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Account

# Transformations of organosilanes by Pt(II) complexes with hemilabile P,N-chelating ligands

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## Abstract

The article reviews the author's own work to enhance the reactivity of Pt(II) complexes towards organosilanes by employing hemilabile chelating ligands $R_2N–R'–PPh_2$ ($P\cap N$). Variation of the groups R and R′ allows to influence the reactivity of the complexes. $(P\cap N)PtMe_2$ reacts with $HSiR_3$ to yield the complexes $(P\cap N)Pt(SiR_3)Me$ and $(P\cap N)Pt(SiR_3)_2$ along with $MeSiR_3$ and methane. An excess of $HSi(OMe)_3$ is catalytically converted into $Si(OMe)_4$. $P\cap N$-substituted Pt(II) complexes also catalyze the formation of disiloxanes from $HSiR_3$ and C–Cl/Si–H exchange reactions. The latter reaction yields dechlorinated hydrocarbons and chlorosilanes. Reaction of $(P\cap N)PtMe_2$ with $ClSiPhMe_2$ results in the stoichiometric formation of $Ph_2Me_4Si_2$, the Pt(IV) complex $(P\cap N)Pt(Cl)Me_3$ and the Pt(II) complex $((P\cap N)Pt(Cl)Me$. The corresponding bisphoshine complex $(dppe)PtMe_2$ undergoes none of these reactions. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Silicon; Platinum; Silyl complexes; Catalysis; Exchange reactions

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## 1. Introduction

Hemilabile ligands are used in coordination chemistry to enhance the reactivity of metal complexes. These are chelating ligands with two different donor centers. The activating effect of such ligands results from the different metal–ligand bond strengths, while one atom remains coordinated to the metal, the more weakly bonded second center de-coordinates more easily and thus creates a vacant coordination site at the metal. This donor atom nevertheless stays in the proximity of the metal because it is tethered to the other donor center. After coordination of a substrate molecule and its reaction at the metal center, the dangling center may re-coordinate with concomitant elimination of a product species. Hemilabile ligands thus promote both oxidative addition and reductive elimination reactions, and many catalytic reactions in organometallic chemistry benefit from their use [1].

Another effect associated with this kind of chelate ligands is not often discussed. Due to the different donor/acceptor properties of the two Lewis basic centers, an unsymmetrical electronic situation is created at the metal, i.e. the sites *trans* to the two donor atoms have different electronic properties. For example, square planar complexes of late transition metals bearing P,N-chelating ligands $(P\cap N)MX_2$ (M = Pd, Pt; X = halide, alkyl, etc.) are known to allow highly stereoselective substitution reactions of the ligands X (see Refs. [2–4] for selected examples).

In the chemistry of metal–silicon compounds, hemilabile auxiliary ligands are hardly used. This is rather surprising because oxidative addition–reductive elimination reactions play a much larger role than in the organometallic chemistry of carbon compounds. In this article, we give an account on our recent investigations to enhance the reactivity of Pt(II) complexes towards silanes by using hemilabile, $\kappa^2$-P,N (chelating) ligands (denoted as $P\cap N$). We will show that the use of such ligands has indeed a remarkable effect on both the outcome and the rate of these reactions.

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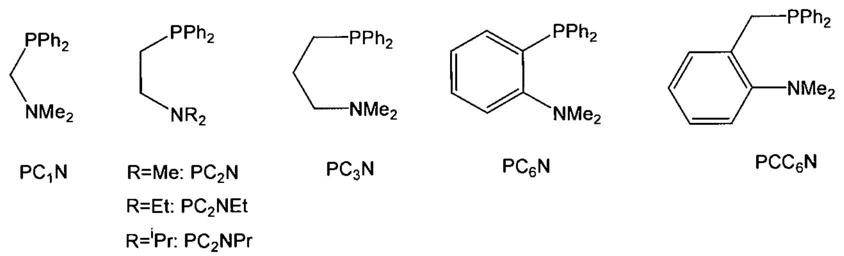
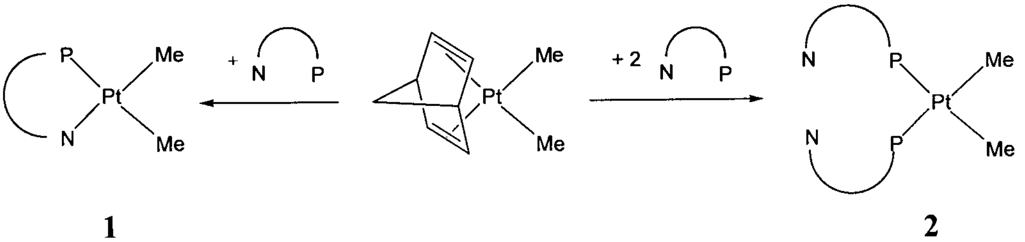


