

PHOTODECOMPOSITION OF PLATINUM AND PALLADIUM ALKYLs: A CIDNP STUDY

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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

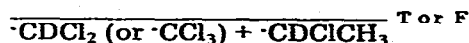
Photolysis of methylplatinum compounds in CDCl₃

Irradiation of (CH₃)₂PtL₂ (L₂ = PPh₃ or diphos) in CDCl₃ with UV light (220–350 nm) causes a number of reactions, as is evident from the NMR spectra. The CIDNP polarized ¹H 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 CH₃D, CH₃CDCl₂ and CH₃CCl₃, and their polarizations have also been found in the photoreaction of CH₃AuPPh₃ in chloroform-*d*. It is known that this CIDNP stems from the radical pairs $\overline{\text{CH}_3\cdot} + \cdot\text{CDCl}_2$ (or $\cdot\text{CCl}_3$) T or F formed according to reactions 1–4*.



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*, indicates that a $\cdot\text{CDClCH}_3$ 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:



(b) The $\cdot\text{CDClCH}_3$ 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, CH₃AuPPh₃, (CH₃)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 $\cdot\text{CDClCH}_3$ radicals upon irradiation with UV light in CDCl₃; the monomethyl compound CH₃PtClL₂ gives no $\cdot\text{CDClCH}_3$. 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 $\cdot\text{CDCl}_2$ radicals at the platinum complex might ultimately lead to formation of propane derivatives. The main product,

* 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 suppression of F-pair formation by radical scavengers, which would cause side reactions in our systems.

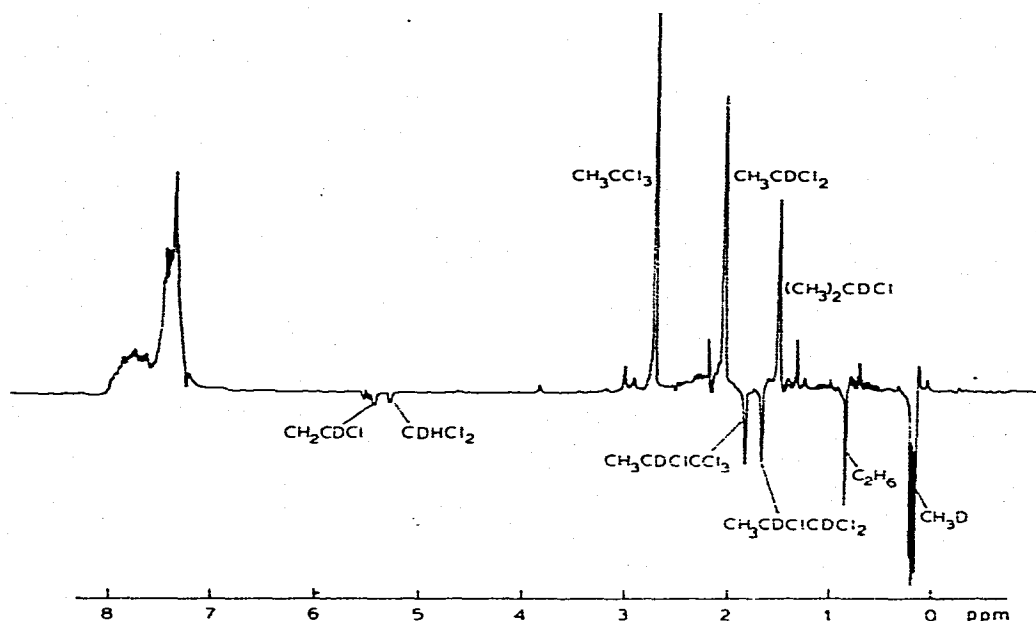


Fig. 1. The ^1H -NMR spectrum of $(\text{diphos})\text{Pt}(\text{CH}_3)_2$ in CDCl_3 with UV irradiation as measured under standard conditions.

however, is CH_3D , and therefore $\cdot\text{CCl}_3$ radicals are formed in far larger amounts than $\cdot\text{CDCl}_2$ radicals. Since no products containing a 2,2-dichloro group are found, it is unlikely that $\cdot\text{CCl}_3$ radicals and, hence, $\cdot\text{CDCl}_2$ radicals would attack a platinum centre to any appreciable extent.

