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ORIGINAL PAPER

An NMR study on the reaction of [(κ^2-P,N)-$Ph_2PCH_2CH_2NMe_2$]$PtMe_2$ with activated chlorocarbons: C–Cl and C–C activation, followed by C–N cleavage of the phosphinoalkylamine ligand and formation of an ylide complex

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Abstract Reaction of [(κ^2-P,N)-$Ph_2PCH_2CH_2NMe_2$]$PtMe_2$ with either ethyl chloroacetate or benzyl chloride results in complex reaction mixtures, which were investigated by a combination of NMR techniques. The reactions are initiated by oxidative addition of either the C–Cl bond or of the C–CH_2Cl bond, respectively. The latter is followed by a rearrangement of the intermediate Pt(IV) complex with concomitant C–N bond cleavage of the phosphinoalkylamine ligand and formation of the ylide complexes Pt[CH_2=PPh_2(vinyl)](NMe_2R)Me_2 (R = COOEt or Ph).

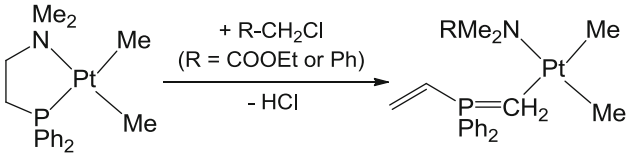
Keywords Platinum complexes · Ylide complexes · Phosphinoalkylamine ligands · C–Cl activation · C–C activation

Introduction

We have previously pointed out that the reactivity of Pt(II) complexes towards organosilanes ([1] and references cited therein) or chlorocarbons [2, 3] is greatly enhanced when heterofunctional chelating ligands R_2N-R′-PPh_2 [4–6] are employed. It was shown, inter alia, that the complex (P∩N)$PtMe_2$ (**1**, P∩N = (κ^2-P,N)-$Ph_2PCH_2CH_2NMe_2$) reacts with CH_xCl_{4-x} by initial oxidative addition of the C–Cl bond (for selected examples of (non-activated) C–Cl bond activation by Pt complexes see Refs. [7–9]). The complexes (P∩N)Pt(Me)Cl (**2**), (P∩N)$Pt(Me)_3Cl$ (**3**) and (P∩N)Pt(CCl=CH_2)Cl were isolated from the reaction with CCl_4 (Fig. 1). The vinyl complex is formed by oxidative addition of CCl_4, followed by MeCl elimination and rearrangement of the thus obtained complex (P∩N)Pt(Me)CCl_3 to (P∩N)Pt(CCl_2Me)Cl, from which HCl is eliminated. Oxidative addition of the eliminated MeCl to **1** gives complex **3**, whereas complex **2** results from addition of HCl to **1** followed by CH_4 elimination or by ethane elimination from **3** (Fig. 1). It was found that reactivity towards **1** decreased in the order $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$. The mechanism of these reactions was also investigated by density functional theory (DFT) calculations [10].

These reactions prompted us to investigate the reactions of compounds with activated C–Cl bonds, such as ethyl chloroacetate or benzyl chloride. These chlorides were chosen because β-elimination is not possible once C–Cl oxidative addition has occurred. The results reported in this article show that apart from the reactions leading to **1**–**3**, a new reaction occurs (Scheme 1) which involves cleavage of the P∩N ligand.

Scheme 1



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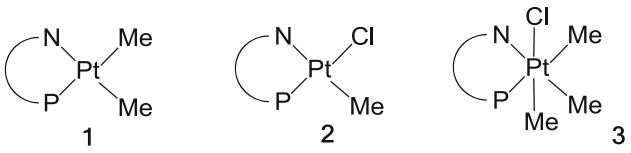


Fig. 1 Complexes **1**–**3**

Results and discussion

The reactions of **1** with ethyl chloroacetate or benzyl chloride at 70 °C in a 1:1 molar ratio were relatively slow. With benzyl chloride, only about 10 % of **1** was consumed after 10 days at 70 °C, whereas the reaction with ethyl chloroacetate was finished after 3 days at the same temperature. Reaction was faster when an excess of the chloride was employed; this did not influence the product distribution. For example, only 10 % of **1** was consumed after 10 days in the reaction with one molar equivalent of benzyl chloride, whereas reaction with a 15-fold excess of benzyl chloride was finished after 1 day (disappearance of the NMR signals of **1**).

