DFT Calculations on the C−Cl/Si−H Exchange Catalyzed by *P*,*N*-Chelated Pt^{II} Complexes

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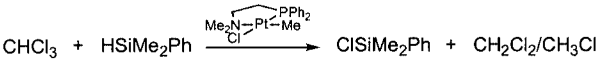
The mechanism of the previously reported C–Cl/Si–H exchange reaction between H_xCCl_{4-x} (x = 0–3) and $HSiMe_2Ph$ catalyzed by [PtMeCl($Ph_2PCH_2CH_2NMe_2$-κ^2*P*,*N*)] [PtMeCl(P∩N)] was investigated by DFT calculations. The energetically less-favored isomer of [PtMeCl(P∩N)], with Cl and P being *cis*, was identified to be the actual catalytic species. The catalytic reaction proceeds by oxidative addition of the silane, de-coordination of the nitrogen atom of the *P*,*N*-chelating ligand, reductive elimination of the chlorosilane and oxidative addition of the C–Cl bond of H_xCCl_{4-x}. The final step is the reductive elimination of the C–H bond with concomitant re-coordination of the nitrogen atom of the *P*,*N*-chelating ligand.

Introduction

We recently reported that the complex [PtMeCl($Ph_2PCH_2CH_2NMe_2$-κ^2*P*,*N*)] [PtMeCl(P∩N)] catalyzes the C−Cl/Si−H exchange reaction between H_xCCl_{4-x} (x = 0−3) and $HSiMe_2Ph$ [Equation (1)].[1] While the chlorinated hydrocarbons are successively dechlorinated, the silane is the chloride sink and $ClSiMe_2Ph$ is formed. The order of reactivity is CCl_4 > $CHCl_3$ > CH_2Cl_2 > CH_3Cl. A related reaction is the [Rh(C_6F_5)(PMe_3)$_3$]-catalyzed hydrodefluorination of C_6F_6 by $HSi(OEt)_3$.[2]



$$CHCl_3 + HSiMe_2Ph \xrightarrow{Me_2N{-}Pt(Cl){-}Me,\ PPh_2} ClSiMe_2Ph + CH_2Cl_2/CH_3Cl \quad (1)$$

A remarkable feature of this reaction is that [PtMeCl(P∩N)], where Cl and P are *trans* in the most stable isomer ("*trans*-[PtMeCl(P∩N)]"),[3,4] does not react with either CCl_4 or $HSiMe_2Ph$ alone on a reasonable time scale. The formation of the catalytic species must be the result of an initial reaction of [PtMeCl(P∩N)] with either $HSiMe_2Ph$ or the chlorinated hydrocarbon. We therefore postulated that the energetically less-favored isomer of [PtMeCl(P∩N)] with *cis* Cl and P ("*cis*-[PtMeCl(P∩N)]") might be the actual catalytic species.[1] To shed light on this question and on the further course of the reaction we performed DFT calculations, which are reported in this article.

Results and Discussion

The theoretical analysis of the catalytic reaction was divided into two parts. In the first part the reaction of both isomers of [PtMeCl(P∩N)] with SiH_4 was analyzed. In the second part the catalytic cycle was studied. SiH_4 and CH_3Cl were used as the reactants to simplify the calculations.

Reaction of [PtMeCl(P∩N)] with SiH_4

When [PtMeCl(P∩N)] is taken as the starting point of the catalytic reaction, the next step must be the reaction with $HSiR_3$. We therefore investigated first the oxidative addition of the silane to the two isomers of [PtMeCl(P∩N)]. Calculations were carried out by method I (see Computational Details) on *P*,*N*-chelated complexes where the chelate ligand was modeled as $PH_2CH_2CH_2NH_2$.