Scheme 1.

## 2. Results and discussion

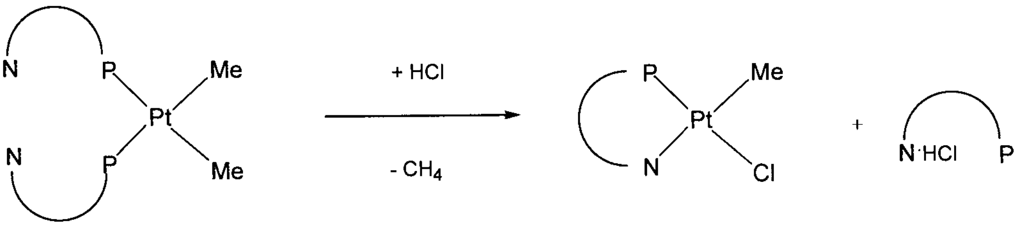
A series of Pt(II) dimethyl complexes with hemilabile P,N-chelating ligands, (P∩N)PtMe$_2$ (**1**), was prepared by reaction of ($\eta^4$-2,5-norbornadiene)dimethyl platinum(II), (nbd)PtMe$_2$, with P∩N (Eq. (1)) [5]. The strength (or weakness) of the Pt–N interaction can be modified by varying the size and flexibility of the chelate ring, the bulkiness of the substituents at nitrogen and the basicity of the nitrogen donor center (Scheme 1). When the Pt–N interaction becomes too weak, another P∩N is added to **1** and complexes **2** are formed instead. This reaction was observed for PC$_1$N. The formation of [($\kappa^1$-P)–Me$_2$NCH$_2$PPh$_2$]$_2$PtMe$_2$ is in contrast with the reactions of dppm-substituted Pt(II) complexes (dppm = Ph$_2$PCH$_2$PPh$_2$) in which chelatation of the dppm ligand is retained. The corresponding complex (PC$_1$N)PtMe$_2$ is possibly too unstable because the strain of a four-membered ring cannot be compensated by the weak Pt–N bond.



**1** **2**

(1)

However, the complex [($\kappa^1$-P)–Me$_2$NCH$_2$PPh$_2$]$_2$-PtMe$_2$ was converted to [($\kappa^2$-P,N)–Me$_2$NCH$_2$PPh$_2$]Pt-(Me)Cl upon reaction with HCl (Eq. (2)) [6].



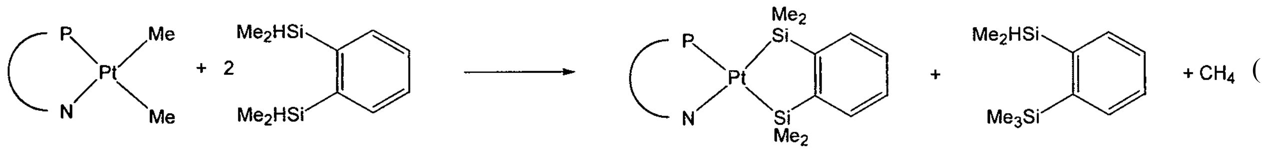
(2)

The Pt–N distances of selected complexes **1** (Table 1) are in the range of the Pt–P distances—or even longer—despite the smaller bond radius of nitrogen compared with phosphorus. The weak Pt–N interaction results in a strengthening of the Pt–Me bond *trans* to N; the Pt–C bond lengths *trans* to N are distinctly shorter than that *trans* to P. The structures show that **1** can be considered T-shaped complexes (R$_3$P)PtMe$_2$, in which the fourth coordination site is screened by a more or less weakly bonded amino group.