When monitoring the reaction by NMR spectroscopy it was observed that a variety of intermediates were formed. Because of the slow reaction, it was possible to identify these intermediates by a combination of various NMR techniques. To this end the reactions were carried out in C_6D_6, and NMR spectra of the reaction mixture were recorded at regular intervals. No attempts were made to isolate the products. Apart from the organic by-products, the outcome of the reactions with ethyl chloroacetate or benzyl chloride was very similar, indicating that the same sequence of reactions takes place. In the following, the NMR experiments with ethyl chloroacetate will be discussed in detail, followed by a brief section on the benzyl chloride experiments. Identification of the intermediates, as discussed in the following, allowed the likely mechanism of the overall reaction to be deduced as will be outlined in the "Conclusions" section.

^{1}H NMR investigations

The main metal-containing product was complex **2**. In the 1:1 reaction with ethyl chloroacetate, ethyl acetate was identified as an organic product after complete consumption of complex **1** (hydrodehalogenation). Neither the methylation product ethyl propionate nor dehalogenative coupling product diethyl succinate was observed by either NMR or GC/MS investigations. The proportion of ethyl acetate (molar ratio of 1:8, as calculated from the integrated signals in the ^{1}H NMR spectrum), however, was too low relative to complex **2**. Closer examination of the ^{1}H NMR spectra revealed two additional features:

1. A singlet at 0.16 ppm was assigned to methane. The only reaction that could yield methane is the reaction of a methyl complex (P∩N)Pt(Me)Z (any group Z) with HCl and concomitant formation of (P∩N)Pt(Cl)Z. The presence of HCl contaminations in the starting compounds can be ruled out, because of the high proportion of the protonated products and the fact that they are only slowly formed. A control experiment carried out between complex **1** and HCl showed that **1** is converted to **2** within seconds even at room temperature. The possible mechanism leading to HCl formation will be elucidated later in the article.
2. Two groups of signals were observed in the olefinic region of the spectra (Fig. 2). Group 1 and 3 represent two protons (according to the integration values) which couple with each other. The signal groups 3 and 4 in Fig. 2 consisted of two doublets of doublets indicative of a vinylic CH group. The phosphorus-decoupled ^{1}H NMR spectrum showed that the additional splitting of the signals is due to the phosphorus atom of the P∩N ligand. In a P/H-HMBC experiment, the vinylic protons correlate with a signal at 21.6 ppm in the ^{31}P NMR spectrum as well as with two signals in the aromatic region of the ^{1}H NMR spectrum. The ^{31}P signal also correlates with two Pt–Me groups.

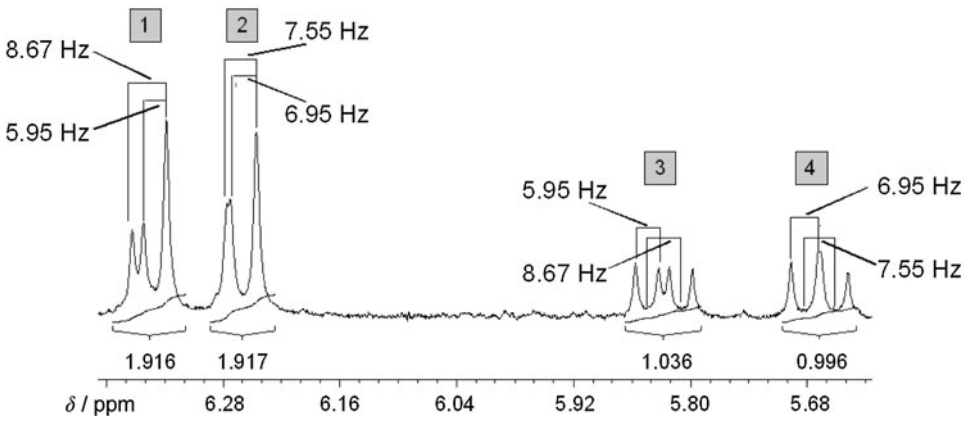


Fig. 2 Vinylic region of the 500 MHz ^{1}H NMR spectrum of the reaction solution between **1** and ethyl chloroacetate

