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Hydrodealkoxylation reactions of silyl ligands at platinum: reactivity of SiH_3 and SiH_2Me complexes†

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The platinum(II) complex [Pt(H)$_2$(dcpe)] (**1**; dcpe = 1,2-bis(dicyclohexylphosphino)ethane) reacts with an excess of the dialkoxymethylsilanes (HSiMe(OR)$_2$; R = Me, Et) to give the bis(silyl) complex [Pt(SiH$_2$Me)$_2$(dcpe)] (**3**) and trialkoxymethylsilanes by hydrodealkoxylation reactions. These rearrangements of the silyl ligands involve Si–O bond activations. The exchange of the alkoxy moieties against silicon-bound hydrogen atoms occurs stepwise. The intermediate complexes [Pt(H){SiMe(OEt)$_2$}(dcpe)] (**5**), [Pt{SiMe(OEt)$_2$}$_2$(dcpe)] (**6**), [Pt{SiHMe(OEt)}$_2$(dcpe)] (**7**) and [Pt{SiHMe(OMe)}$_2$(dcpe)] (**8**) were detected. Treatment of the complex **1** with an excess of dichloromethylsilane yields the bis(silyl) complex [Pt(SiMeCl$_2$)$_2$(dcpe)] (**9**). The hydrido silyl complex [Pt(H)(SiMeCl$_2$)(dcpe)] (**10**) was identified as an intermediate. The reactions of the complexes [Pt(SiH$_3$)$_2$(dcpe)] (**2**) and [Pt(SiH$_2$Me)$_2$(dcpe)] (**3**) with iodomethane lead to a transfer of the SiH$_3$ and SiH$_2$Me ligands. Methylsilane and dimethylsilane, respectively, as well as the platinum diiodo complex [Pt(I)$_2$(dcpe)] (**11**) were identified as main products.

Introduction

The oxidative addition of silicon–hydrogen bonds to transition-metal complexes and the formation of silyl complexes and/or silylene complexes are considered to be important key steps in transition-metal-mediated silylations, like hydrosilylation[1,2] and bis(silylation)[3] reactions as well as the redistribution of substituents at silanes.[4–9] In particular, the redistribution reactions can involve the cleavage of fairly stable Si–C, Si–O or Si–N bonds. For instance, titanocene complexes are reported to catalyse the redistribution of alkoxysilanes.[10] The reaction of dimethyltitanocene with tertiary alkoxysilanes to give the binuclear complex [Cp$_4$Ti$_2$(μ-HSiH$_2$)$_2$] involves the redistribution of silicon-bound alkoxy groups and hydrogen atoms at silyl ligands.[11–13] Though mechanistically, the reaction pathway of this conversion is speculative. Comparable rearrangement reactions of alkoxysilanes are known at hafnium and zirconium complexes.[14] The addition of alkoxysilanes HSiR′(OMe)$_2$ to the hafnium silyl chlorido complex [Hf{Si(SiMe$_3$)$_3$}(Cl)(Cp)(Cp*)] proceeds *via* a metal-mediated redistribution of the alkoxysilane and yields the complexes [Hf(SiH$_2$Me)(Cl)(Cp)(Cp*)] (R′ = Me) and [Hf(SiH$_3$)(Cl)(Cp)(Cp*)] (R′ = OMe).[14] Again the reaction steps for these rearrangements of the silyl ligand are unclear. Note also that Schmidbaur *et al.* reported a transition-metal-free conversion of aryl trialkoxysilanes into hydrogen rich arylsilanes ArSiH$_3$ and interesting RO/H ligand redistributions were found.[15,16] Beck and Benkeser reported a metal-mediated redistribution at silanes which involves an exchange of chloro and methyl groups.[17] Thus, chloroplatinic acid can catalyse the redistribution of SiMeR′$_3$ and HSiCl$_3$ yielding SiR′$_3$Cl and HSiMeCl$_2$ (R′ = alkyl) *via* Si–C bond cleavage reactions.