Table 1
Typical bond lengths (in pm) and angles (°) in complexes (P∩N)PtMe$_2$

| P∩N | PC$_2$N | PC$_2$NPr | PC$_3$N |
|---|---|---|---|
| *Bond lengths* | | | |
| Pt–C (*trans* P) | 206.9(8) | 210.2(6) | 210.3(9) |
| Pt–C (*trans* N) | 203.7(9) | 204.5(7) | 203.4(1) |
| Pt–N | 221.0(7) | 230.2(5) | 223.9(8) |
| Pt–P | 224.3(2) | 224.6(2) | 224.2(2) |
| *Bond angles* | | | |
| N–Pt–P | 84.6(1) | 84.0(1) | 95.5(2) |
| P–Pt–C (*cis*) | 96.5(2) | 93.2(3) | 89.4(4) |
| N–Pt–C (*cis*) | 92.0(2) | 96.7(2) | 91.0(4) |
| C–Pt–C | 87.0(3) | 86.0(3) | 84.1(5) |

Reaction of (P∩N)PtMe$_2$ (P∩N = PC$_1$N, PC$_2$N, PC$_6$N) with 1,2-bis(dimethylsilyl)benzene yielded cyclic bis(silyl) complexes (Eq. (3)) [5]. This reaction is remarkable for two reasons.



(3)

1. The corresponding chelating bisphosphine complex (dppe)PtMe$_2$ did not react with 1,2-bis(dimethylsilyl)benzene under the same conditions, i.e. the P$\cap$N chelating ligands enhance the reactivity of the dimethyl platinum complex considerably.
2. For the complete reaction of the dimethyl complexes, two equivalents of 1,2-bis(dimethylsilyl)benzene were necessary, and one equivalent of 1-dimethylsilyl-2-trimethylsilyl-benzene was formed as a by-product along with methane. The latter finding implies that the formation of the bis(silyl) complex from the hydrogenosilane was not a simple methyl–silyl exchange with the concomitant formation of methane but instead a more complex process.

The X-ray structure analysis of the cyclic bis(silyl) complex (Fig. 1) shows again that the weak Pt–N interaction results in a strengthening of the bond *trans* to nitrogen; the Pt–Si bond length *trans* to N is distinctly shorter than that *trans* to P.

Formation of both methane and a methylsilane, with the methyl groups originating from the Pt–Me ligands, was also observed when other hydrogenosilanes were reacted with (P$\cap$N)PtMe$_2$ (again, (dppe)PtMe$_2$ did not react) [7,8]. The reactivity of the complexes depends on the employed P$\cap$N ligand and increases in the order PC$_2$NPr $\gg$ PC$_3$N $\gg$ PC$_2$Net > PC$_2$N.

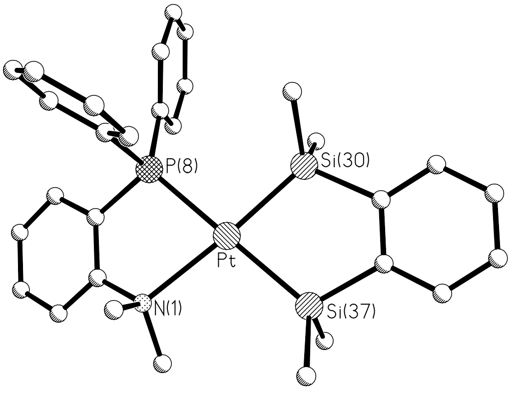
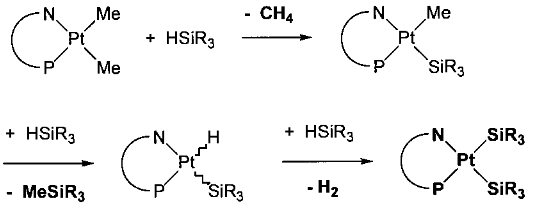


Fig. 1. Molecular structure of [($\kappa^2$-P,N)–Me$_2$NC$_6$H$_4$PPh$_2$]Pt[($\kappa^2$-Si,Si)–Me$_2$SiC$_6$H$_4$SiMe$_2$]. Pt–Si (*trans* P) 237.2(2), Pt–Si (*trans* N) 230.4(2), Pt–N 236.8(5), Pt–P 230.3(2) pm, N–Pt–P 79.1(1), Si–Pt–Si 82.51(6)°.