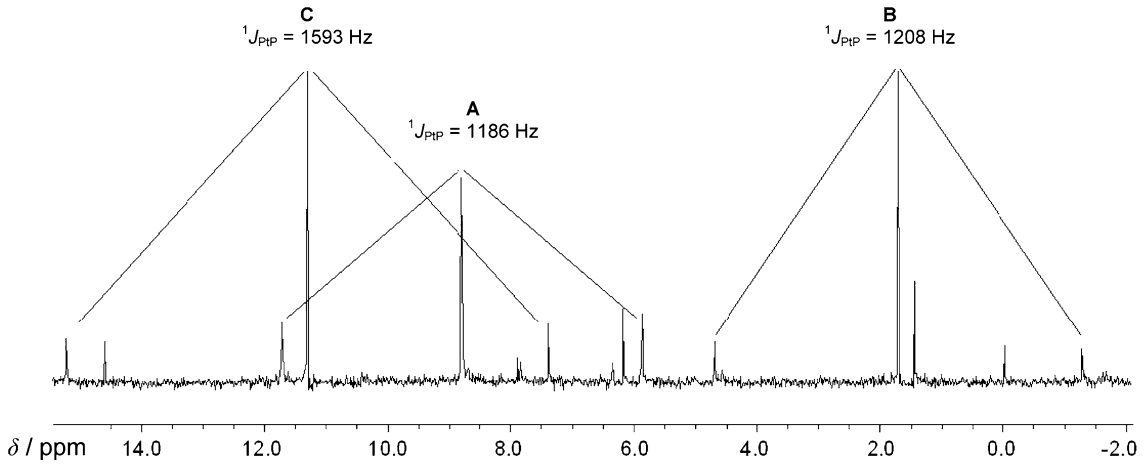


Fig. 3 ^{31}P NMR signals of octahedral Pt complexes formed by reaction of **1** with ethyl chloroacetate

^{31}P NMR investigations

To gain deeper insight in the reactions taking place another experiment with two equivalents of ethyl chloroacetate was carried out. The mixture was only heated to 70 °C for 1 h to investigate the reaction at an early stage, where the ^{31}P NMR signals of the different Pt complex intermediates can be observed. These signals can be divided into three groups, which will be discussed separately in the following: the region of 0–12 ppm typical of octahedral complexes, the region of 26–40 ppm typical of square planar complexes and the peak at 21.2 ppm. The last of these is the only peak which is also observed at the end of the reaction.

Octahedral complexes

The ^{31}P NMR spectrum showed three signals with platinum satellites in the region of octahedral Pt complexes (0–12 ppm, complexes A, B and C, Fig. 3).

Complex A is **3**, formed by oxidative addition of CH_3Cl to **1**, as previously reported [2]. P/H-HMBC measurement showed that the ^{31}P NMR signals of complex B couple with protons at 0.41 and 1.68 ppm. According to an APT NMR measurement, the two ligands of complex B are CH_3 groups. The chemical shift indicated that the signal at 0.41 ppm is a CH_3 group out of the P–Pt–N plane. The peak at 1.68 ppm has a coupling constant $^3J_{PtH} = 73$ Hz, typical for a CH_3 ligand in the *trans* position to the nitrogen of the P,N ligand (as in **3**). The corresponding ^{31}P NMR signal is shifted upfield relative to complex **3**; this is typical for replacing the ligand *trans* to phosphorus by a group with lower *trans* influence [11]. Since there is obviously no organic ligand in this position, this ligand could be chlorine, which has a very weak *trans* influence [12]. Therefore, complex B appears to be (P∩N)$PtMe_2Cl_2$ (**4**), formed by reaction of **3** with HCl (Fig. 4).

Complex C is visible in the two-dimensional NMR spectrum (Fig. 5) at $\delta_{Pt} = -1{,}410$ ppm. P/H-HMBC measurement showed that the ^{31}P NMR signal of complex C couples with proton signals in the ^{1}H NMR spectrum at 0.53 and 2.04 ppm and another signal at 2.98 ppm. The resonance at 0.53 ppm apparently belongs to a CH_3 group out of the P–Pt–N plane; the other signal at 2.04 ppm has a Pt–P coupling constant of $^3J_{PtH} = 70$ Hz and is therefore in the *trans* position to the nitrogen of the P,N ligand. The peak at 2.98 ppm was assigned to a CH_2 group. The ligand in the *trans* position to the phosphorus can definitely not be chlorine, because this would shift the ^{31}Pt signal upfield relative to that of complex **3**. Also J_{PtP} of 1,593 Hz is remarkably high compared to J_{PtP} of 1,208 Hz in **4**, where the chlorine is located *trans* to the phosphorus. A possible explanation for these unusual observations could be that the H_2ClC–COOEt bond was activated, yielding complex **5**. This interpretation was also supported by a C/H-HMBC measurement, where no coupling was observed between the protons of the CH_2Cl ligand and the ethyl CH_2 carbon of the COOEt group (this coupling is observed in ethyl chloroacetate). Oxidative addition of a C_{CO}–C bond to a Rh centre was, for example, described by Suggs and Jun [13].

