A Comparison of the Reactivity of Chloroalkanes and Chlorosilanes towards Activated Pt^{II} Complexes by DFT Calculations

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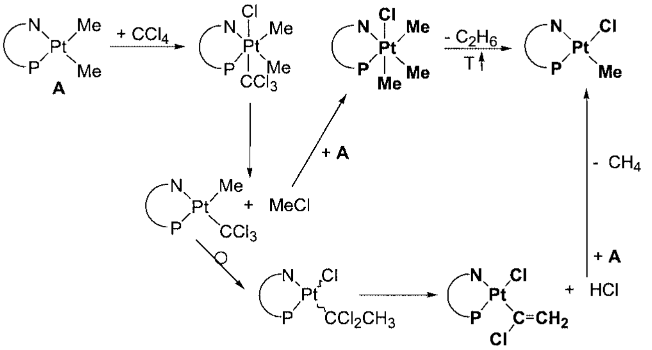
The pathways of the C–Cl bond activation of CCl_4 and CH_3Cl by the 14-electron Pt^{II} complexes $[PtMe_2(PH_3)]$ or the corresponding reactions of $SiCl_4$ and SiH_3Cl with $[PtMe(SiH_3)(PH_3)]$ were investigated by DFT calculations. The complexes $[Pt(EH_3)Me(PH_3)]$ (E = C, Si) are models for $[Pt(EH_3)Me\{(\kappa^2\text{-}P,N)\text{-}Ph_2PCH_2CH_2NMe_2\}]$, with hemilabile P,N chelating ligands, used in practical experiments. While the reaction of $[Pt(EH_3)Me(PH_3)]$ with ECl_4 results in an EH_3/ECl_3 exchange, reaction of $[Pt(EH_3)Me(PH_3)]$ with EH_3Cl results in the elimination of E_2H_6. Both reactions proceed via a five-coordinate Pt^{IV} intermediate. The elimination of Si_2H_6 is endothermic.

Introduction

Hemilabile chelating ligands (A∩B) are used in coordination chemistry to enhance the reactivity of metal complexes.[1] The activating effect of such ligands results from the different metal−ligand bond strengths: while one atom (A) remains coordinated to the metal, a more weakly bonded second center (B) decoordinates more easily and reversibly.

Coordinatively and electronically unsaturated complexes play a key role in many stoichiometric and catalytic reactions of Pt^{II} complexes based on oxidative addition/reductive elimination reactions. Three-coordinate Pt^{II} complexes are often required for the initial oxidative addition reactions.[2] They are generally transient species generated in situ by ligand elimination from the square-planar precursor complexes. After oxidative addition has occurred, five-coordinate Pt^{IV} complexes are key intermediates in the product-forming reductive elimination reactions.[3] The use of hemilabile chelating ligands should therefore promote both oxidative addition reactions starting from the Pt^{II} complexes and reductive elimination reactions from the corresponding Pt^{IV} intermediates.

In the chemistry of metal-silicon compounds hemilabile ligands have hardly been used. In a series of papers, we have recently shown that the reactivity of Pt^{II} complexes towards silanes is greatly enhanced by using hemilabile chelating ligands of the type $\kappa^2\text{-}Ph_2P{-}X{-}NR_2$ (denoted as P∩N).[4] Furthermore, these complexes were also found to activate C−Cl bonds.[5,6] The outcome of the reactions of $[PtMe_2\{(\kappa^2\text{-}P,N)\text{-}Ph_2PCH_2CH_2NMe_2\}]$ (**A**) with $CH_{4-n}Cl_n$ (n = 1−4) on one hand and with $PhMe_2SiCl$ on the other showed remarkable differences. In the reaction with CCl_4, the complexes [Pt(Cl)Me(P∩N)], $[Pt(Cl)Me_3(P∩N)]$ and $[Pt(Cl)C(Cl){=}CH_2(P∩N)]$ were formed at room temperature. A suggested reaction mechanism is shown in Scheme 1 (the final products are drawn in bold). In this reaction, the complex [Pt(Cl)Me(P∩N)] can be formed by two different routes. At room temperature, this complex was only obtained by reaction of **A** with the HCl cleaved in the reaction forming the vinylidene complex. Ethane elimination from $[Pt(Cl)Me_3(P∩N)]$ with concomitant formation of [Pt(Cl)Me(P∩N)] occurred only in boiling benzene.



Scheme 1

The analogous reactions of $CHCl_3$ and CH_2Cl_2 with [Pt(Cl)Me(P∩N)] were much slower, but resulted in analogous products; CH_3Cl only reacts slowly with $[PtMe_2(P∩N)]$ in a hot benzene solution to form $[Pt(Cl)Me_3(P∩N)]$ and [Pt(Cl)Me(P∩N)], and thus does not fit into the sequence.