Scheme 2.

The experimental findings suggest the mechanism depicted in Scheme 2 (the obtained products are drawn in bold). Addition of the hydrogenosilane to the Pt atom with concomitant elimination of methane leads to the formation of a methyl(silyl) complex, which was spectroscopically observed in some reactions. The geometry of the methyl(silyl) complex (P$\cap$N)Pt(Me)SiR$_3$ (C *trans* to P) was clearly derived from the NMR spectra and is a consequence of the much larger *trans* effect of the silyl ligand compared with methyl. According to MO calculations, the T-shaped complex (H$_3$P)Pt(CH$_3$)SiH$_3$ with Si *trans* to P is 47.8 kJ mol$^{-1}$ higher in energy than the isomer with C *trans* to P [9].

After addition of the second silane molecule to the methyl(silyl) complex, the remaining methyl ligand is not eliminated as methane but instead as methylsilane to give the corresponding hydrido(silyl) complex. Reductive elimination of MeSiR$_3$ from the intermediate methyl(silyl) complex and formation of a Pt(0) intermediate can be ruled out because the observed methyl(silyl) complexes are stable in the absence of HSiR$_3$. The elimination of a methylsilane from intermediate Pt(IV) complexes containing hydrido, methyl and silyl ligands is rather surprising. However, related reactions have already been observed. Methane and MeSiEt$_3$ were obtained in a 4:1 ratio when (Me$_3$P)$_3$Ir(Me)(H)SiEt$_3$ was heated to 100 °C [10], and treatment of [($\kappa^2$-P,Si)–Me$_2$SiCH$_2$CH$_2$PPh$_2$](Me$_3$P)$_2$Ir(H)Me with RSiH$_3$ led to the formation of [($\kappa^2$-P,Si)–Me$_2$SiCH$_2$CH$_2$PPh$_2$]-(Me$_3$P)$_2$IrH$_2$ and MeRSiH$_2$ [11].

The final step in Scheme 2 is the reaction of the intermediate hydrido(silyl) complex with a third equivalent of the hydrogenosilane, followed by elimination of H$_2$, which yields the bis(silyl) complex. The fact that hydrido(silyl) complexes were not observed does not contradict this mechanism, as their reaction with the silane is probably too fast to be observed. The formation of bis(silyl) complexes from hydrogenosilanes and hydrido silyl complexes by hydrogen elimination is a known reaction in the chemistry of metal–silicon compounds [12].

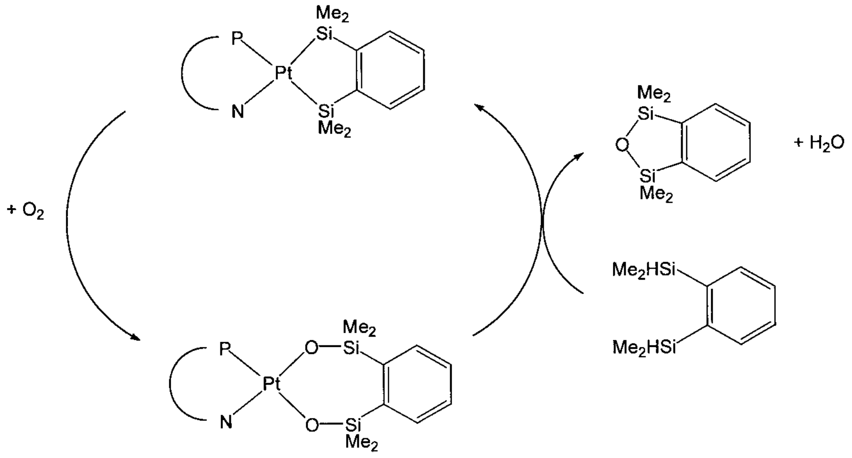
In the reactions of (P$\cap$N)PtMe$_2$ with hydrogenosilanes, other organosilicon products were identified in addition to the methylsilane. For example, [($\kappa^2$-P,N)–Me$_2$NCH$_2$CH$_2$PPh$_2$]PtMe$_2$ reacted with HSi-(OMe)$_3$ to yield the Pt(II) complexes [($\kappa^2$-P,N)–Me$_2$-