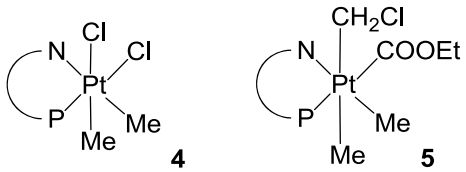
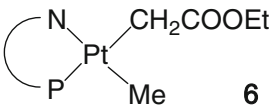


Fig. 4 Complexes **4** and **5**

Square-planar complexes

Three compounds were observed in the range of planar Pt(II) complexes in the ^{31}P NMR spectrum (Fig. 6), viz. the known complexes **1** and **2** and a new complex **6**.



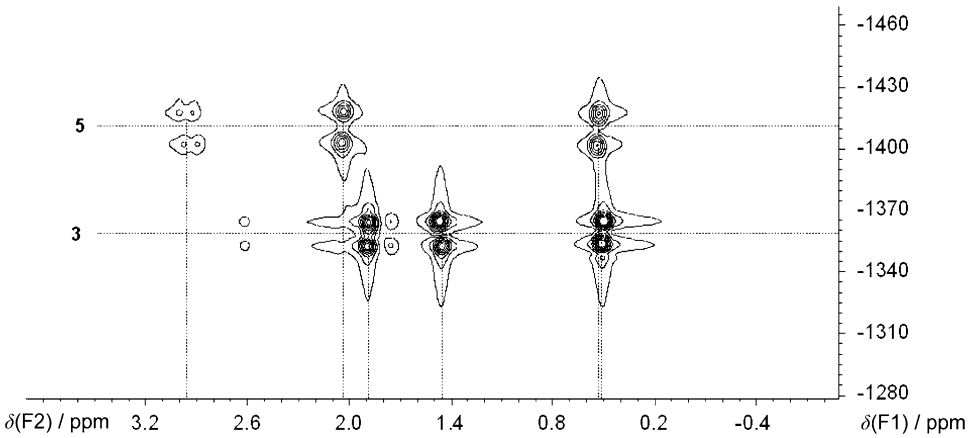


Fig. 5 Pt/H correlation NMR of the region showing the ^{1}H signals of octahedral complexes

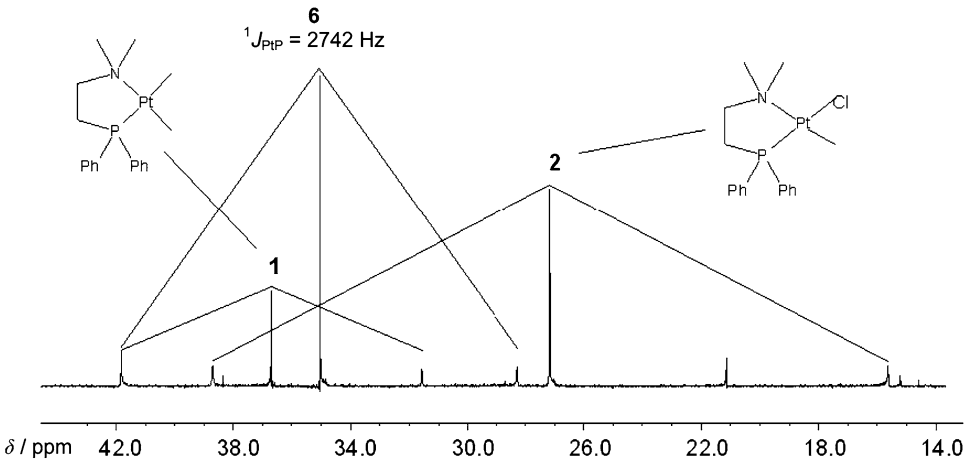


Fig. 6 ^{31}P NMR signals in the shift range of the planar complexes in the reaction mixture of **1** with ethyl chloroacetate

