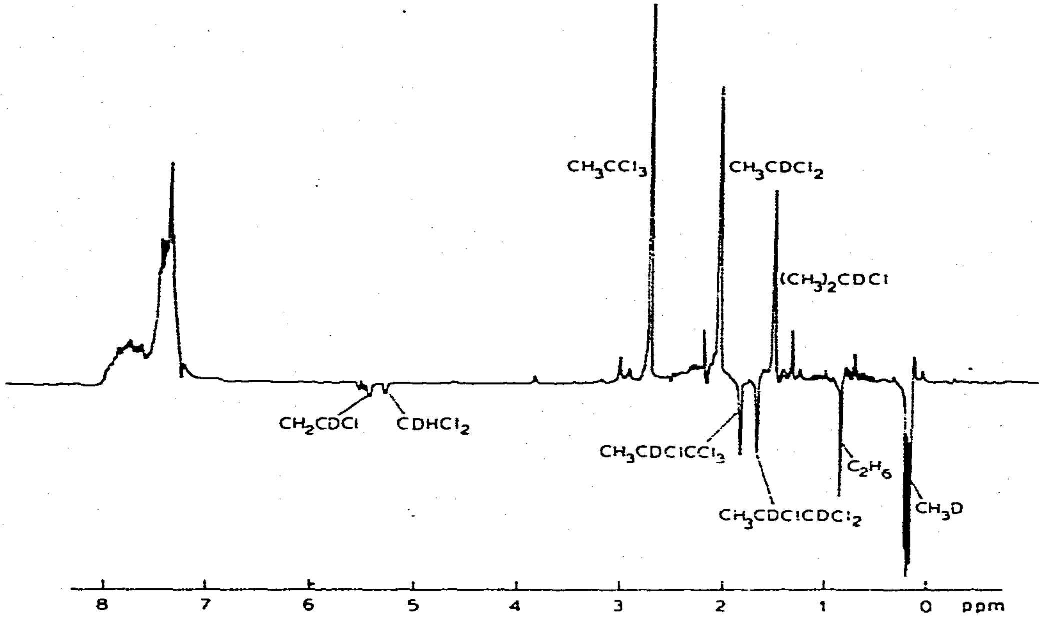


Fig. 1. The ^{1}H-NMR spectrum of (diphos)Pt(CH$_3$)$_2$ in CDCl$_3$ with UV irradiation as measured under standard conditions.

however, is CH$_3$D, and therefore $\cdot$CCl$_3$ radicals are formed in far larger amounts than $\cdot$CDCl$_2$ radicals. Since no products containing a 2,2-dichloro group are found, it is unlikely that $\cdot$CCl$_3$ radicals and, hence, $\cdot$CDCl$_2$ radicals would attack a platinum centre to any appreciable extent.

(e) During the photolysis CDCl$_2$CCl$_3$ is formed, although it does not show up in the ^{1}H NMR spectrum owing to the absence of protons. This product might be expected to react with (CH$_3$)$_2$PtL$_2$ under the prevailing conditions to give the

TABLE 1

CIDNP SPECTRAL DATA OF THE PHOTOLYSIS OF (CH$_3$)$_2$PtL$_2$ IN CDCl$_3$

Compound	Emission (E) or enhanced absorption (A)	δ (ppm)
CHCl$_3$	E	7.27
CH$_2$CDCl	E	5.40—5.50
CHDCl$_2$	E	5.28
Unknown, small	A	3.02
CH$_3$CCl$_3$	A	2.71
CH$_3$CDCl$_2$	A	2.06
CH$_3$CDClCCl$_3$	E	1.86
CH$_3$CDClCDCl$_2$	E	1.69
(CH$_3$)$_2$CDCl	A	1.52
CH$_3$CD$_2$Cl	A	1.47[a]
CH$_3$D	E	0.20

[a] Weak, questionable.