$NCH_2CH_2PPh_2]Pt[Si(OMe)_3]Me$ and $[(\kappa^2\text{-}P,N)\text{–}Me_2NCH_2CH_2PPh_2]Pt[Si(OMe)_3]_2$ along with methyltrimethoxysilane, tetramethoxysilane, and small amounts of pentamethoxydisiloxane and hexamethoxydisiloxane. The formation of $Si(OMe)_4$ is catalytic, i.e. when $HSi(OMe)_3$ is added to the reaction mixture once the reaction is completed, formation of $Si(OMe)_4$ is resumed [7]. The redistribution of methyl, phenyl and silyl groups was also observed [8].

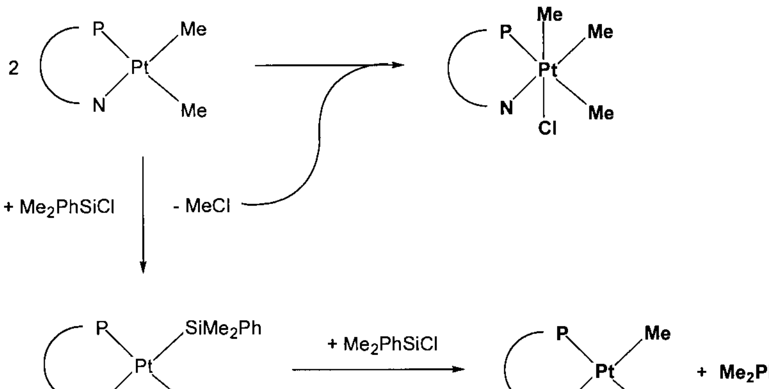
The mechanism of the $Si(OMe)_4$ formation is still unclear. Scrambling reactions of silicon substituents in metal silyl complexes are not uncommon and are usually explained by intermediate silylene complexes [13]. Formation of a $L_nPt[{=}Si(OMe)_2][Si(OMe)_3](OMe)$ intermediate by migration of one methoxy group from silicon to the metal is possibly facilitated by the hemilabile P∩N ligand. $Si(OMe)_4$ is then formed by reductive elimination of the methoxy and the $Si(OMe)_3$ ligands. An alternative would be a direct transfer of a methoxy group between two neighboring $Si(OMe)_3$ ligands [14]. This sequence of reactions must occur at one of the intermediate complexes, because the bis(silyl) complex $[(\kappa^2\text{-}P,N)\text{–}Me_2NCH_2CH_2PPh_2]Pt[Si(OMe)_3]_2$ is stable after completion of the reaction.

When (P∩N)$PtMe_2$ was reacted with 1,2-bis(dimethylsilyl)benzene, small amounts of 1,1,3,3-tetramethyl-4,5-benzo-2-oxa-1,3-disilacyclopent-4-ene were formed as a by-product due to the presence of traces of oxygen. A closer investigation of this reaction revealed that the primarily formed bis(silyl) complex $(PC_6N)Pt[o\text{-}(Me_2Si)_2C_6H_4]$ reacted with oxygen to give the corresponding bis(siloxy) complex $(PC_6N)Pt[o\text{-}(OMe_2Si)_2\text{-}C_6H_4]$, which was isolated and structurally characterized. In the presence of air and a catalytic amount of (P∩N)$PtMe_2$, 1,2-bis(dimethylsilyl)benzene was catalytically converted to the cyclic siloxane (Scheme 3) [15]. This is the first example that siloxy complexes were observed as intermediates in a catalytic silane oxidation reaction.