We reported on remarkable hydrodealkoxylation reactions which involve the formation of [Pt(SiH$_3$)$_2$(dcpe)] (**2**) after treatment of [Pt(H)$_2$(dcpe)] (**1**) with an excess of trialkoxysilanes (HSi(OR)$_3$; R = Me, Et) at room temperature.[18] The identification of intermediate silyl complexes by NMR spectroscopy gave an insight into the rearrangement reactions at silyl ligands and revealed a repetitive activation of Si–O bonds at silyl ligands and the generation of free tetraalkoxysilane. The two SiH$_3$ ligands are formed stepwise. Intermediate complexes bearing Si(OR)$_3$, SiH(OR)$_2$ and SiH$_2$(OR) ligands were detected.

Herein we present the synthesis of [Pt(SiH$_2$Me)$_2$(dcpe)] (**3**) by hydrodealkoxylation reactions of dialkoxymethylsilanes (HSiMe(OR)$_2$; R = Me, Et). The methyl moiety of the dialkoxymethylsilyl ligands does not undergo any exchange reactions like the alkoxy moiety. Treatment of the complexes [Pt(SiH$_3$)$_2$(dcpe)] (**2**) and [Pt(SiH$_2$Me)$_2$(dcpe)] (**3**) with iodomethane led to the formation of methylsilane and dimethylsilane, respectively.

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Results and discussion

Synthesis of [Pt(SiH$_2$Me)$_2$(dcpe)] (3) by hydrodealkoxylation reactions

Treatment of the platinum dihydrido complex [Pt(H)$_2$(dcpe)] (**1**), which was generated *in situ* by a reaction of [Pt(Cl)$_2$(dcpe)] (**4**) with lithium triethylborohydride,[18–21] with an excess of dimethoxymethyl- or diethoxymethylsilane at room temperature yielded solely the platinum bis(silyl) complex [Pt(SiH$_2$Me)$_2$(dcpe)] (**3**) and trimethoxymethylsilane or triethoxymethylsilane, respectively (Scheme 1). The generation of SiMe(OR)$_3$ (R = Me, Et) was confirmed by ^{29}Si{^{1}H} and ^{1}H,^{29}Si HMBC NMR spectroscopy.[22]

This reaction pattern is in contrast to well-known Si–H bond activation reactions at platinum complexes which involve the formation of hydrido silyl complexes after elimination of H$_2$.[1,2,23–28] Note that the reaction of [Pt(PEt$_3$)$_3$] with an excess of triethoxysilane yields the isomeric compounds *trans*- and *cis*-[Pt(H){Si(OEt)$_3$}(PEt$_3$)$_2$].[24]

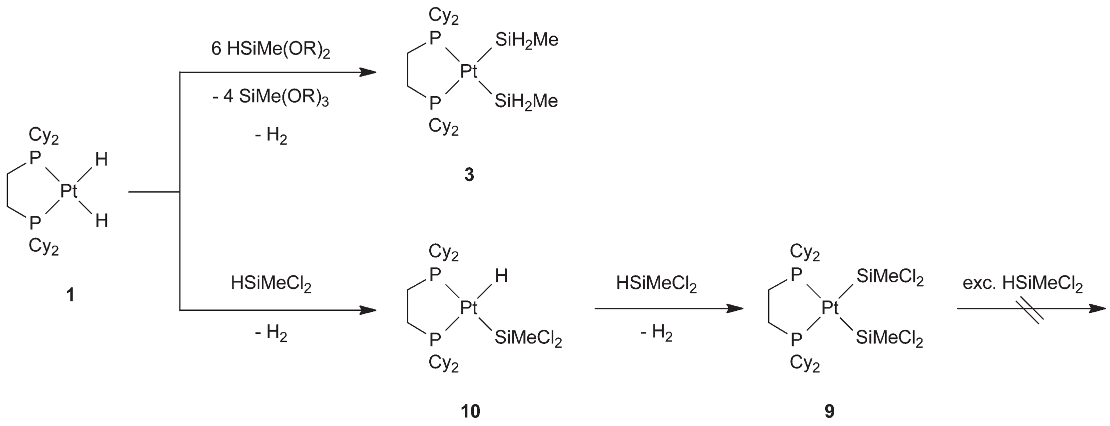
Complex **3** is soluble in tetrahydrofuran and insoluble in hexane. In benzene or toluene complex **3** precipitates after one day as a solid powder or crystallizes. Compound **3** was characterized by NMR spectroscopy, LIFDI mass spectroscopy, single-crystal X-ray analysis and elemental analysis.