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

TABLE 1
CIDNP SPECTRAL DATA OF THE PHOTOLYSIS OF $(\text{CH}_3)_2\text{PtL}_2$ IN CDCl_3

Compound	Emission (E) or enhanced absorption (A)	δ (ppm)
CHCl_3	E	7.27
CH_2CDCl	E	5.40–5.50
CHDCl_2	E	5.28
Unknown, small	A	3.02
CH_3CCl_3	A	2.71
CH_3CDCl_2	A	2.06
$\text{CH}_3\text{CDClCCl}_3$	E	1.86
$\text{CH}_3\text{CDClCDCl}_2$	E	1.69
$(\text{CH}_3)_2\text{CDCl}$	A	1.52
$\text{CH}_3\text{CD}_2\text{Cl}$	A	1.47 ^a
CH_3D	E	0.20

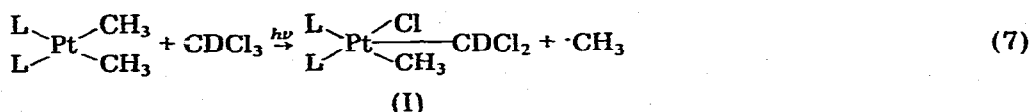
^a Weak, questionable.

propane derivatives found. However, when $\text{CHCl}_2\text{CCl}_3$ was added to $(\text{CH}_3)_2\text{PtL}_2$ (molar ratio 3/2) in CDCl_3 prior to irradiation, no product having the composition $\text{CH}_3\text{CHClCCl}_3$ was observed during photolysis, whereas the deuterio analogue $\text{CH}_3\text{CDClCCl}_3$ was still present. Therefore there is no reaction between $\text{CDCl}_2\text{CCl}_3$ and $(\text{CH}_3)_2\text{PtL}_2$ 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:



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



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.



The characteristic absorptions of $(\text{CH}_3)\text{PtClL}_2$ are found in the final ^1H NMR spectrum (*cis*- $\text{CH}_3\text{PtClL}_2$ when $\text{L}_2 = \text{diphos}$ ** and *trans*- $\text{CH}_3\text{PtClL}_2$ when $\text{L} = \text{PPh}_3$).

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



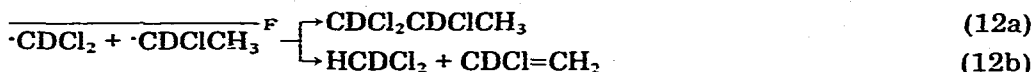
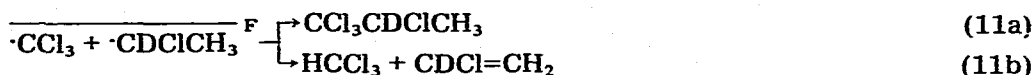
This reaction can be envisaged as an intramolecular insertion of a carbene into a platinum–carbon bond with a chlorocarbene–platinum compound as the carbenoid. Subsequently, the α -chloroethyl radical leaves the platinum complex (eq. 10).



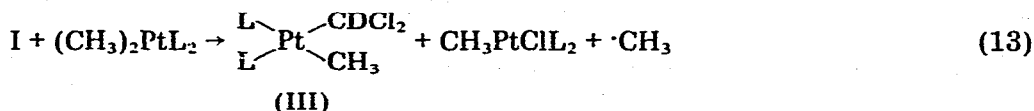
Free encounters of radicals result in polarization of the products according to eq. 11 and 12.

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

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



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.



Compound III could then give the carbene displacement:



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 $\text{CHCl}_2\text{CCl}_3$ (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.