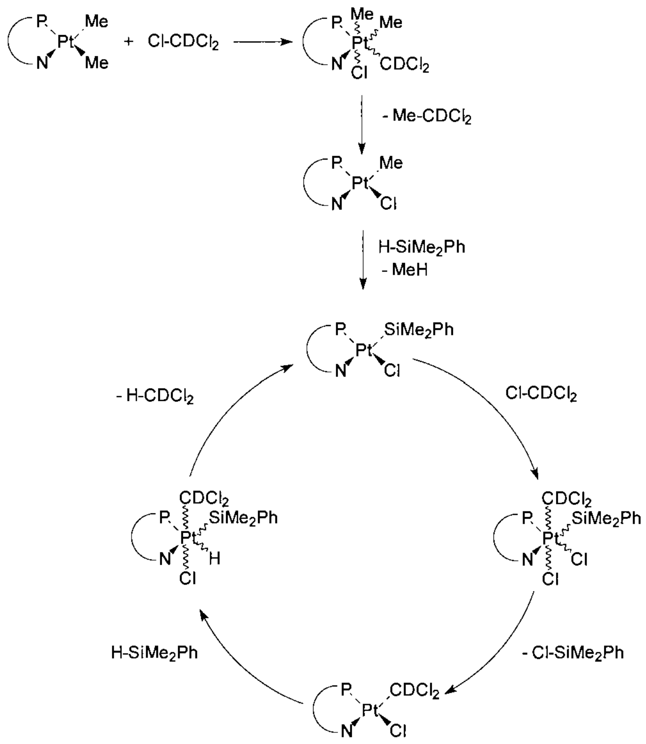
The reactivity of $[(\kappa^2\text{-}P,N)\text{–}Ph_2PCH_2CH_2CH_2NMe_2]\text{-}PtMe_2$ towards hydrogenostannanes was completely different. Instead of the methyl–silyl exchange and redistribution reactions observed for hydrogenosilanes, catalytic dehydrogenative dimerization occurred when



Scheme 3.



Scheme 4.



Scheme 5.

$HSnBu_3$ was reacted (Eq. (4)). The reaction must proceed by a different mechanism because no $MeSnBu_3$ was observed. This reaction is also catalyzed by $(dppe)PtMe_2$, however, the $(P\cap N)PtMe_2$ complex is more active [8].

$$2HSnBu_3 \xrightarrow{\text{cat. }(P\cap N)PtMe_2} Sn_2Bu_6 + H_2 \qquad (4)$$

The complexes $(P\cap N)PtMe_2$ not only activate Si–H bonds but also Si–Cl bonds. For example, $PC_2N$ was reacted stoichiometrically with $PhMe_2SiCl$ to give the disilane $Ph_2Me_4Si_2$ quantitatively, and the Pt(IV) complex $PC_2N$ and the Pt(II) complex $PC_2N$ in a 1:4 ratio [6]. A possible reaction mechanism is shown in Scheme 4 (the observed products are drawn in bold).

The overall mechanism is probably very much related to the mechanism of the hydrogenosilane reaction (Scheme 2). In the first step, the Si–X ($X = H$, Cl) bond is added to the platinum atom, and the corresponding methyl(silyl) complex is formed by $CH_3X$ elimination. Addition of a second Si–Cl bond may lead to an intermediate with the same overall composition, i.e. $(P\cap N)Pt(Me)(SiR_3)_2X$. While $MeSiR_3$ is eliminated for $X = H$, a disilane is eliminated for $X = Cl$; $Me_3SiPh$ was not observed in the reaction of $PhMe_2SiCl$. A possible explanation for this different elimination behavior from the postulated Pt(IV) intermediate may be a different stereochemistry caused by a different *trans*-preference of Cl and H. The Pt(IV) product $[(\kappa^2\text{-}P,N)\text{–}Ph_2PCH_2CH_2NR_2]Pt(Cl)Me_3$ is formed by reaction of methyl chloride, eliminated in the first step reacts with the starting dimethyl complex as verified by a control experiment.