Complex **3** has been synthesized before by Fink *et al.* on a different route.[29] Reaction of [Pt(H)$_2$(dcpe)] with 1,2-dimethyldisilane at −25 °C leads initially to a hydrido disilanyl complex by Si–H bond activation. After warming up to room temperature the silyl ligand migrates and the complex **3** is formed. The NMR data of **3** were reported, but some values differ from our data significantly due to a different solvent which was used and some coupling constants were missing.[29]

The ^{31}P{^{1}H} NMR spectrum of **3** shows a singlet with ^{195}Pt satellites at δ = 73.8 ppm. The phosphorus–platinum coupling constant of $^1J_{P,Pt}$ = 1558 Hz is in accordance with a platinum(II) metal centre.[30,31] The silicon-bound hydrogen atoms give rise to a multiplet with satellites in the ^{1}H NMR spectrum at δ = 4.04 ppm which transforms into a quartet with ^{29}Si and ^{195}Pt satellites upon phosphorus decoupling. The hydrogen–silicon coupling constant of $^1J_{H,Si}$ = 161 Hz proves the presence of a SiH unit. The hydrogen–hydrogen coupling constant of $^3J_{H,H}$ = 4.5 Hz is also found for the signal at δ = 0.31 ppm for the hydrogen atoms of the methyl groups. The chemical shifts in the ^{1}H NMR spectrum are comparable to those of other complexes with SiH$_2$Me or SiHMe$_2$ ligands.[11,32–34] The ^{29}Si{^{1}H} NMR spectrum displays a doublet of doublets at δ = −40.1 ppm due to the coupling of the silicon atoms to the phosphorus atoms in the *trans* and *cis* position. The data are in accordance with the cross-peaks found in the ^{1}H, ^{29}Si HMBC NMR and ^{1}H, ^{31}P HMBC NMR spectra. The LIFDI MS spectra reveals a peak at *m*/*z* = 707 which can be assigned to the molecular ion [M]$^+$ and a peak at *m*/*z* = 662 which corresponds to the fragment ion [M − {SiH$_2$Me}]$^+$.

The molecular structure of **3** was confirmed by single-crystal X-ray analysis (Fig. 1). Selected bond lengths and angles are summarized in Table 1. The structure reveals a distorted square-planar arrangement of the chelating phosphine ligand and the two silyl ligands at the platinum centre. The silicon-bound hydrogen atoms were located in the difference Fourier map and were refined isotropically. The platinum–silicon bond lengths of 2.3724(14) Å and 2.3539(13) Å are comparable to those in the complex [Pt(SiHMe$_2$)$_2$(dcpe)] [2.3741(9) Å, 2.3654(10) Å],[32] which was synthesized by the reaction of [Pt(η^2-C$_2$H$_4$)(dcpe)] with 1,1,2,2-tetramethyldisilane, but are longer compared to those in the complex [Pt(SiH$_3$)$_2$(dcpe)] (**2**) [2.3500(7) Å, 2.3408(6) Å].[18] The Pt–P bond lengths of 2.3152(13) Å and 2.3181(12) Å are similar to those of [Pt(SiHMe$_2$)$_2$(dcpe)] [2.3125(8) Å, 2.3213(8) Å][32] and slightly longer as the corresponding bonds in the complex **2** [2.3045(5) Å, 2.3075(6) Å].[18] The bite angle of the chelating phosphine ligand P1–Pt1–P2 is 86.76(4)° and compares well with those reported for [Pt(SiHMe$_2$)$_2$(dcpe)] [85.94(3)°][32] and for complex **2** [86.992(19)°].[18]

The conversion of **1** into **3** with dimethoxymethylsilane is finished within one hour at room temperature. With diethoxymethylsilane the reaction needs 24 hours to be completed and in this case it was possible to detect the three intermediates [Pt(H){SiMe(OEt)$_2$}(dcpe)] (**5**), [Pt{SiMe(OEt)$_2$}$_2$(dcpe)] (**6**) and



Scheme 1 Reactions of [Pt(H)$_2$(dcpe)] (**1**) with an excess of dialkoxymethylsilane and dichloromethylsilane; R = Me, Et.