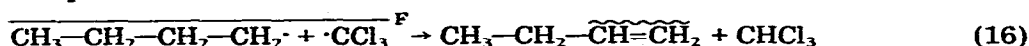
Irradiation of alkylplatinum compounds in chloroform

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) $\text{Pt}(\text{C}_2\text{H}_5)_2$, no platinum carbenoid species is formed. For example, upon irradiation in CDCl_3 , $(\text{Et}_3\text{P})_2\text{Pt}(\text{CH}_2\text{Ph})_2$ shows an enhanced absorption of $\text{CDCl}_2\text{CH}_2\text{Ph}$ 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.



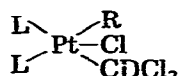
Other compounds that have been studied are (disphos) $\text{Pt}(\text{C}_2\text{H}_5)_2$, $(\text{PPh}_3)_2\text{Pt}(\text{n-C}_4\text{H}_9)_2$ and $(\text{PPh}_3)_2\text{Pt}(\text{n-C}_8\text{H}_{17})_2$. In CDCl_3 the butyl and octyl compounds give the expected CIDNP spectra with emissions for chloroform and dichloromethane, emissions and absorptions for butene-1 and octene-1 respectively, en-

hanced absorptions for the β -protons in $-\text{CH}_2-\text{CDCl}_2$ 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.



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 , $\text{CH}_3\text{CH}_2\text{CCl}_3$, $\text{CH}_3\text{CH}_2\text{CDCl}_2$, $\text{C}_2\text{H}_5\text{D}$). In addition, very weak polarizations due to $\text{CH}_3\text{CH}_2\text{CDClCDCl}_2$ and $\text{CH}_3\text{CH}_2\text{CDClCCl}_3$ 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 $\cdot\text{CH}_3$ or $\cdot\text{CDCl}_2$ radical) than when R is another alkyl group. The loss of a $\cdot\text{CDCl}_2$ 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 with 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.



The enhanced absorption could be explained by reaction 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 , $\text{CH}_3\text{CDClCDCl}_2$ and $\text{CH}_3\text{CDClCCl}_3$. 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, $(\text{diphos})\text{Pd}(\text{CH}_3)_2$ 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

$$\text{M}(\text{CH}_3)_2 \rightarrow \text{M} \cdot \text{CH}_2 + \text{CH}_4 \quad (19)$$

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 $\text{CH}_3\text{CDClCH}_3$, a chain growth product from $\text{CH}_3 \cdot \text{CDClCH}_3$, which raises the question why so little of the more common chain-growth products ($\text{CH}_3\text{CDClCDCl}_2$ and $\text{CH}_3\text{CDClCCl}_3$) 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.

$(\text{Diphos})\text{Pd}(\text{CH}_3)\text{Cl}$ 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 $(\text{Et}_3\text{P})_2\text{Pd}(\text{CH}_3)_2$ 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 $(\text{Et}_3\text{P})_2\text{Pd}(\text{CH}_3)_2$ 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 , $\text{L}_2\text{Pt}(\text{CH}_3)_2$, $\text{L}_2\text{Pt}(\text{C}_2\text{H}_5)_2$, $\text{L}_2\text{Pt}(\text{C}_4\text{H}_9)_2$, $\text{L}_2\text{Pt}(\text{C}_6\text{H}_{11})_2$, $\text{L}_2\text{Pt}(\text{CH}_2\text{Ph})_2$, where $\text{L} = \text{PPh}_3$ or $\text{L}_2 = \text{diphos} = \text{bis}(1,2\text{-diphenylphosphino})\text{ethane}$ were prepared according to literature procedures [11]. $(\text{Diphos})\text{Pt}(\text{CH}_3)\text{Cl}$ was prepared by dissolving $(\text{diphos})\text{Pt}(\text{CH}_3)_2$ (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(CH₃)₂ was prepared from the corresponding chloride and methyllithium. The CIDNP-NMR signal assigned to CDCl=CH₂ was compared to the NMR spectrum of an authentic sample of CDCl=CH₂ which confirmed the assignment. CDCl=CH₂ was prepared by treating CHCl=CH₂ with butyllithium at -110°C in pentane/diethyl ether/tetrahydrofuran, followed by treatment with CH₃OD. CH₃CHClCHCl₂ was prepared by careful chlorination of CH₃CH=CHCl in CCl₄ 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 NiSO₄ 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 T₁ measurements.