Reaction of SiH_4 with *trans*-[PtMeCl(P∩N)] (1)

The energy required to form $\mathbf{TS}_{1-2}$ from **1** and SiH_4 is 23.6 kcal/mol (Figure 1). A Pt−Si bond of 2.456 Å and a

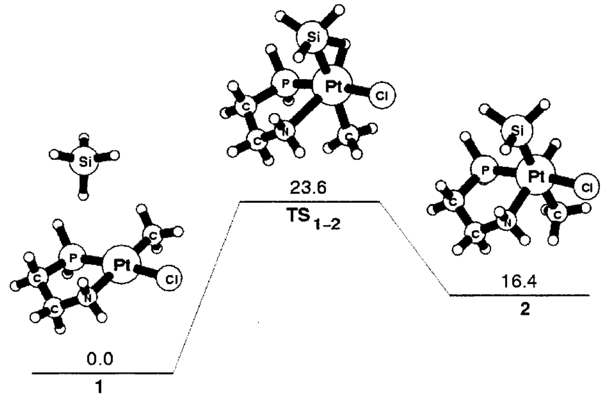


Figure 1. Reaction for the reaction of SiH_4 with **1**; energies in kcal/mol

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Pt−H bond of 1.582 Å are formed. The Pt−N bond length is increased to 2.686 Å in $\mathbf{TS}_{1-2}$ compared to 2.267 Å in **1**. The eventually formed Pt^{III} complex **2** is 16.4 kcal/mol higher in energy than the reactants **1** and SiH_4. This, and the high activation energy of 23.6 kcal/mol for the initial reaction step, seems to be the reason why no reaction is observed between **1** and $HSiMe_2Ph$.

Reaction of SiH_4 with cis-[PtMeCl(P∩N)] (3)

The activation energy required to form $\mathbf{TS}_{3-4}$ (22.7 kcal/mol; Figure 2) is similar to that for *trans*-[PtMeCl(P∩N)]. The formed Pt−Si bond in $\mathbf{TS}_{3-4}$ (2.736 Å) and the Pt−H bond (1.827 Å) are much longer than the bonds in the corresponding complex $\mathbf{TS}_{1-2}$ in the previous reaction. This means that the interaction of the SiH_4 molecule with the platinum center is weaker. This is also reflected in a shorter Pt−N bond length of 2.248 Å. The reaction of **3** with SiH_4 eventually results in the six-coordinate Pt^{III} complex **4**, releasing 13.1 kcal/mol. Complex **4**, with the silyl ligand *trans* to Cl, is lower in energy than isomer **1** with the silyl ligand *trans* to a methyl ligand.

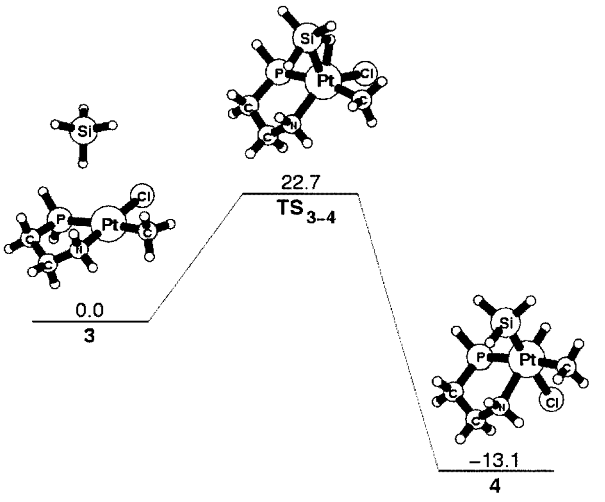


Figure 2. Reaction for the reaction of SiH_4 with **3**; energies in kcal/mol

It appears that the formation of *cis*-[PtMeCl(P∩N)] is necessary for the catalytic reaction to occur. The energy difference between the more stable *trans*-[PtMeCl(P∩N)] (**1**) and *cis*-[PtMeCl(P∩N)] (**3**) is 9.7 kcal/mol, which means that both isomers could be present in the equilibrium. This is in agreement with the fact that hydridosilanes do not react with [PtMeCl(P∩N)], since the activation energy for the reaction of the hydridosilane (22.7 kcal/mol) is quite high. However, when CCl_4 is present, a Cl/H exchange reaction can occur giving the catalytic cycle.

Catalytic Cycle

The mechanism of the Cl/H exchange reaction is examined in this section. The complete cycle was modeled in four steps as described in the following sections. In this part of the work, a much simpler model was used to describe the involved complexes — the *P,N*-chelating ligand was replaced by a PH_3 and an NH_3 ligand, and method II was used.