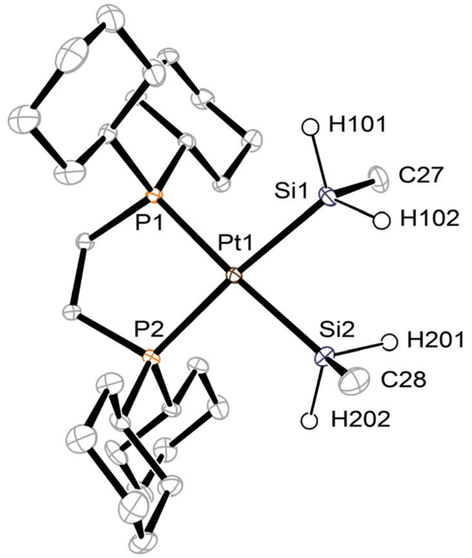


Fig. 1 An ORTEP diagram of **3**. The ellipsoids are drawn to 50% probability level. The hydrogen atoms, except the silicon-bound, are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for $\mathbf{3}\cdot C_6H_6$ with estimated standard deviations in parentheses

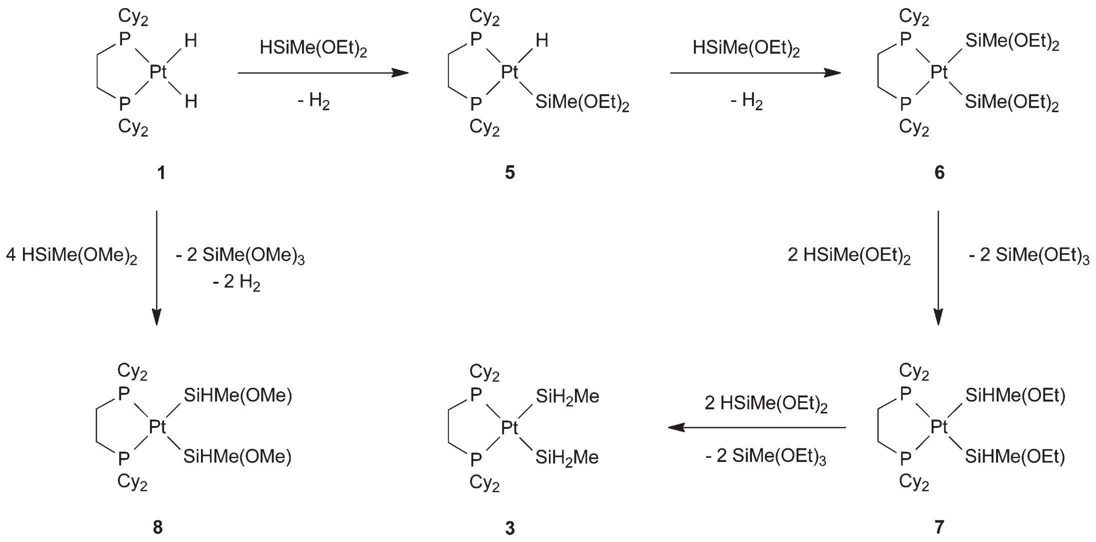
Bond lengths [Å]		Bond angles [°]	
Pt1–Si1	2.3724(14)	P1–Pt1–P2	86.76(4)
Pt1–Si2	2.3539(13)	P1–Pt1–Si1	97.21(5)
Pt1–P1	2.3152(13)	P1–Pt1–Si2	172.46(4)
Pt1–P2	2.3181(12)	P2–Pt1–Si1	174.84(5)
Si1–C27	1.905(5)	P2–Pt1–Si2	95.22(5)
Si2–C28	1.887(5)	Si1–Pt1–Si2	80.43(5)
		C27–Si1–Pt1	115.05(18)
		C28–Si2–Pt1	118.45(19)

[Pt{SiHMe(OEt)}$_2$(dcpe)] (**7**) by monitoring the reaction by NMR spectroscopy (Scheme 2). Such varying reaction times for various alkoxysilanes were also observed for the zirconium-mediated redistribution of dialkoxymethylsilane to methylsilane and trialkoxymethylsilane.[14]