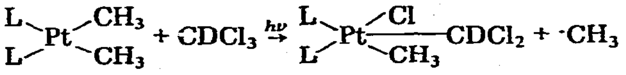
propane derivatives found. However, when $CHCl_2CCl_3$ was added to $(CH_3)_2PtL_2$ (molar ratio 3/2) in $CDCl_3$ prior to irradiation, no product having the composition $CH_3CHClCCl_3$ was observed during photolysis, whereas the deuterio analogue $CH_3CDClCCl_3$ was still present. Therefore there is no reaction between $CDCl_2CCl_3$ and $(CH_3)_2PtL_2$ which can explain the formation of the peculiar products.

(f) In an inert solvent such as C_6D_6 no fast homolysis is observed, which means that reactions 5 and 6 are unlikely to be the first steps in the photolysis:

$$(CH_3)_2PtL_2 \xrightarrow{h\nu} (CH_3)PtL_2 + {}^{\cdot}CH_3 \qquad (5)$$

$$(CH_3)PtL_2 + CDCl_3 \rightarrow (CH_3)(CDCl_2)PtClL_2 \qquad (6)$$

The following sequence of reactions (eq. 7—14) is in accord with all the above observations *:



$$L_2Pt(CH_3)_2 + CDCl_3 \xrightarrow{h\nu} L_2Pt(Cl)(CDCl_2)(CH_3) + {}^{\cdot}CH_3 \qquad (7)$$

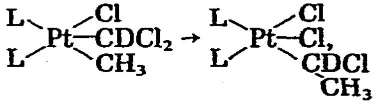
(I)

The first intermediate (I) is a trivalent platinum species. According to observation c one methyl group is lost in the first step, and there must be another methyl group left at the platinum. The intermediacy of a platinum(IV) species obtained by oxidative addition of $CDCl_3$ to platinum(II) with rapid loss of a methyl radical cannot be precluded as an alternative to reaction 7. Compound I either decomposes eq. 8 or reacts further eq. 9.

$$I \rightarrow (CH_3)PtClL_2 + {}^{\cdot}CDCl_2 \qquad (8)$$

The characteristic absorptions of $(CH_3)PtClL_2$ are found in the final ^1H NMR spectrum (*cis*-CH_3PtClL_2 when L_2 = diphos ** and *trans*-CH_3PtClL_2 when L = PPh_3).

The key reaction leading to the propane derivatives and vinyl chloride-d_1 is:



$$L_2Pt(Cl)(CDCl_2)(CH_3) \rightarrow L_2Pt(Cl)(Cl)(CDClCH_3) \qquad (9)$$

(I) (II)

This reaction can be envisaged as an intramolecular insertion of a carbene into a platinum—carbon bond with a chlorocarbene—platinum compound as the carbenoid. Subsequently, the α-chloroethyl radical leaves the platinum complex (eq. 10).

$$II \rightarrow L_2PtCl_2 + {}^{\cdot}CDClCH_3 \qquad (10)$$

Free encounters of radicals result in polarization of the products according to eq. 11 and 12.

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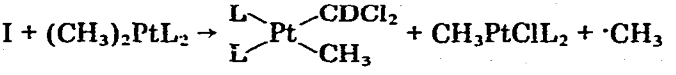
* We have no information about the nature of the photo-excitation.

** diphos = 1,2-bis(diphenylphosphino)ethane.

$$\overline{\cdot CCl_3 + \cdot CDClCH_3}^{\,F} \left\{ \begin{array}{ll} \rightarrow CCl_3CDClCH_3 & (11a) \\ \rightarrow HCCl_3 + CDCl{=}CH_2 & (11b) \end{array} \right.$$

$$\overline{\cdot CDCl_2 + \cdot CDClCH_3}^{\,F} \left\{ \begin{array}{ll} \rightarrow CDCl_2CDClCH_3 & (12a) \\ \rightarrow HCDCl_2 + CDCl{=}CH_2 & (12b) \end{array} \right.$$

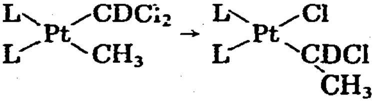
The possibility of slight modifications in reactions 9 and 10 cannot be entirely ruled out. Formation of a platinum(II) species from I via an abstraction of a chlorine radical by either an organic radical or dimethylplatinum is a reasonable alternative, e.g. eq. 13.