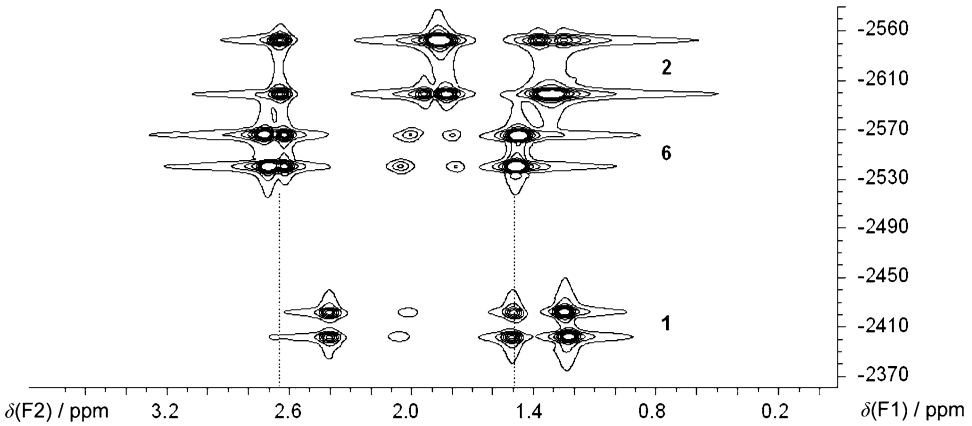


Fig. 7 Pt/H correlation measurement of the planar complexes formed in the reaction of **1** with ethyl chloroacetate

A Pt/H correlation spectrum was measured (Fig. 7) to determine the composition of **6**. Two new ligand signals appeared at 1.31 and 2.51 ppm. According to APT NMR, the first is a methyl group, the second a CH_2 group (resulting in a larger J_{PtP} of 2,742 Hz compared to 2,070 Hz in **1**). In a 2D C/H spectrum the CH_2 group shows correlations with COO, CH_2 and CH_3 groups. Therefore, this signal appears to belong to an ethoxycarbonylmethyl ligand, and the composition of **6** is (P∩N)Pt(Me)(CH_2COOEt), formed by methyl chloride elimination from the octahedral intermediate (P∩N)Pt(Me)$_2$(CH_2COOEt)Cl.

Complex **6** apparently does not undergo oxidative addition of another ethyl chloroacetate, because diethyl