The ^{31}P{^{1}H} NMR spectrum of **5** displays two doublets with ^{195}Pt satellites at δ = 83.3 ppm ($^1J_{\mathrm{P,Pt}}$ = 1403 Hz) and δ = 73.7 ppm ($^1J_{\mathrm{P,Pt}}$ = 2044 Hz) for the two inequivalent phosphorus atoms. The phosphorus–phosphorus coupling constant of $^2J_{\mathrm{P,P}}$ = 2 Hz is fairly small when compared to typical coupling constants for square-planar coordinated hydrido silyl platinum complexes.[23,24,32,35] The difference in the P–Pt coupling constants arises from the strong *trans* influence of the silyl ligand.[36] For the phosphorus atom in the *trans* position to the silicon atom the $^1J_{\mathrm{P,Pt}}$ coupling constant is smaller (1403 Hz) than for the phosphorus atom in the *trans* position to the hydrido ligand (2044 Hz). The hydrido ligand gives rise to a doublet of doublets with ^{195}Pt satellites in the ^{1}H NMR spectrum at δ = −1.12 ppm. The hydrogen–platinum coupling constant of $^1J_{\mathrm{H,Pt}}$ = 1020 Hz indicates the presence of a platinum-bound hydrogen atom.

The ^{31}P{^{1}H} NMR spectrum for the platinum bis(silyl) complex **6** shows a singlet with ^{195}Pt satellites at δ = 74.4 ppm ($^1J_{\mathrm{P,Pt}}$ = 1342 Hz). The ^{1}H NMR spectrum displays a signal at δ = 0.36 ppm for the hydrogen atoms of the methyl groups. These signals are in accordance with the cross-peaks found in the ^{1}H, ^{29}Si HMBC and the ^{31}P, ^{29}Si HMBC NMR spectra. Fig. 2 depicts part of the ^{1}H, ^{29}Si HMBC NMR spectrum displaying the cross-peak connecting the signal for the silicon atoms and the signal for the OCH$_2$ units. The $^1J_{\mathrm{Si,Pt}}$ and $^2J_{\mathrm{Si,P}\text{-}trans}$ coupling constants are also revealed.

The platinum bis(silyl) complex **7** with two SiHMe(OEt) ligands is chiral and one diastereomer gives rise to a singlet with ^{195}Pt satellites in the ^{31}P{^{1}H} NMR spectrum at δ = 76.4 ppm ($^1J_{\mathrm{P,Pt}}$ = 1445 Hz). The ^{1}H NMR spectrum displays a



Scheme 2 Detected intermediates during the formation of [Pt(SiH$_2$Me)$_2$(dcpe)] (**3**).

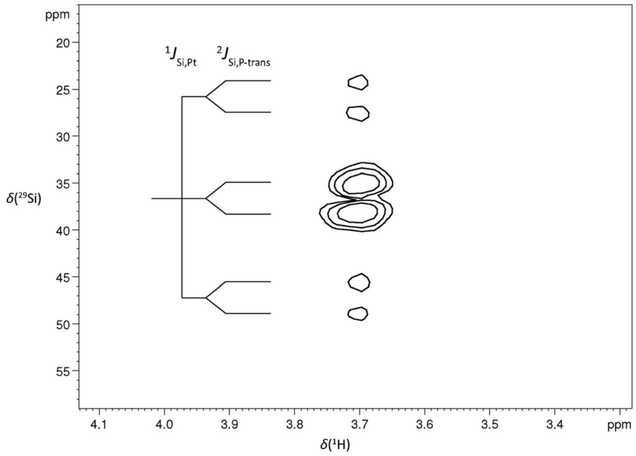
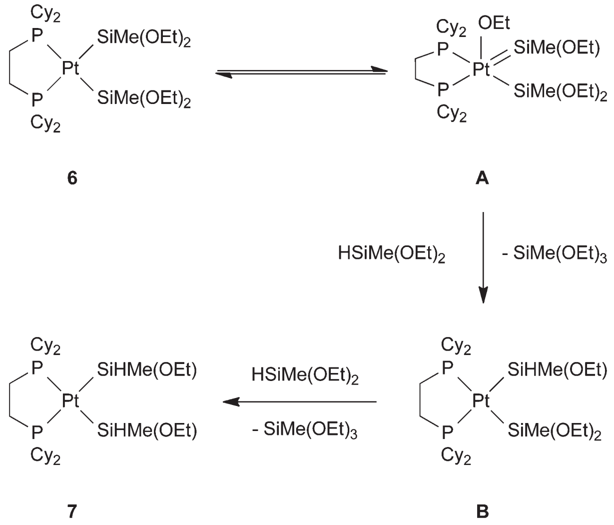


Fig. 2 Part of the ${}^1H$, ${}^{29}Si$ HMBC NMR spectrum of [Pt{SiMe(OEt)$_2$}$_2$(dcpe)] (**6**).