In contrast, when $[PtMe_2\{(\kappa^2\text{-}P,N)\text{-}Ph_2PCH_2CH_2NMe_2\}]$ was reacted with $PhMe_2SiCl$, the disilane $Ph_2Me_4Si_2$ was

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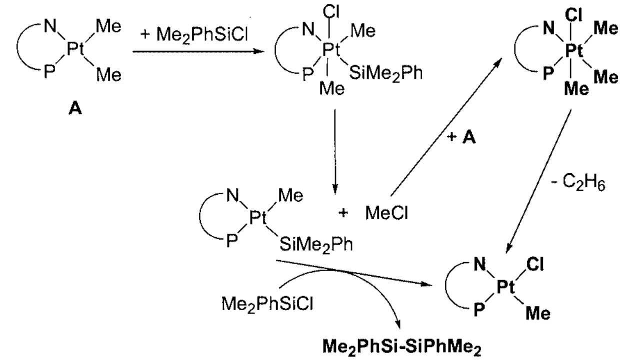


Scheme 2

formed quantitatively, together with the Pt^{IV} complex [Pt(Cl)Me$_3$(P∩N)] and the Pt^{II} complex [Pt(Cl)Me(P∩N)]. A possible reaction mechanism is shown in Scheme 2 (the final products are again drawn in bold).

The practical results suggested that the initial steps are the same in both the reaction of CCl$_4$ and PhMe$_2$SiCl. However, the [PtMe(SiMe$_2$Ph)(P∩N)] intermediate in the latter reaction reacted with another equivalent of PhMe$_2$SiCl to give the disilane, while the corresponding intermediate [Pt(CCl$_3$)Me(P∩N)] did not undergo C−C coupling.

These observations prompted us to investigate the pathways of the C−Cl and Si−Cl activation by the complexes [PtMe$_2$(P∩N)] using DFT calculations. While several theoretical calculations on the oxidative addition of silicon-element bonds to unsaturated PtL$_2$ (d^{10}) complexes have been performed,[7] little theoretical work has been carried out on such reactions with unsaturated d^8 PtLX$_2$ complexes.

Results and Discussion

As was already discussed in our earlier work,[8,9] at the key stage of the reaction the amino group of the chelating P∩N ligand was considered to be decoordinated, and therefore the chelate ligand was replaced by a PH$_3$ group in the calculations. In the four- and six-coordinate complexes, the chelating P∩N ligand was replaced by a PH$_3$ and NH$_3$ group. Further simplification was used in the reactions where the molecules Me$_2$PhSiCl or Me$_2$PhSiH were involved. These were replaced by H$_3$SiCl and H$_3$SiH respectively.

Reaction of CCl$_4$ with [PtMe$_2$(PH$_3$)] (1)

As a first step in the reaction of [PtMe$_2$(P∩N)] with CCl$_4$, the oxidative addition of a C−Cl bond was suggested, followed by elimination of methyl chloride. The three-coordinate complex **1** and CCl$_4$ initially form the precursor complex **PC**$_{1-2}$. This reaction requires 6.1 kcal/mol. In the distorted square-planar complex thus formed, the platinum atom interacts with CCl$_4$ through a weak Pt−Cl interaction (Pt−Cl 2.690 Å; Figure 1). The associated C−Cl bond is only slightly stretched from 1.793 Å in CCl$_4$ to 1.832 Å in **PC**$_{1-2}$.

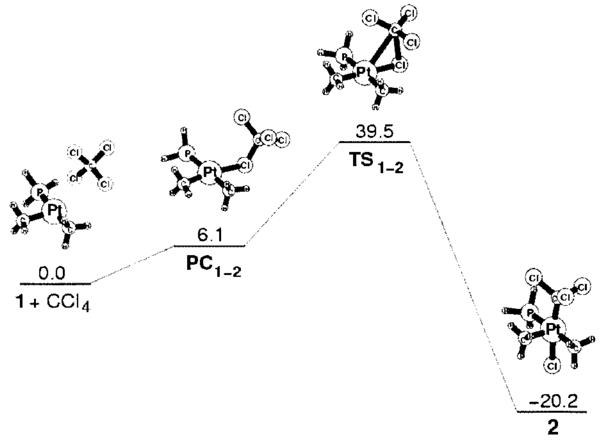


Figure 1. Reaction profile for the oxidative addition of CCl$_4$ to **1**; energies in kcal/mol