Oxidative Addition of SiH_4 to $[PtMeCl(PH_3)(NH_3)]$ (5)

The starting point is the catalytic active complex **5** (Figure 3), which is analogous to the previously discussed *cis*-[PtMeCl(P∩N)] (**3**). Complex **5** reacts with SiH_4 to form the transition state $\mathbf{TS}_{5-6}$. The energy required is 24.5 kcal/mol. In $\mathbf{TS}_{5-6}$ a Pt−Si bond of 2.739 Å and a Pt−H bond of 1.822 Å are formed and, as a result, the Si−H bond is stretched to 1.601 Å. The Pt−N bond length is 2.248 Å, therefore the addition of SiH_4 to $\mathbf{TS}_{5-6}$ happens when the *P,N*-ligand is closed. The relaxation of $\mathbf{TS}_{5-6}$ leads to the octahedral Pt^{III} complex $[Pt(Me)H(SiH_3)Cl(PH_3)(NH_3)]$ (**6**). Upon formation of the six-coordinate complex the Pt−Si and Pt−H bonds are shortened to 2.353 and 1.560 Å, respectively, while all other bonds are lengthened. This frees 35.5 kcal/mol, and therefore the energy of **6** is 11.0 kcal/mol lower than that of the starting compounds. Up to this point, the reaction profile is very similar to that discussed before (Figure 3), which shows that the simplification introduced by replacing the chelating $H_2NCH_2CH_2PH_2$ ligand by single NH_3 and PH_3 ligands does not affect the outcome of the calculations very much.

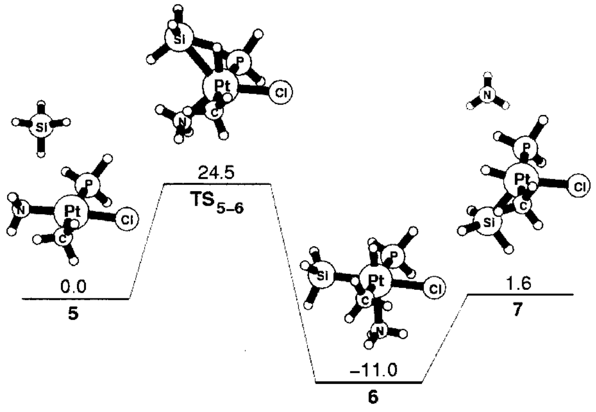


Figure 3. Reaction profile for the oxidative SiH_4 addition to **5**; energies in kcal/mol

The only way for **6** to undergo further reaction is by loss of the NH_3 ligand, which in the real system is the opening of the *P,N*-chelate. The relaxation of **6** after eliminating the NH_3 ligand leads to $[Pt(Me)H(SiH_3)Cl(PH_3)]$ (**7**) which can be described as a distorted trigonal bipyramid. The formation of **7** from **6** is endothermic, and an energy of 12.6 kcal/mol is required for this process.

Reductive H_3SiCl Elimination from 7

The transition state $\mathbf{TS}_{7-8}$ (Figure 4) is formed from **7** by the reorientation of the SiH_3 group towards the chloro ligand, with concomitant increase of the Pt−Si bond length from 2.336 to 2.615 Å and that of the Pt−Cl bond from

2.423 to 2.554 Å. The other bond lengths are shortened. The formation of a Si−Cl bond is observed, with a bond length of 2.303 Å in the transition state.