$$I + (CH_3)_2PtL_2 \rightarrow L_2Pt(CDCl_2)(CH_3) + CH_3PtClL_2 + \cdot CH_3 \tag{13}$$

(III)

Compound III could then give the carbene displacement:



$$L_2Pt(CDCl_2)(CH_3) \rightarrow L_2Pt(Cl)(CDClCH_3) \tag{14}$$

(III) (IV)

In connection with this, it is of interest that other experiments [9] have shown that reaction 14 does indeed occur with compound III. Loss of the α-chloroethyl radical from IV then requires a second light-induced reaction. This may also be the case for reaction 10.

In order to facilitate the identification of the products we also ran experiments in mixtures of C_6D_6 and $CHCl_3$. The same products (though non-deuterated) were observed, together with $CHCl_2CCl_3$ (enhanced absorption at 5.92 ppm) formed as a result of a free-encounter combination of the solvent-derived radicals. In $CHCl_3$ the ratio of the polarizations of tetrachloropropane and trichloropropane is higher than the ratio of the same polarizations in the deuterio analogues.

Irradiation of alkylplatinum compounds in chloroform

Platinum compounds containing alkyl groups other than methyl react with chloroform in very much the same way as many other alkylmetals. Except possibly for (disphos)Pt$(C_2H_5)_2$, no platinum carbenoid species is formed. For example, upon irradiation in $CDCl_3$, $(Et_3P)_2Pt(CH_2Ph)_2$ shows an enhanced absorption of $CDCl_2CH_2Ph$ at δ 3.47 ppm, an emission of dibenzyl at δ 2.90 ppm, several polarized signals in the aromatic region, and an emission of $CHDCl_2$ at δ 5.28 ppm. The reactions are identical with reactions 1 and 3, completed by eq. 15 as deuterium abstraction (eq. 2) cannot compete with combination reaction 15.

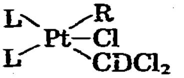
$$2\,\widetilde{PhCH_2}\cdot \rightarrow \widetilde{PhCH_2CH_2Ph} \tag{15}$$

Other compounds that have been studied are (disphos)Pt$(C_2H_5)_2$, $(PPh_3)_2$Pt$(n\text{-}C_4H_9)_2$ and $(PPh_3)_2$Pt$(n\text{-}C_8H_{17})_2$. In $CDCl_3$ the butyl and octyl compounds give the expected CIDNP spectra with emissions for chloroform and dichloromethane, emissions and absorptions for butene-1 and octene-1 respectively, enhanced absorptions for the β-protons in $—CH_2—CDCl_2$ and emissions for the γ-protons in the same compounds, together with the complex polarization for the alkanes formed. Pure net effects are found in accordance with reactions 1—4. The polarization of chloroform stems from reaction 16.

$$\overline{CH_3—CH_2—CH_2—CH_2\cdot + \cdot CCl_3}^{F} \rightarrow CH_3—CH_2—\widetilde{CH}=\widetilde{CH}_2 + CHCl_3 \qquad (16)$$

There is less overlap of the absorptions and emissions from the (disphos)Pt-$(C_2H_5)_2$ compound, and most of the peaks can be assigned to the products expected ($CHCl_3$, C_2H_4, $CDHCl_2$, $CH_3CH_2CCl_3$, $CH_3CH_2CDCl_2$, C_2H_5D). In addition, very weak polarizations due to $CH_3CH_2CDClCDCl_2$ and $CH_3CH_2CDClCCl_3$ are found, indicating that a carbenoid migration takes place to a correspondingly small extent.

The difference in reaction pathways between methylplatinum and other alkylplatinum derivatives can be rationalized as follows. The difference lies in the lifetime of the intermediate formed in the first step (eq. 7).