The transition state structure **TS**$_{1-2}$ is formed by closing of the Pt−Cl−C angle from 118.7° in **PC**$_{1-2}$ to 74.5° in **TS**$_{1-2}$, corresponding to the formation of a new Pt−C bond. The C−Cl bond is now stretched to 2.788 Å, and the Pt−Cl bond is reduced to 2.481 Å. Additionally the C−Pt−Cl angle is increased from 170.9° in **PC**$_{1-2}$ to 178.8° in **TS**$_{1-2}$. The energy required for this change is 33.4 kcal/mol, which is quite high. On the other hand, the relaxation to [Pt(CCl$_3$)(Cl)Me$_2$(PH$_3$)] (**2**) liberates 59.7 kcal/mol. This high value is a result of the rearrangements during the relaxation to intermediate **2**, where the chlorine atom moves into the *trans* position to the CCl$_3$ group. The rearrangement of the chlorine is an effect of the stronger *trans* effect of the methyl group compared to the CCl$_3$ group.[8] The overall reaction of **1** with CCl$_4$ is best described as an oxidative addition via a three-center transition state. As expected from the different electronegativities, the Pt−Cl interaction develops faster than the Pt−C interaction.

The geometry optimization on the reactant side of **TS**$_{3-4}$ leads to the square-pyramidal complex [Pt(CCl$_3$)(Cl)Me$_2$(PH$_3$)] (**3**) which is nearly equivalent to **2**. This shows that the two reaction profiles in Figure 1 and Figure 2 are connected. Hence the next stage of the reaction mechanism, which eventually leads to a reductive elimination of methyl chloride, begins with **3** (Figure 2). The energy required to form **TS**$_{3-4}$ from intermediate **3** is 35.8 kcal/mol. The geometric changes on the way from **3** to **4** + ClCH$_3$ mirror those during the oxidative addition of CCl$_4$, i.e. the Cl−Pt−C angle closes from 96.1° in **3** to 53.9° in **TS**$_{3-4}$, and the Pt−C bond is stretched from 2.072 Å to 2.603 Å. The change in the Pt−Cl bond length from 2.414 Å to 2.461 Å is much smaller. Through the changes in the geometry, a weak C−Cl interaction with 2.298 Å is formed.

The Pt−C bond is broken during the relaxation to **PC**$_{3-4}$, and the C−Cl bond is fully formed. The bond length of 1.821 Å is close to the final C−Cl bond length of 1.806 Å in MeCl. The Pt−Cl bond length is increased to

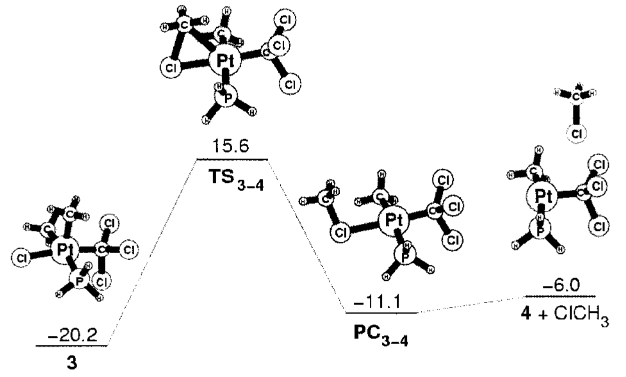
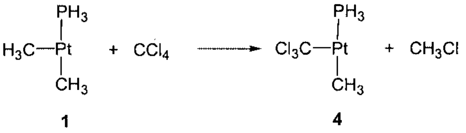


Figure 2. Continuing reaction profile for the reaction of **1** with CCl_4 (elimination of MeCl); energies in kcal/mol

2.617 Å and the energy released by the relaxation is 26.7 kcal/mol. MeCl is eventually fully dissociated. The last step is endothermic by +5.1 kcal/mol, but the whole reaction [Equation (1)] is exothermic by −6.0 kcal/mol.



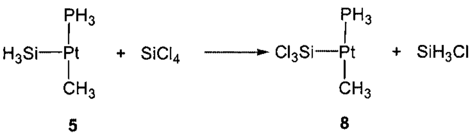
$$\mathrm{H_3C{-}}\overset{\mathrm{PH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Pt}}} + \mathrm{CCl_4} \longrightarrow \mathrm{Cl_3C{-}}\overset{\mathrm{PH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Pt}}} + \mathrm{CH_3Cl} \qquad (1)$$

1 **4**

The formation of **4** is the key step for the reaction of CCl_4 with the dimethylplatinum complex **1**. This, in turn, allows further reactions to happen (Scheme 1), all of which are exothermic. Although there is a high activation energy barrier for the oxidative CCl_4 addition to **1**, these following exothermic reactions produce enough energy for this barrier to be overcome.[9]

Reaction of $SiCl_4$ with $[Pt(SiH_3)Me(PH_3)]$ (5)