Scheme 3 Postulated mechanism for the hydrodealkoxylation steps for the generating of complex **7**.

multiplet with satellites at $\delta = 6.05$ ppm for the silicon-bound hydrogen atoms. Upon phosphorus decoupling the signal again transforms into a quartet with satellites. The hydrogen–silicon coupling constant of ${}^1J_{H,Si} = 202$ Hz indicates a Si–H moiety. The ${}^{29}Si\{{}^1H\}$ NMR spectrum shows a doublet of doublets at $\delta = 39.7$ ppm due to the coupling to the phosphorus atoms. The cross-peaks found in the ${}^1H$, ${}^{29}Si$ HMBC NMR spectrum are in accordance with these signals. A second diastereomer of **7** shows in the ${}^{31}P\{{}^1H\}$ NMR spectrum a signal with ${}^{195}Pt$ satellites at $\delta = 73.4$ ppm. The ${}^{29}Si\{{}^1H\}$ NMR spectrum reveals a doublet of doublet at $\delta = 38.8$ ppm.

Similar intermediates are supposed for the formation of **3** with HSiMe(OMe)$_2$ for which the reaction time is much shorter. However, the addition of only four equivalents dimethoxymethylsilane to the dihydrido complex **1** gave the bis(silyl) complex [Pt{SiHMe(OMe)}$_2$(dcpe)] (**8**), which is comparable to the intermediate **7** formed during the reaction with HSiMe(OEt)$_2$ (Scheme 2). The reaction solution did not contain any complex **3**, but **8** reacts with more dimethoxymethylsilane to yield **3**. The NMR data of **8** are comparable to those of complex **7**. The LIFDI data of **8** reveal a peak at $m/z = 767$ which can be assigned to the molecular ion $[M]^+$ and a peak at $m/z = 692$ which corresponds to the fragment ion $[M - \{SiHMe(OMe)\}]^+$.

The following reaction pathway can be illustrated based on these observations (Scheme 2). The activation of the Si–H bond of diethoxymethylsilane gives the hydrido silyl complex **5** and the release of dihydrogen. Another equivalent of the silane yields the bis(silyl) complex **6** and dihydrogen again. Further addition of silane leads to a rearrangement of the substituents at the silyl ligands and an exchange of the alkoxy moieties to silicon-bound hydrogen atoms which is associated with the formation of trialkoxymethylsilane. These rearrangements involve repetitive Si–O bond activations. The complexes **7**, **8** and **3** are generated by such hydrodealkoxylation reactions. Note that the ${}^{31}P\{{}^1H\}$ NMR spectra of the reaction solutions reveal additional small doublets with ${}^2J_{P,P}$ coupling constants which might be assigned to complexes with two different silyl ligands such as **B** (Scheme 3).

This mechanism sequence is comparable to the stepwise formation of [Pt(SiH$_3$)$_2$(dcpe)] (**2**).[18] It is conceivable that the hydrodealkoxylation steps involve a migration of an ethoxy group resulting in the generation of the silylene complex **A** (Scheme 3). Alternatively a dissociation of the OEt$^-$ group might lead to the cationic silyl(silylene) platinum complex [Pt{SiMe(OEt)$_2$}{=SiMe(OEt)}(dcpe)]OEt. The addition of diethoxymethylsilane across a M=Si bond would then give a silicon-bound hydrogen atom at the silyl ligand of the complex **B** and trialkoxymethylsilane. Note that Berry *et al.* suggested comparable rearrangement steps at silyl ligands.[37] For the redistribution of methyl groups and X in the complexes [Cp$_2$W(SiMe$_3$)(SiR$_2$X)] (R = iPr, CH$_3$, CD$_3$; X = Cl, OSO$_2$CF$_3$) a dissociation of X$^-$ and the formation of a cationic silyl(silylene) tungsten intermediate was proposed. A dissociation of a triflat group of a silyl ligand by cleavage of a Si–O bond to form a silylene ligand was also postulated by Tilley *et al.*[38] A silylene ligand might in addition be stabilized by an intramolecular interaction of an alkoxy group of the neighboring silyl ligand with the silylene ligand.[5,8,39–41] We have no indication for reaction steps which involve an α-hydrogen abstraction from a silyl ligand.[38,42] The methyl groups bound at the silyl ligands also do not rearrange and remain at the silicon atom.