This intermediate is more stable towards decomposition when R is CH_3 (i.e. loss of $\cdot CH_3$ or $\cdot CDCl_2$ radical) than when R is another alkyl group. The loss of a $\cdot CDCl_2$ radical is expected to be only slightly influenced by replacement of methyl by ethyl, and therefore the relatively high bond strength of platinum—methyl with respect to platinum—ethyl must be one of the main factors contributing to the relatively long lifetime of the methyl intermediate. Provided that the carbene migration itself is not faster for the methyl than for the ethyl derivative (as would be expected), the slower homolysis of the methyl derivatives could well explain why the "growth" reaction is almost exclusively found for the methyl compounds.

Irradiation of alkylplatinum compounds in benzene

Irradiation of L_2PtR_2 ($L = PPh_3$, and R = benzyl, methyl) in C_6D_6 for 5 min gave no detectable reaction. However, irradiation of L_2PtR_2 will $R = C_2H_5$ gave rise to polarized signals for butane and ethane. Butane showed an A/E multiplet effect, which indicates that the radical pair is a triplet or a free-encounter one. The enhanced absorption for ethane is rather unusual since this so-called net effect [7] can only result from a pair of radicals with different *g*-values. No polarized ethene was observed, which precludes a reaction of the type of eq. 17.

$$R\cdot + \cdot C_2H_5 \rightarrow RH + C_2H_4 \qquad (17)$$

The enhanced absorption could be explained by reaction 18.

$$L_2Pt(C_2H_5)_2 \xrightarrow{h\nu} \overline{L_2Pt(C_2H_5)\cdot + \cdot C_2H_5} \qquad (18)$$

However, firm conclusions cannot be made about the origin of these enhanced absorptions, which may be caused by several other factors.

Irradiation of alkylpalladium compounds

Upon irradiation in $CDCl_3$ *cis*-$(Et_3P)_2Pd(CH_3)_2$ affords CIDNP spectra similar to those of the dimethylplatinum compounds, the polarized products being CH_3D, C_2H_6, CH_3CDCl_2, CH_3CCl_3, $CH_3CDClCDCl_2$ and $CH_3CDClCCl_3$. The polarizations of the latter two products are weak and the expected CH_2CDCl product is absent. We suggest that these phenomena can be explained in terms of reaction sequences similar to those observed with the platinum compounds.

Surprisingly, (diphos)Pd$(CH_3)_2$ reacts somewhat differently. The signals of tetrachloro- and trichloro-propane are extremely weak and several additional polarized signals are observed, viz. a strong absorption at δ 2.19 ppm, intermediate absorptions at 1.52 (D triplet) and 5.48 ppm, and small emissions at 2.52, 2.29 and 1.27 ppm. Furthermore CH_4 is formed (enhanced absorption or not polarized), which may point to a non-radical photodecomposition, and it is tempting to describe this as an analogue of the thermal decomposition of several dimethylmetal compounds (eq. 19) since the monomethyl derivative shows no

$$M(CH_3)_2 \rightarrow M \cdot CH_2 + CH_4 \qquad (19)$$

CH_4 formation, indicating that the proton stems from the second methyl group rather than from the phosphine ligand. The triplet at δ 1.52 ppm is assigned to $CH_3CDClCH_3$, a chain growth product from $CH_3 \cdot CDClCH_3$, which raises the question why so little of the more common chain-growth products ($CH_3CDClCDCl_2$ and $CH_3CDClCCl_3$) is formed. The enhanced absorption at δ 2.19 ppm is probably due to an addition of methyl radicals to the phenyl groups of the diphos ligand. The absorption at δ 5.48 ppm may be due to ethylene. The signs of the polarizations in this system are contradictory, however, and several reactions must be taking place simultaneously.

(Diphos)Pd(CH_3)Cl gives a straightforward photoreaction of type 1—4, which need not be discussed in detail. It is interesting to note that although several methylmetal compounds give the same reactions and radical pairs, the intensity ratios differ from one system to another.