Though not yet practically investigated, the reaction between the three-coordinate complex **5** and $SiCl_4$ was also investigated for comparison. This is the silicon analogue to the previously discussed reaction, i.e. the SiH_3 group in the starting complex **5** is replaced by a $SiCl_3$ ligand [Equation (2)]. We have previously shown that the energetically preferred structure of the T-shaped complex **5** is the one where PH_3 and CH_3 are *trans* to each other.[8]



$$\mathrm{H_3Si{-}}\overset{\mathrm{PH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Pt}}} + \mathrm{SiCl_4} \longrightarrow \mathrm{Cl_3Si{-}}\overset{\mathrm{PH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Pt}}} + \mathrm{SiH_3Cl} \qquad (2)$$

5 **8**

Complex **5** reacts with $SiCl_4$ to form the precursor complex $\mathbf{PC_{5-6}}$. The reaction requires 8.5 kcal/mol, and a weak Pt−Cl bond is formed. The Pt−Cl distance in $\mathbf{PC_{5-6}}$ (3.127 Å) is considerably longer than the corresponding distance in the reaction with CCl_4 (precursor complex $\mathbf{PC_{1-2}}$). This is due to the SiH_3 group in $\mathbf{PC_{5-6}}$ having a stronger *trans* effect than the methyl group in the *trans* position in $\mathbf{PC_{1-2}}$. The associated Si−Cl bond length (2.059 Å) is nearly unchanged relative to the free $SiCl_4$ molecule (2.047 Å).

As in the CCl_4 reaction, the Pt−Si bond forms by closing of the Pt−Cl−Si angle from 116.5° in $\mathbf{PC_{5-6}}$ to 65.2° in $\mathbf{TS_{5-6}}$, stretching of the Si−Cl bond to 2.205 Å and reducing the Pt−Cl bond length to 2.654 Å.

Compared to the reaction with CCl_4, the incoming $SiCl_4$ molecule is not as distorted in the transition-state structure as the CCl_4 molecule was. As a result, the energy required for this change is, at 11.8 kcal/mol, much lower than the 33.4 kcal/mol required for the reaction with CCl_4. On the other hand the relaxation to $[Pt(Cl)Me(SiH_3)(SiCl_3)(PH_3)]$ (**6**) liberates only 18.9 kcal/mol. A rearrangement occurs during the relaxation to the intermediate **6**, where the chlorine atom moves *trans* to the $SiCl_3$ group, analogous to the CCl_4 reaction. This is again an effect of the stronger *trans* effect of the SiH_3 group compared to the $SiCl_3$ group. It is interesting to note that the formation of the intermediate **6** is slightly endothermic, in comparison to the analogous reaction with CCl_4, where the formation of the intermediate **2/3** was exothermic.

The geometry optimization on the reactant side of $\mathbf{TS_{7-8}}$ leads to the five-coordinate complex $[Pt(Cl)Me(SiH_3)(SiCl_3)(PH_3)]$ (**7**) which is equivalent to **6**. Although the energy difference is 0.7 kcal/mol, the assumption that the two reaction profiles in Figure 3 and Figure 4 are connected is still valid. The energy required to form $\mathbf{TS_{7-8}}$ from **7** is

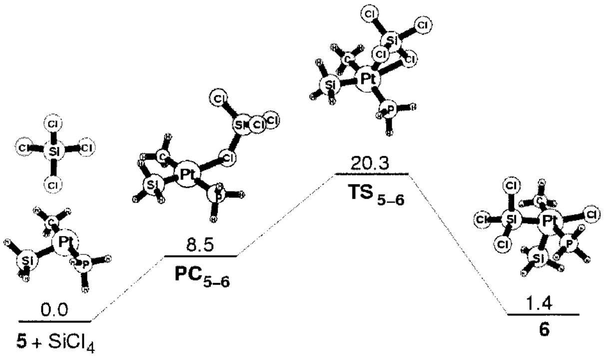


Figure 3. Reaction profile for the reaction of **5** with $SiCl_4$; energies in kcal/mol

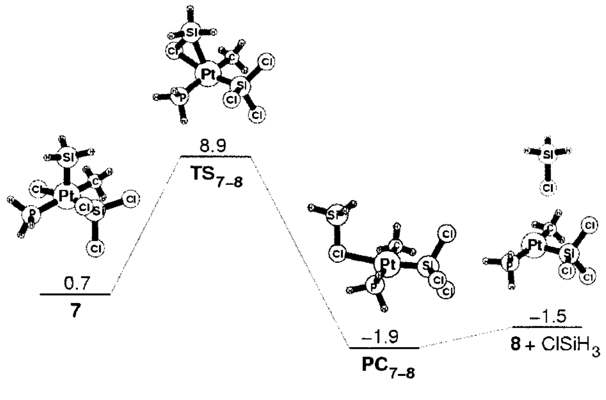


Figure 4. Continuing reaction profile for the reaction of **5** with $SiCl_4$ (elimination of H_3SiCl); energies in kcal/mol

8.2 kcal/mol. This is again much less than in the CCl_4 reaction. The Cl−Pt−Si angle is changed from 101.5° in **7** to 52.8° in $\mathbf{TS}_{7-8}$, the Pt−Si bond is stretched from 2.360 Å to 2.644 Å, and a weak Si−Cl bond (2.318 Å) is formed. The change in the Pt−Cl bond length (from 2.439 Å to 2.567 Å) is much larger than for the case of CCl_4.