Although this is not the topic of this account, it should be mentioned in passing that the complexes $(P\cap N)PtMe_2$ not only activate Si–Cl bonds, but also C–Cl bonds, and a very interesting spectrum of products, i.e. the complexes $(P\cap N)Pt(Cl)Me$, $(P\cap N)Pt(Cl)Me_3$ and $(P\cap N)Pt(Cl)C(Cl){=}CH_2$, was found in their reaction with $CCl_4$ [16]. The activation of both Si–H and C–Cl bonds in the same reaction led to the development of a highly efficient catalytic Si–H/C–Cl exchange reaction (Eq. (5)) [17].

$$PhMe_2SiH + HCCl_3 \xrightarrow{\text{cat. }(P\cap N)PtMe_2} PhMe_2SiCl + H_2CCl_2/CH_3Cl/CH_4 \qquad (5)$$

The chloro(methyl) complexes $[(\kappa^2\text{-}P,N)\text{–}Ph_2PCH_2CH_2NR_2]Pt(Cl)Me$ ($R = Me$, Et, $^i$Pr), which are obtained by reaction of $(P\cap N)PtMe_2$ with HCl or (nbd)Pt(Cl)Me with $P\cap N$ [18], are even more active as catalysts than the dimethyl complexes. The catalytic activity increases in the series $R = Me < Et < {}^iPr$, i.e. parallel to the weakening of the Pt–N interaction. This catalytic reaction is again not observed with $(dppe)PtMe_2$. For spectroscopic reasons, the only employed silane so far was $PhMe_2SiH$. However, we expect other silanes to react similarly. When this account was written, the reaction was tested for allyl chloride, $Ph_3CCl$, $CHCl_3$, 1,1,2,2-tetrachloroethane and $H_2CCl_2$; the reactivity of the chlorides decreased in the given order. A consequence of decreasing reactivity of the chlorides is that $CDCl_3$ can be selectively converted in mono-deuterated $HDCCl_2$ when the activity of the $(P\cap N)Pt(Cl)Me$ is properly tuned by choosing the right $P\cap N$ ligand.

A possible reaction mechanism leading to the Si–H/C–Cl exchange is given in Scheme 5. After the initial formation of the chloro(methyl) complex from the dimethyl complex, a chloro(silyl) complex is obtained by a methyl–silyl exchange reaction as discussed above. This complex is probably a member of the catalytic cycle, which proceeds through oxidative addition of a C–Cl bond and reductive elimination of the chlorosilane followed by oxidative addition of a Si–H bond and elimination of the C–H compound. Theoretical calculations have shown that the driving force for the overall reaction is the formation of the very stable Si–Cl bond [9]. New systems to convert critical halogen-containing organic compounds in to more innocent compounds based on this reaction can be envisaged.

## 3. Conclusions

The above results clearly demonstrate that metal-mediated stoichiometric or catalytic reactions of organosilanes can be promoted by employing hemilabile chelating ligands. The reactivity of the complexes can be somewhat varied by modifying the properties of the P,N-chelating ligand (kind and length of spacer group between P and N; substituents at *N*).

The calculated enthalpies for the reaction of $SiH_4$ with $[(\kappa^2\text{-P,N})\text{–}H_2PCH_2CH_2NH_2]PtMe_2$ ($\Delta E = -111.2$ kJ $mol^{-1}$) or $(H_3P)_2PtMe_2$ ($\Delta E = -103.3$ kJ $mol^{-1}$) to the corresponding methyl(silyl) complexes are very similar [9] (it can be assumed that the reaction enthalpy for $[(\kappa^2\text{-P,P})\text{–}H_2PCH_2CH_2PH_2]PtMe_2$ is of the same magnitude). Nevertheless, no reactions were observed between $(dppe)_2PtMe_2$ complexes and silanes, while the corresponding $(P \cap N)PtMe_2$ complexes react rapidly. This implies that the latter reaction is driven by the easier cleavage of the Pt–N bond.

The redistribution reactions mentioned above indicate that the opening of a coordination site not only promotes oxidative addition and possibly σ-bond metathesis reactions, but—different to carbon compounds—also induces migrations of silicon substituents with the concomitant formation of silylene complex intermediates. It was pointed out by Tilley et al. that the transfer of a silyl substituent from silicon to platinum is easier in three- than in four-coordinated complexes [19]. The formation of the three-coordinate complex is of course easier with a $P \cap N$ ligand than with two $PR_3$ or a bisphosphine ligand.

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