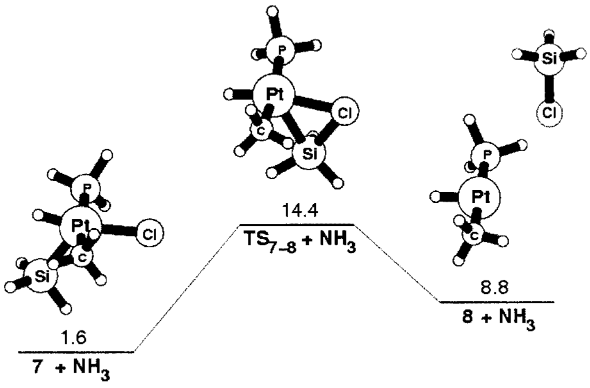


Figure 4. Reaction profile for the reductive H_3SiCl elimination from **7**; energies in kcal/mol

The three-coordinate complex [PtMeH(PH_3)] (**8**) is obtained by elimination of H_3SiCl from TS_{7-8}. An energy of 7.2 kcal/mol is required to eliminate H_3SiCl from **7**. The hydrido ligand in the trigonal-planar complex **8** is *cis* to the phosphorus atom.

Oxidative CH_3Cl Addition to 8

In $\mathbf{TS}_{8-9}$, formed from the oxidative addition of CH_3Cl to **8** (Figure 5), the C−Cl bond is stretched from 1.806 Å in CH_3Cl to 2.284 Å and new Pt−C and Pt−Cl bonds develop (Pt−C: 2.575 Å; Pt−Cl: 2.501 Å). The Pt−P, Pt−C and Pt−H bond lengths are slightly lengthened. The formation of $\mathbf{TS}_{8-9}$ requires 24.9 kcal/mol, which is quite high. On the other hand the relaxation to [Pt(Cl)$Me_2H(PH_3)$] (**9**) frees 36.4 kcal/mol. The five-coordinate complex **9** is a result of the reorientation of the incoming CH_3 group.

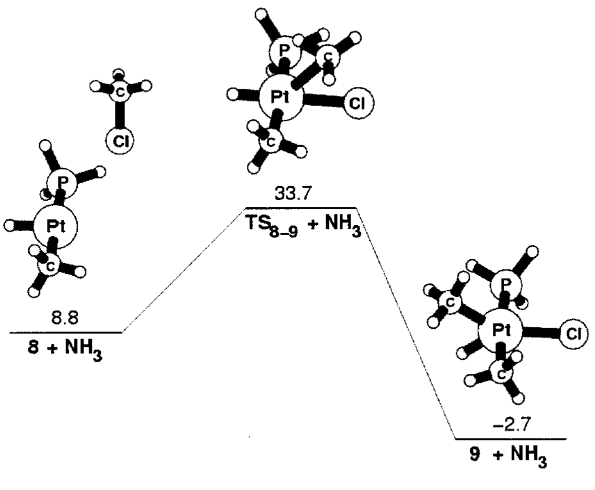


Figure 5. Reaction profile for the oxidative CH_3Cl addition to **8**; energies in kcal/mol

Reductive CH_4 Elimination from 9

The final step, the reductive CH_4 elimination, starts from the five-coordinate complex **9** (Figure 6). Only minor geometric changes are required to form $\mathbf{TS}_{9\text{-}10}$, where the new C−H bond is formed (1.552 Å). The related Pt−H and Pt−C bonds are stretched to 1.585 Å and 2.181 Å respectively. The Cl−Pt−H angle is opened from 139.9° to 153.1° and the Cl−Pt−C angle from 147.6° to 161.2°. An energy of 2.5 kcal/mol is freed by dissociating the CH_4 molecule and, as a result, the three-coordinate complex [PtMeCl(PH_3)] (**10**) is formed.