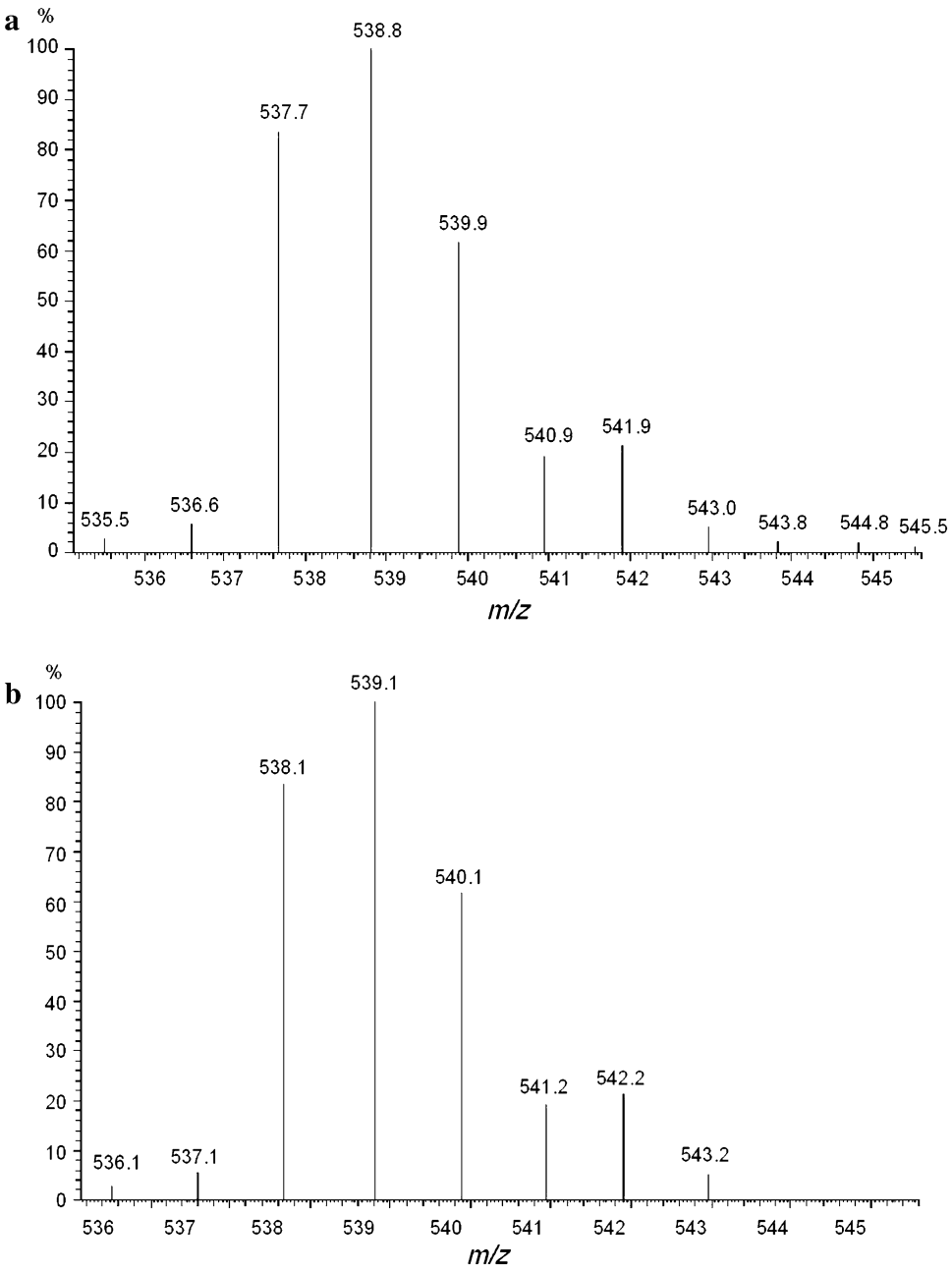


Fig. 8 **a** Isotope pattern of the unknown signal and **b** calculated pattern of $C_{20}H_{26}NO_2PPt + H^+$

succinate (formed by reductive elimination) was not observed in the reaction mixture. Reaction with HCl, yielding complex **2** and ethyl acetate, is the main reaction pathway for **6** instead.

The resonance at 21.2 ppm

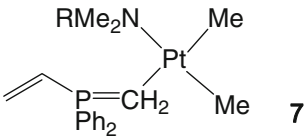
The experiments discussed in this article show that the HCl-producing reaction yields a complex containing a coordinated amino group as well as a vinyl group bonded to a phosphorus atom. The ^{31}P NMR signal at 21.2 ppm corresponds to chemical shifts reported in the literature for ylide complexes [14, 15]. Mass spectrometry with chemical ionisation provided the final proof for the formation of an ylide complex.

Mass spectrometry investigations

This method was chosen to generate complex ions with low fragmentation, because some fragments of the other complexes formed in the reaction are identical. The measurements were performed on the reaction mixtures of complex **1** with ethyl

chloroacetate in a molar ratio of 1:2. The mixture was heated until **1**, **2** and the possible ylide complex were observed in the ^{31}P NMR spectrum. The crude mass spectrum showed four signal groups: complexes **1** and **2**, complex **1** less one CH_3 group, and a group of unknown signals, possibly belonging to the ylide complex. A background file, containing the spectrum of the complexes **1** and **2**, was subtracted from the spectrum to reveal the isotope pattern of the unknown signal (Fig. 8).

For the complex from the reaction with ethyl chloroacetate, the elemental composition $C_{20}H_{26}NO_2PPt$ was thus determined. Considering all facts from the NMR spectra (especially the splitting of the vinylic protons in Fig. 2), the signal appears to belong to a doubly demethylated fragment of the ylide complex $Pt[CH_2{=}PPh_2(vinyl)](NMe_2COOEt)Me_2$ (**7**, R = COOEt).



7

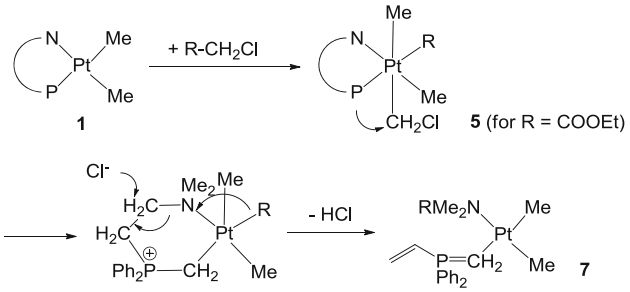
Reaction of benzyl chloride

The analogous products were observed during the (slower) reaction of **1** with benzyl chloride. The only differences were (i) that the analogue of intermediate **5** was not observed spectroscopically, i.e. its reaction to give **7** is apparently faster, and (ii) that both dibenzyl and toluene were identified as organic products in the ^{1}H NMR spectrum of the reaction solution. Dibenzyl is the product of dehalogenative coupling, and toluene that of hydrodehalogenation. Thus contrary to complex **6**, the corresponding complex $(P{\cap}N)Pt(Me)CH_2Ph$ can also undergo oxidative addition of a second benzyl chloride molecule, followed by elimination of dibenzyl and formation of **2**, in addition to the reaction with HCl, yielding complex **2** and toluene. Since there is no doubt about the formation of **7**, it is safe to assume the same mechanisms as in the case of ethyl chloroacetate (with different reaction rates). The mass spectrum of the reaction with benzyl chloride was only slightly different from that of the reaction with ethyl chloroacetate. It led to the elemental composition $C_{23}H_{26}NPPt$ and assignment to the demethylated fragment of the ylide complex $Pt[CH_2{=}PPh_2(vinyl)](NMe_2Ph)Me_2$ (**7**, R = Ph).