Photolysis of $(Et_3P)_2Pd(CH_3)_2$ in C_6D_6 leads to CH_4 as the only observed product. A reaction of type 19 must be responsible. The NMR observations agree with the well-known fact that palladium alkyls are more prone to photolytic decomposition than platinum alkyls.

Thermal decomposition of $(Et_3P_2)Pd(CH_3)_2$ at 100°C is known [10] to give mainly ethane, and only small amounts of ethylene and methane, via a process which at the time was supposed to be a radical reaction. Thermal decomposition studied by NMR revealed no CIDNP to confirm this supposition. In the absence of experimental data the formation of C_2H_6 could be better explained as being due to a reductive elimination.

Experimental

Synthesis

The starting materials L_2PtCl_2, $L_2Pt(CH_3)_2$, $L_2Pt(C_2H_5)_2$, $L_2Pt(C_4H_9)_2$, $L_2Pt(C_8H_{17})_2$, $L_2Pt(CH_2Ph)_2$, where L = PPh_3 or L_2 = diphos = bis(1,2-diphenylphosphino)ethane were prepared according to literature procedures [11]. (Diphos)Pt(CH_3)Cl was prepared by dissolving (diphos)Pt$(CH_3)_2$ (1.0 mmol) under argon in 40 ml of dry benzene. Then 150 μl of CH_3OH was added, followed by 1.0 mmol of acetyl chloride. After 2 h stirring and standing overnight the crystals were filtered off (yield 92%). (Diphos)Pd$(CH_3)_2$ was prepared from the corresponding chloride and methyllithium. The CIDNP-NMR signal assigned to $CDCl{=}CH_2$ was compared to the NMR spectrum of an authentic sample of $CDCl{=}CH_2$ which confirmed the assignment. $CDCl{=}CH_2$ was prepared by treating $CHCl{=}CH_2$ with butyllithium at −110°C in pentane/diethyl ether/tetrahydrofuran, followed by treatment with CH_3OD. $CH_3CHClCHCl_2$ was prepared by careful chlorination of $CH_3CH{=}CHCl$ in CCl_4 at 0°C.

Measurements

^1H NMR measurements were run on a Bruker WH-90 NMR spectrometer in the Fourier transform mode. Small pulse angles ($<40°$) were used to preserve the multiplet effects in the CIDNP spectra. Photodecomposition with concomitant recording of the ^1H NMR spectra was performed with a Philips SP-1000 lamp using a $NiSO_4$water solution as a filter (220—350 nm). The light beam was focussed with two lenses and directed into the probe via a quartz light pipe (diameter 8 mm, length 30 cm). In a standard procedure the sample was irradiated for 45 sec while ten spectra were accumulated over the last 35 sec. In some cases the photoreactions and the CIDNP decay after the light had been switched off were followed by collecting the spectra separately on a disk using a program for T_1 measurements.

^{1}*H NMR spectra data*

The chemical shifts, measured in $CDCl_3$, are given in δ, ppm downfield from tetramethylsilane. The compounds are listed in order of increasing number of carbon atoms. CH_3D, 0.20; CH_2Cl_2, 5.28; C_2H_6, 0.86; $CDCl{=}CH_2$, 5.40 and 5.48 multiplets, J(H—D *trans*) 2 Hz, J(H—D *cis*) 1 Hz, J(H—H) ≈ 2 Hz; CH_3CH_2Cl, 1.49 and 3.56; CH_3CHCl_2, 2.06 and 5.85; CH_3CCl_3, 2.72; $CH_2ClCHCl_2$, 3.97 and 5.74; $CHCl_2CCl_3$, 6.09; $CH_3CH_2CDCl_2$, 1.10 and 2.19; $CH_3CH_2CCl_3$, 1.28 and 2.70; $CH_3CHClCHCl_2$, 1.69, 4.34 and 5.85; $(CH_3)_2CCl_2$, 2.17; $(CH_3)_2CDCl$, 1.52; $CH_3CHClCCl_3$, 1.85 and 4.61; $CH_3CCl_2CCl_3$, 2.51; $C_6H_5CH_2CDCl_2$, 3.47.