During the relaxation of $\mathbf{TS}_{7-8}$ to $\mathbf{PC}_{7-8}$, the Pt−C bond is broken and the Si−Cl bond is fully formed. The bond length of 2.114 Å is close to that of 2.081 Å in the H_3SiCl molecule. The Pt−Cl bond is lengthened to 2.849 Å and the energy released by the relaxation is 10.8 kcal/mol. Finally the H_3SiCl molecule is fully dissociated. The whole reaction [Equation (2)] is slightly exothermic by −1.5 kcal/mol.

Reaction of CH_3Cl with $[PtMe_2(NH_3)(PH_3)]$ (9)

Practical experiments have shown that a six-coordinate Pt^{IV} complex is formed in the reaction of $[PtMe_2(P\cap N)]$ with MeCl [Equation (3)] in contrast to the reaction with CCl_4.[5] For the calculation of the reaction profile (Figure 5), the four-coordinate complex **9** was taken as a starting point. The first step in the reaction with MeCl is the formation of the four-coordinate precursor $\mathbf{PC}_{9-10}$, which requires 14.5 kcal/mol. For the formation of this precursor complex the nitrogen must decoordinate, and a weak Pt−Cl bond (2.709 Å) must form.

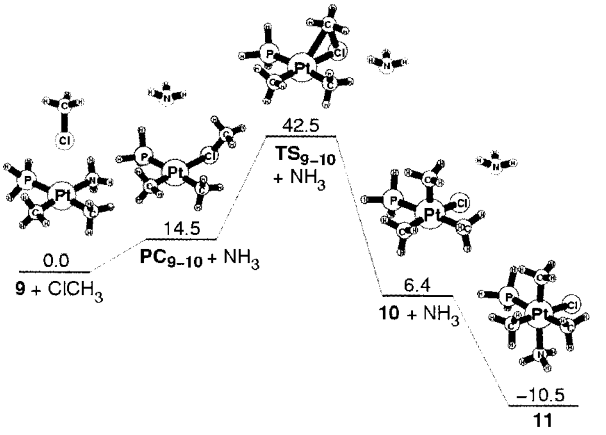
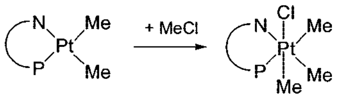


Figure 5. Reaction profile for the reaction of **9** with CH_3Cl; energies in kcal/mol



(3)

The energy required to form $\mathbf{TS}_{9-10}$ from $\mathbf{PC}_{9-10}$ is 28.0 kcal/mol, which is lower than the 33.4 kcal/mol for the case of CCl_4. In $\mathbf{TS}_{9-10}$ the carbon atom approaches the platinum atom (Pt−C 2.580 Å), while the corresponding C−Cl bond is stretched to 2.270 Å. The Pt−Cl bond is now 2.526 Å, and the Cl−Pt−C angle is 52.8°. During the relaxation to $[Pt(Cl)Me_3(PH_3)]$ (**10**) the Pt−C bond length is decreased to 2.063 Å while the C−Cl bond is broken. The Pt−Cl bond is now 2.466 Å and the Cl−Pt−C angle is 105.2°. Noticeably, the chlorine is not re-orientated as in the case of **2** (Figure 1). This is due to the fact that the incoming alkyl ligand is the same as the existing alkyl ligands (i.e. the chlorine is already *trans* to a methyl group).

The six-coordinate complex $[Pt(Cl)Me_3(NH_3)(PH_3)]$ (**11**) is formed through the re-coordination of the nitrogen. Here the platinum has an octahedral geometry as seen in the corresponding crystal structure of $[Pt(Cl)Me_3\{(\kappa^2\text{-}P,N)\text{-}Ph_2PCH_2CH_2NMe_2\}]$.[5] The reaction to form **11** is exothermic by −10.5 kcal/mol. The six-coordinate complex **11** is the only reaction product, because formation of a vinylidene complex is not possible. Elimination of MeCl would just reverse the reaction, but would not lead to the formation of a new complex.