Conclusions

Reaction of $(P{\cap}N)PtMe_2$ with either benzyl chloride or ethyl chloroacetate resulted in complex reaction mixtures. In addition to the oxidative addition of the C–Cl bonds and associated consecutive reactions, which were already observed for non-activated C–Cl bonds, new reactions were observed which can be explained by alternative oxidative addition of the C–CH_2Cl bond.

Scheme 2

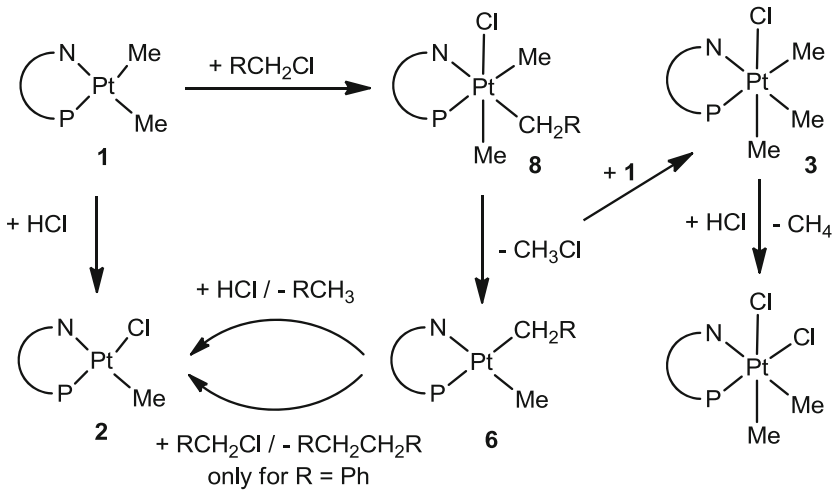


On the basis of these results, the following sequence of reactions is postulated. The HCl-producing reaction is due to initial C–C bond activation, i.e. oxidative addition of the R–C bond of R–CH_2Cl (R = Ph or COOEt) to the Pt atom. The resultant CH_2X ligand of the (observed) complex **5** is then attacked by the phosphorus atom of the chelating ligand resulting in a cyclic phosphonium intermediate, followed by migration of the group R from the metal to the amino group and abstraction of a proton (by the cleaved chloride) from the CH_2 group next to the nitrogen atom (Scheme 2) to result in the observed ylide complex **7**. To the best of our knowledge this sequence of reactions, resulting in the cleavage of the P∩N ligand, has not been observed before. Reaction of the phosphane with the CH_2X ligand might be related to the reaction of $Pt(PPh_3)_4$ with CH_2ClI which results in the formation of the cationic ylide complex *cis*-$Pt(CH_2PPh_3)Cl(PPh_3)_2$ [15].

During this reaction HCl is developed, which can either react with the starting complex **1** to give **2** directly, the trimethyl complex **3** to produce methane and **4** (both compounds were identified), or with complex **6** through formation of RCH_3 (toluene or ethyl acetate).

The starting complex **1** also reacts with RCH_2Cl by activation of the C–Cl bond, as previously reported [2, 3]. The formed octahedral intermediate **8** eliminates CH_3Cl which subsequently reacts with complex **1** to form **3** (Scheme 3). As judged by the observed organic products, **2** can be formed from **6** either by addition of HCl and elimination of RCH_3 (R = Ph or COOEt) or, in the reaction of benzyl chloride, also by oxidative addition of a second $PhCH_2Cl$ molecule, followed by dibenzyl elimination.

Scheme 3



Experimental

All compounds were handled under Ar atmosphere using standard Schlenk techniques. All solvents were dried by standard methods. The NMR solvents were stored over molecular sieve (4 Å). The NMR tubes were treated with dichlorodimethylsilane to prevent the SiOH groups from reacting with the educts and the complexes.

NMR experiments were performed on Bruker Avance 250 and 300 MHz spectrometers and on a Bruker Avance III 500 MHz spectrometer at room temperature. ^{13}C, ^{31}P and ^{195}Pt NMR spectra were proton decoupled. All pulse programs were obtained from the Bruker software library. Mass spectra were measured on a Thermo Scientific ITQ 1100 with chemical ionisation. Signals of unreacted educts are not listed.