¹H NMR spectra data

The chemical shifts, measured in CDCl₃, are given in δ, ppm downfield from tetramethylsilane. The compounds are listed in order of increasing number of carbon atoms. CH₃D, 0.20; CH₂Cl₂, 5.28; C₂H₆, 0.86; CDCl=CH₂, 5.40 and 5.48 multiplets, *J*(H–D *trans*) 2 Hz, *J*(H–D *cis*) 1 Hz, *J*(H–H) ≈ 2 Hz; CH₃CH₂Cl, 1.49 and 3.56; CH₃CHCl₂, 2.06 and 5.85; CH₃CCl₃, 2.72; CH₂ClCHCl₂, 3.97 and 5.74; CHCl₂CCl₃, 6.09; CH₃CH₂CDCl₂, 1.10 and 2.19; CH₃CH₂CCl₃, 1.28 and 2.70; CH₃CHClCHCl₂, 1.69, 4.34 and 5.85; (CH₃)₂CCl₂, 2.17; (CH₃)₂CDCl, 1.52; CH₃CHClCCl₃, 1.85 and 4.61; CH₃CCl₂CCl₃, 2.51; C₆H₅CH₂CDCl₂, 3.47.

¹H NMR photo-CIDNP spectral data

L₂Pt(CH₃)₂ in CDCl₃, see Table 1 and Figure 1.

(Diphos)Pt(C₂H₅)₂ in CDCl₃: emissions CHCl₃, C₂H₄, CHDCl₂, $\widetilde{\text{CH}}_3\text{CH}_2\text{CDCl}_2$, $\widetilde{\text{CH}}_3\text{CH}_2\text{CCl}_3$, CH₃ $\widetilde{\text{CH}}_2\text{D}$; absorptions CH₃ $\widetilde{\text{CH}}_2\text{CDCl}_2$, CH₃ $\widetilde{\text{CH}}_2\text{CCl}_3$, $\widetilde{\text{CH}}_3\text{CH}_2\text{D}$; many smaller polarized signals in the aliphatic and chloroaliphatic region tentatively assigned to "carbenoid" insertion products.

(PPh₃)₂Pt(C₂H₅)₂ in C₆D₆: butane A/E multiplet effect, ethane absorption. (diphos)PtCl(C₂H₅) in CDCl₃: emissions, CHCl₃, C₂H₄, CHDCl₂, CH₃ $\widetilde{\text{CH}}_2\text{Cl}$ (weak), $\widetilde{\text{CH}}_3\text{CH}_2\text{CDCl}_2$, $\widetilde{\text{CH}}_3\text{CH}_2\text{CCl}_3$; absorptions, CH₃ $\widetilde{\text{CH}}_2\text{CDCl}_2$, CH₃ $\widetilde{\text{CH}}_2\text{CDCl}_2$, $\widetilde{\text{CH}}_3\text{CH}_2\text{Cl}$ (weak), C₂H₅D.

(Diphos)PtCl(CH₃) and (diphos)PdCl(CH₃) in CDCl₃: emissions C₂H₆, CH₃D; absorptions CH₃CCl₃ and CH₃CDCl₂.

(Et₃P)₂Pt(CH₂Ph)₂ in CDCl₃: absorption PhCH₂CDCl₂; emissions CHDCl₂ and PhCH₂CH₂Ph.

(Ph₃P)₂Pt(n-C₄H₉)₂ in CDCl₃: emissions CHCl₃, butene, CHDCl₂, butyl-CDCl₂, butane; absorptions butene, butyl-CDCl₂, butane, butyl-CCl₃.

$(\text{Ph}_3\text{P})_2\text{Pt}(\text{n-C}_8\text{H}_{17})_2$ in CDCl_3 : same as preceding compound with butyl = octyl.
 $(\text{Diphos})\text{Pd}(\text{CH}_3)_2$ in CDCl_3 : (assignment tentative) absorptions $(\text{CH}_3)_2\text{CDCl}$, C_2H_4 , 2.19 (unknown); CH_4 ; emissions 2.52, 2.29 and 1.27 (unknown).

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