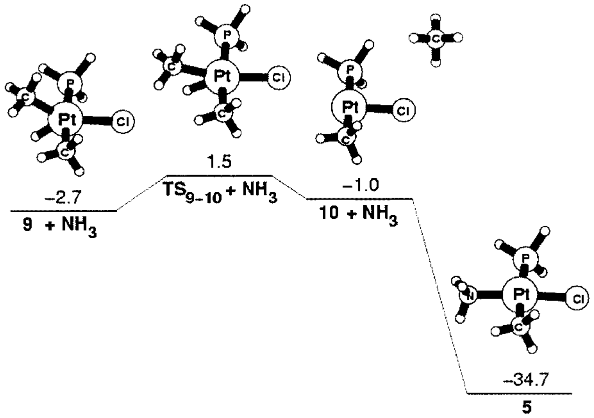


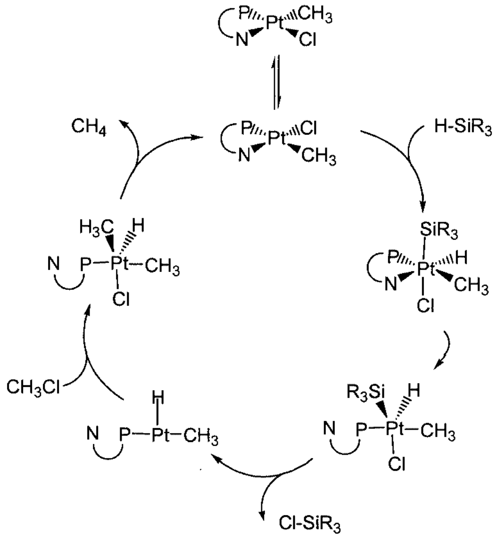
Figure 6. Reaction profile for the reductive CH_4 elimination from **9**; energies in kcal/mol

To close the catalytic cycle, the re-coordination of the NH_3 group is needed (representing the closing of the *P,N*-ligand in the real system). This frees 33.7 kcal/mol and results in the re-formation of the four-coordinate complex **5**, which is the starting point of the catalytic cycle.

Conclusions

Since no intermediates were observed in the [PtMeCl(P∩N)]-catalyzed C−Cl/Si−H exchange between H_xCCl_{4-x} and $HSiMe_2Ph$,[1] theoretical calculations were carried out to elucidate the reaction mechanism and the stereochemistry of the intermediates. Based on these calculations, the mechanism shown in Scheme 1 is proposed, which largely corresponds to our initial suggestion.[1]

The formation of *cis*-[PtMeCl(P∩N)] (**3**) is obviously necessary for the catalytic reaction to occur. This isomer is 9.7 kcal/mol less stable than *trans*-[PtMeCl(P∩N)] (**1**), but its reaction with SiH_4 turns out to be energetically more favorable. The oxidative addition of SiH_4 results in an octahedral Pt^{III} complex, therefore it is not necessary for the NH_3 ligand (corresponding to the amino group of the *P,N*-chelating ligand in the real system) to be eliminated for the reaction to occur. De-coordination of the amino group only occurs after the addition of the silane, and all the subsequent steps in the catalytic cycle — elimination of SiH_3Cl, addition of CH_3Cl and elimination of CH_4 — proceed via three- or five-coordinate complexes. The amino group is re-



Scheme 1

coordinated in the final step, where the starting complex *cis*-[PtMeCl(P∩N)] (**3**) is regenerated.

The methyl group stays *trans* to phosphorus during the whole reaction. This is obviously a particularly favorable orientation of the ligands, since five-coordinate intermediates with analogous geometries have also been found in the reaction of [PtMe$_2$(P∩N)] and [Pt(SiH$_3$)Me(P∩N)] with chlorinated hydrocarbons and chlorosilanes.[5]

A final point to be made is the importance of the hydrido-methyl intermediate **8**. We have recently postulated such an intermediate, based on spectroscopic evidence, in the reaction of [PtMe$_2$(P∩N)] with HSiEt$_3$ and HSiMePh$_2$. In the first step of this reaction [PtMeH(P∩N)] and Me-SiR$_3$ are formed; the hydrido-methyl complex may react with a second molecule of silane to give [Pt(SiR$_3$)-Me(P∩N)] and H$_2$.[6]

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.[7,8] The relativistic effective core potential and basis set of Preuss and co-workers (which is available in the Gaussian 98 software package as the SDD basis set) was used in Methods I and II for platinum.[9] In Method I, the 6-311G++(d) basis set was used for all atoms, except platinum. In Method II, the 6-31G++(d) basis set was used for all atoms, except platinum. Vibrational mode analyses were carried out to confirm that optimized geometries on the potential-energy surfaces correspond to a local minimum without an imaginary frequency mode, or a saddle point with only one imaginary mode. Corrections for zero-point vibrational energies were taken into account in the stationary structures obtained. All the calculations were carried out with the Gaussian 98 package.[10]

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