Reaction with ethyl chloroacetate

Ethyl chloroacetate (5.1 mg, 0.042 mmol) was added at room temperature to 10 mg of **1** (0.021 mmol) in 0.6 cm^3 of C_6D_6. NMR spectra were recorded at regular intervals. The following NMR data are from the reaction mixture while the reaction was still on-going. Therefore, not all compounds discussed in the "Results and discussion" section are represented. ^1H NMR: $\delta = 0.16$ (s, CH_4), 0.41 (d, with satellites, $^3J_{PH} = 7$ Hz, $^2J_{PtH} = 50$ Hz, CH_3-Pt, **4**), 0.50 (d, with satellites, $^3J_{PH} = 7.8$ Hz, $^2J_{PtH} = 71$ Hz, CH_3-Pt, **3**), 0.53 (d, with satellites, $^3J_{PH} = 6.7$ Hz, $^2J_{PtH} = 69$ Hz, CH_3-Pt, **8**), 0.80 (s, CH_3CH_3), 1.31 (d, with satellites, $^3J_{PH} = 3.3$ Hz, $^2J_{PtH} = 74$ Hz, CH_3-Pt, **2**), 1.47 (d, with satellites, $^3J_{PH} = 8$ Hz, $^2J_{PtH} = 62$ Hz, CH_3-Pt, **3**), 1.68 (d, with satellites, $^3J_{PH} = 6.8$ Hz, $^2J_{PtH} = 73$ Hz, CH_3-Pt, **4**), 1.89 (d, with satellites, $^3J_{PH} = 7.0$ Hz, $^2J_{PtH} = 72$ Hz, CH_3-Pt, **3**), 2.04 (d, with satellites, $^3J_{PH} = 5.5$ Hz, $^2J_{PtH} = 71$ Hz, CH_3-Pt, **8**), 2.51 (s, with satellites, $^3J_{PtP} = 11.9$ Hz, CH_3-N, **2**), 2.74 (s, $PhCH_2CH_2Ph$), 2.98 (m, CH_2-Pt, **8**), 5.74, 6.27 and 6.34 (see Fig. 2, $^3J_{PH} = 23.8$ Hz, P–CH=CH_2, **7**), 7.04 and 7.53 (m, C_{arom}, **2**) ppm; ^{31}P NMR: $\delta = 1.7$ (s with satellites, $^1J_{PtP} = 1{,}208$ Hz, **4**), 8.8 (s with satellites, $^1J_{PtP} = 1{,}183$ Hz, **3**), 11.3 (s with satellites, $^1J_{PtP} = 1{,}587$ Hz, **8**), 21.6 ppm; ^{13}C NMR: $\delta = -9.96$ (CH_3-Pt, **4**), −8.61 (CH_3-Pt, **3**), −7.83 (CH_3-Pt, **8**), 17.29 (CH_3-Pt, **3**), 27.61 (CH_3-Pt, **6**), 29.87 (CH_2-Pt, **8**) ppm; ^{195}Pt NMR: $\delta = -4{,}173$ (**6**), −2,977 (**3**), −3,030 (**8**) ppm.

Reaction with benzyl chloride

Benzyl chloride (2.7 mg, 0.021 mmol) was added at room temperature to 10 mg of **1** (0.021 mmol) in 0.6 cm^3 of C_6D_6. NMR spectra were recorded at regular intervals. The following NMR data are from the reaction mixture while the reaction was still on-going. Therefore, not all compounds discussed in the "Results and discussion" section are represented. ^1H NMR: $\delta = 0.16$ (s, CH_4), 0.80 (s, CH_3CH_3), 1.31 (d, with satellites, $^3J_{PH} = 3.3$ Hz, $^2J_{PtH} = 74$ Hz, CH_3-Pt, **2**), 2.11 (s, Ph-CH_3), 2.51 (s, with satellites, CH_3-N, **2**), 2.74 (s, $PhCH_2CH_2Ph$), 5.74, 6.27 and 6.34 (see Fig. 2, $^3J_{PH} = 23.8$ Hz, P–CH=CH_2, **7**), 7.04 (m, C_{arom}, **2**), 7.53 (m, C_{arom}, **2**) ppm; ^{31}P NMR: $\delta = 20.1$ (s, **7**), 27.1 (s with satellites, $^1J_{PtP} = 4{,}675$ Hz, **2**), 21.6 ppm; GC/MS: $T_{start} = 80$ °C, $T_{end} = 280$ °C, rate = 10 °C/min. Time: 2.13 min ($m/z = 106, 105, 93, 92, 91$, $C_6H_5CH_2CH_3$), 12.33 min ($m/z = 183, 182, 92, 91$, $C_6H_5CH_2CH_2C_6H_5$).

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