Although the reaction to form **11** is exothermic, the practical results showed that ethane elimination can occur at elevated temperatures. The profile of this reaction is shown in Figure 6. Starting from the six-coordinate complex **11**, the five-coordinate intermediate $[Pt(Cl)Me_3(PH_3)]$ (**12**) is formed through the de-coordination of the nitrogen. This has a trigonal-bipyramidal geometry instead of a square-pyramidal geometry as in **10**. However, the trigonal-bipyramidal structure is only 0.4 kcal/mol higher in energy than the square-pyramidal structure. The formation of **12** needs 17.3 kcal/mol, and the C−C distance in **12** is 2.662 Å indicating that the two carbons approach each other.

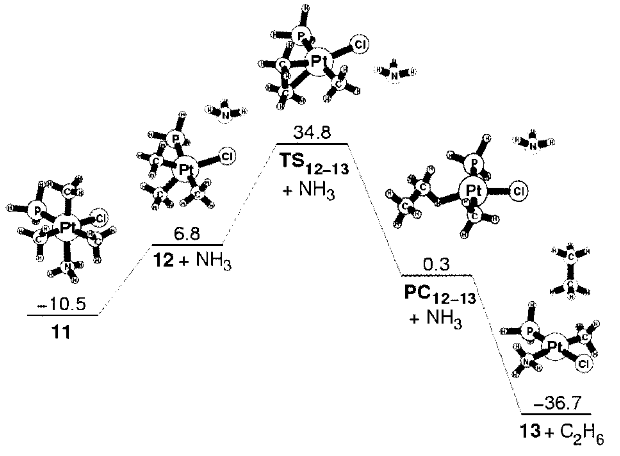


Figure 6. Elimination of ethane from **11**; energies in kcal/mol

An energy of 28.0 kcal/mol is required to form the transition state $\mathbf{TS}_{12-13}$. During this process both Pt−C bonds are lengthened, while a C−C bond (1.908 Å) is formed. On the other hand, the Pt−Cl bond is decreased from 2.443 Å in **12** to 2.367 Å in $\mathbf{TS}_{12-13}$. As shown in Figure 6, the vector of the outgoing C_2H_6 molecule is perpendicular to the plane of the remaining three-coordinate platinum complex. The C−C bond length of 1.530 Å and the Pt−C bond of 2.614 Å suggests that in the complex $\mathbf{PC}_{12-13}$ the ethane is fully formed. In the final step the nitrogen is re-coordinated, an energy of 37.0 kcal/mol is released and the complex $[Pt(Cl)Me(NH_3)(PH_3)]$ (**13**) is formed, where the chlorine is in the energetically favored *trans*-position to the phosphorus. Reductive elimination of ethane from the six-coordinate complex **11** releases an overall energy of 26.2 kcal/mol.

Reaction of SiH_3Cl with $[PtMe(SiH_3)(PH_3)]$ (5)

For a further comparison with the carbon complexes, and due to interesting practical results (the formation of disilane), the corresponding reaction with SiH_3Cl and the platinum complex **5** [Equation (4)] was investigated. Starting from reactants **5** and SiH_3Cl the precursor $\mathbf{PC_{5-14}}$ is formed. This requires 1.3 kcal/mol (Figure 7).

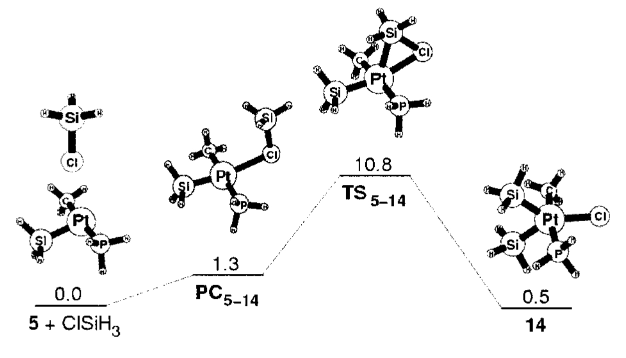
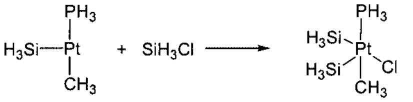


Figure 7. Reaction profile for the reaction **5** with SiH_3Cl; energies in kcal/mol



5

$$H_3Si{-}Pt(PH_3)(CH_3) + SiH_3Cl \longrightarrow (H_3Si)_2Pt(PH_3)(Cl)(CH_3) \qquad (4)$$

In the complex $\mathbf{PC}_{5-14}$, the chlorine of SiH_3Cl interacts weakly with the platinum (Pt−Cl 2.964 Å). Owing to the Pt−Cl interaction, the Si−Cl bond is weakened and stretched from 2.082 Å to 2.103 Å. The SiH_3Cl molecule approaches the platinum complex not quite perpendicularly to the Pt−Si bond but instead it tips slightly towards the carbon atom, giving a Si−Pt−Cl−Si dihedral angle of 27.7°.