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

$L_2Pt(CH_3)_2$ in $CDCl_3$, see Table 1 and Figure 1.

(Diphos)Pt $(C_2H_5)_2$ in $CDCl_3$: emissions $CHCl_3$, C_2H_4, $CHDCl_2$, $\widetilde{CH_3}CH_2CDCl_2$, $\widetilde{CH_3}CH_2CCl_3$, $CH_3\widetilde{CH_2}D$; absorptions $CH_3\widetilde{CH_2}CDCl_2$, $CH_3\widetilde{CH_2}CCl_3$, $\widetilde{CH_3}CH_2D$; many smaller polarized signals in the aliphatic and chloroaliphatic region tentatively assigned to "carbenoid" insertion products.

$(PPh_3)_2Pt$ $(C_2H_5)_2$ in C_6D_6: butane A/E multiplet effect, ethane absorption. (diphos) $PtCl(C_2H_5)$ in $CDCl_3$: emissions, $CHCl_3$, C_2H_4, $CHDCl_2$, $CH_3\widetilde{CH_2}Cl$ (weak), $\widetilde{CH_3}CH_2CDCl_2$, $\widetilde{CH_3}CH_2CCl_3$; absorptions, $CH_3\widetilde{CH_2}CDCl_2$, $CH_3\widetilde{CH_2}CDCl_2$, $\widetilde{CH_3}CH_2Cl$ (weak), C_2H_5D.

(Diphos)$PtCl(CH_3)$ and (diphos)$PdCl(CH_3)$ in $CDCl_3$: emissions C_2H_6, CH_3D; absorptions CH_3CCl_3 and CH_3CDCl_2.

$(Et_3P)_2Pt(CH_2Ph)_2$ in $CDCl_3$: absorption $PhCH_2CDCl_2$; emissions $CHDCl_2$ and $PhCH_2CH_2Ph$.

$(Ph_3P)_2Pt(n\text{-}C_4H_9)_2$ in $CDCl_3$: emissions $CHCl_3$, butene, $CHDCl_2$, butyl-$CDCl_2$, butane; absorptions butene, butyl-$CDCl_2$, butane, butyl-CCl_3.

$(Ph_3P)_2Pt(n\text{-}C_8H_{17})_2$ in $CDCl_3$: same as preceding compound with butyl = octyl.

(Diphos)$Pd(CH_3)_2$ in $CDCl_3$: (assignment tentative) absorptions $(CH_3)_2CDCl$, C_2H_4, 2.19 (unknown); CH_4; emissions 2.52, 2.29 and 1.27 (unknown).

References

1 G.M. Whitesides, J.F. Gaasch and E.R. Stedronsky, J. Amer. Chem. Soc., 94 (1972) 5258.
2 G.M. Whitesides, E.J. Panek and E.R. Stedronsky, J. Amer. Chem. Soc., 94 (1972) 232.
3 M.F. Semmelhack and L. Ryono, Tetrahedron Lett., (1973) 2967.
4 M.P. Brown, R.J. Puddephatt and C.E.E. Upton, J. Chem. Soc. Dalton, (1974) 2457.
5 F.S. D'yachkovskii and N.E. Khrushch, Zh. Obschch. Khim., 41 (1971) 1779.
6 A. Hudson, M.F. Lappert, P.W. Lednor and B.K. Nicholson, J. Chem. Soc. Chem. Commun., (1974) 966.
7 P.W.N.M. van Leeuwen, R. Kaptein, R. Huis and C.F. Roobeek, J. Organometal. Chem., 104 (1976) C44.
8 A.R. Lepley and G.L. Closs (Eds.), Chemically Induced Magnetic Polarization, John Wiley, New York, 1973.
9 P.W.N.M. van Leeuwen, C.F. Roobeek and R. Huis, J. Organometal. Chem., 142 (1977) 243.
10 G. Calvin and G.E. Coates, J. Chem. Soc., (1960) 2008.
11 J. Chatt and B.L. Shaw, J. Chem. Soc., (1959) 705.