In the transition state $\mathbf{TS}_{5-14}$ the Pt−Cl bond is further decreased to 2.608 Å, and the formation of a 2.599 Å long Pt−Si interaction can be observed. On the other hand, the Si−Cl bond is increased from 2.103 Å in $\mathbf{PC}_{5-14}$ to 2.316 Å in $\mathbf{TS}_{5-14}$. The energy required to form the transition state $\mathbf{TS}_{5-14}$ from the precursor $\mathbf{PC}_{5-14}$ is 9.5 kcal/mol.

The distorted trigonal-bipyramidal complex $[Pt(Cl)Me(SiH_3)_2(PH_3)]$ (**14**) is formed from $\mathbf{TS}_{5-14}$, and 10.3 kcal/mol is released. During this process the Si−Cl bond is broken and the Pt−Si bond is fully formed. The final complex **14** consists of two equivalent SiH_3 groups. The geometry optimization on the reactant side of $\mathbf{TS}_{15-16}$ leads to the five-coordinate complex $[Pt(Cl)Me(SiH_3)_2(PH_3)]$ (**15**), which is equivalent to **14**, with the SiH_3 and the Cl ligand in the trigonal plane.

The Si−Si distance of 3.026 Å in **15** is reduced to 2.492 Å in $\mathbf{TS}_{15-16}$ (Figure 8). In $\mathbf{TS}_{15-16}$ a 1.988 Å long Pt−H bond is formed, concurrently the corresponding Si−H bond increases from 1.488 Å to 1.564 Å and the Pt−Si bond is lengthened to 2.452 Å. The other Pt−Si bond (2.652 Å) is even longer. The energy required to form $\mathbf{TS}_{15-16}$, which can mainly be assigned to the formation of the Si−Si bond, is 30.1 kcal/mol. The five-coordinate complex $[Pt(Cl)(H)Me(Si_2H_5)(PH_3)]$ (**16**) is formed freeing 19.9 kcal/mol. During the relaxation the Si−Si bond is reduced to 2.359 Å, and the Pt−H bond is fully formed with a bond length of 1.577 Å. The Si−Pt−H angle is 70.2° and the H−Pt−Cl angle 165.4°.

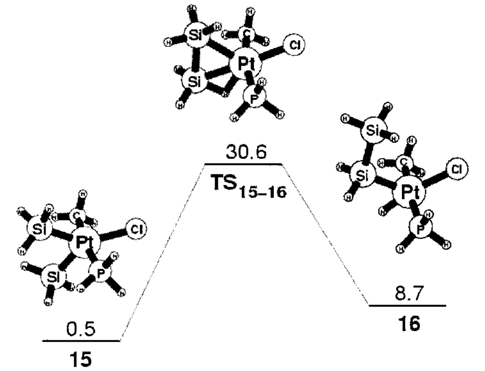


Figure 8. Continuing reaction profile for the reaction of **5** with $ClSiH_3$; energies in kcal/mol

The obvious final step would be the elimination of the disilane Si_2H_6. This step has not been calculated, but instead the comparable elimination of SiH_4 starting from $[Pt(Cl)(H)Me(SiH_3)(PH_3)]$ (**17**) (Figure 9) was calculated.

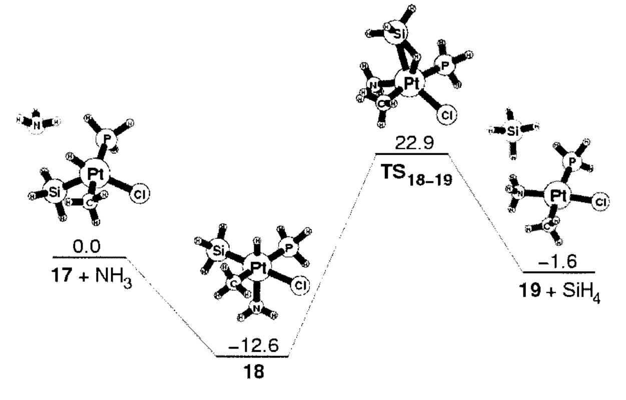


Figure 9. Reaction profile for the reaction of **17** with SiH_4; energies in kcal/mol

In the first step the nitrogen is re-coordinated to form the six-coordinate complex **18**, freeing 12.6 kcal/mol; 35.5 kcal/mol is required to form the transition state structure $\mathbf{TS}_{18-19}$. In $\mathbf{TS}_{18-19}$ the nitrogen is still coordinated, therefore the formation of the six-coordinate intermediate **18** is necessary to allow the reductive elimination of SiH_4. The elimination of SiH_4 and formation of $[Pt(Cl)Me(NH_3)(PH_3)]$ (**19**) frees 24.5 kcal/mol. Although **19** is the energetically less favorable isomer (compared to **13**) the reaction energy is slightly exothermic at −1.6 kcal/

mol. Rearrangement to the energetically favored isomer **13** would liberate an additional 9.0 kcal/mol. It is assumed that **16** can react in the same way as **17**, forming the disilane Si_2H_6.

In the practical experiment, the dimethylplatinum complex $[PtMe_2(P{\cap}N)]$ was reacted with $ClSiMe_2Ph$. In the first step of this reaction the methylsilylplatinum complex $[PtMe(SiMe_2Ph)(P{\cap}N)]$ was formed, and the freed MeCl reacted with still available $[PtMe_2(P{\cap}N)]$ as described previously. The latter reaction is exothermic, which enables the total reaction to occur. It should be noted that in the reaction of $[PtMe_2(P{\cap}N)]$ with $ClSiMe_2Ph$ no hydrido silyl complex (corresponding to **16**) can be formed, because no hydrogen substituents are present. However, the energetics of the overall reaction for the elimination of the disilane directly from **15** (without the intermediacy of **16**) should be very similar to that calculated above.

Conclusions

A comparison of the chlorosilane and chloroalkane reactions with the three-coordinate Pt^{II} complexes shows that the reactions proceed in a geometrically very similar manner. A weak Pt−Cl interaction develops first, which then proceeds to a three-center transition state. The transition-state structures of incoming silanes are less disturbed than those of the corresponding carbon compounds. As a result the activation energies for CCl_4 and CH_3Cl (39.5 and 42.5 kcal/mol, respectively) are much higher than that for $SiCl_4$ and SiH_3Cl (20.3 and 10.8 kcal/mol). On the other hand, the product side relaxation of the transition state structures of the carbon compounds frees 59.7 kcal/mol for CCl_4 and 36.1 kcal/mol for CH_3Cl, which is much more than the 18.9 kcal/mol for $SiCl_4$, and 10.3 kcal/mol for SiH_3Cl.

For the distorted square-pyramidal intermediates **2**, **6**, **10** and **14** (Figures 1, 3, 5 and 7) the following points can be made: (i) When the substituents on the incoming alkyl or silyl group are different from that of the group in the T-shaped precursor complex (CCl_3 and $SiCl_3$ vs. CH_3 and SiH_3) then a rearrangement occurs, which puts the incoming groups (Cl and CCl_3 or $SiCl_3$) *trans* to each other in the square plane, i.e. the *axial* position of the square pyramid is occupied by a CH_3 or SiH_3 ligand, respectively; (ii) When the incoming alkyl or silyl group is the same as the ligand already present (CH_3 or SiH_3), then the incoming groups (Cl and CH_3 or SiH_3) are *cis* (axial/equatorial) in the square-pyramidal intermediate.

Starting from these intermediates (**2**, **6**, **10** and **14**), the reductive elimination of a C−Cl or Si−Cl bond is apparently preferred over the elimination of a C−C or Si−Si bond. When the incoming alkyl or silyl group is the same as the ligand already bonded to the T-shaped precursor complex, reductive C−Cl or Si−Cl elimination would only reverse the reaction.

The differences in the reactivity of CCl_4 and $Me_2PhSiCl$ found in the practical experiments (Scheme 1 and 2) can thus be traced back to the exothermic nature of the reaction leading from $[Pt(CCl_3)Me(P{\cap}N)]$ (corresponding to **4**) to the vinylidene complex $[Pt(Cl)(CCl{=}CH_2)(P{\cap}N)]$ and HCl {which further reacts with $[PtMe_2(P{\cap}N)]$ in an exothermic reaction}. For the corresponding silyl complex (corresponding to **8**) this reaction is not possible, because it would lead to a highly energetic Si=C bond. This reaction is also not possible for $[PtMe_2(P{\cap}N)]$ (no chlorine present that can rearrange), therefore formation of **11** and elimination of ethane (at higher temperatures) is the only reaction possibility.

Computational Details

The geometry optimizations of the equilibrium geometries and transition structures were performed using the B3LYP version of DFT, which is comprised of Becke's hybrid three-parameter exchange functional and the correlation functional of Lee, Yang and Parr.[10,11] The 6-31G++(d) basis set was used an all atoms for the calculations. The relativistic effective core potential and basis set of Preuss and co-workers (which is available in the Gaussian 98 software package as SDD basis set) was used for platinum.[12] Vibrational mode analyses were carried out to confirm that on potential energy surfaces optimized geometries correspond to a local minimum without an imaginary frequency mode or a saddle point with only one imaginary mode. Corrections of zero-point vibrational energies were taken into account in stationary structures obtained. All of the calculations were carried out with the Gaussian 98 package of electronic structure programs.[13]

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