Studies on hydrodechlorination reactions of dichloromethylsilane at complex 1

To investigate potential hydrodechlorination reactions at silyl ligands, the dihydrido complex [Pt(H)$_2$(dcpe)] (**1**) was treated with an excess of dichloromethylsilane at room temperature. This yielded the platinum bis(silyl) complex [Pt(SiMeCl$_2$)$_2$(dcpe)] (**9**) and dihydrogen (Scheme 1). The hydrido silyl complex [Pt(H)(SiMeCl$_2$)(dcpe)] (**10**) was identified as an intermediate.

The complex **9** was characterized by NMR spectroscopy, LIFDI mass spectroscopy and single-crystal X-ray analysis. The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum shows a singlet with $^{195}\mathrm{Pt}$ satellites at $\delta = 68.8$ ppm. The phosphorus–platinum coupling constant of $^{1}J_{\mathrm{P,Pt}} = 1628$ Hz indicates a platinum(II)metal centre.[30,31] The $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR spectrum reveals a doublet of doublets at $\delta = 61.3$ ppm for the two silicon atoms in the *trans* and *cis* position to phosphorus atoms. The $^{1}\mathrm{H}$, $^{29}\mathrm{Si}$ HMBC NMR spectrum displays a cross-peak connecting the signal for the silicon atoms and the signal for the hydrogen atoms of the methyl groups. The LIFDI data reveal a peak at $m/z = 794$ which can be assigned to the fragment ion $[\mathrm{M} - \mathrm{Cl} - \mathrm{CH_3}]^{+}$.

The molecular structure of **9** was confirmed by single-crystal X-ray analysis and is illustrated in Fig. 3. Selected bond lengths and angles are listed in Table 2. The asymmetric cell unit includes two crystallographically independent molecules, which show only minor differences in bond lengths and angles. Therefore, only one of the molecules is shown and discussed. The platinum atom is coordinated by two silyl ligands and the chelating phosphine ligand. The platinum–silicon bond lengths of 2.3435(19) Å and 2.344(2) Å are longer than those in the comparable complex $[\mathrm{Pt(SiMeCl_2)_2(cod)}]$ [2.3090(11) Å][43] and shorter than of those in the complex **3** [2.3724(14) Å, 2.3539(13) Å]. The platinum–phosphorus bond lengths of 2.3374(17) Å and 2.3406(17) Å are longer than those of complex **3** [2.3152(13) Å, 2.3181(12) Å].

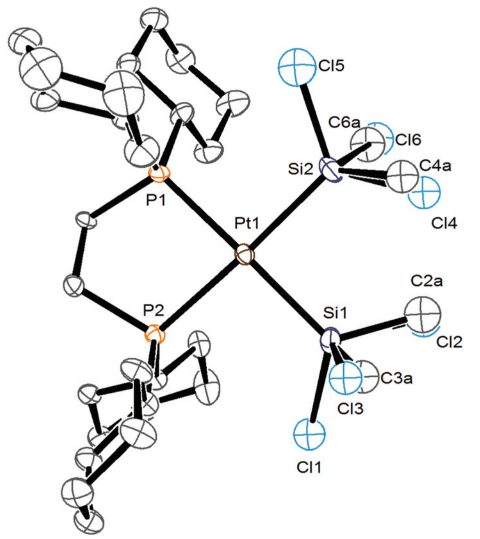


Fig. 3 An ORTEP diagram of **9**. The ellipsoids are drawn to 50% probability level. The hydrogen atoms are omitted for clarity. The asymmetric unit cell contains two crystallographically independent molecules; only one of them is shown. Both molecules show disorder of the methyl and chlorine substituents.

Table 2 Selected bond lengths (Å) and angles (°) for $\mathbf{9}\cdot\mathrm{C_6H_6}$ with estimated standard deviations in parentheses

Bond lengths [Å]		Bond angles [°]	
Pt1–Si1	2.3435(19)	P1–Pt1–P2	84.30(6)
Pt1–Si2	2.344(2)	P1–Pt1–Si1	176.35(6)
Pt1–P1	2.3374(17)	P1–Pt1–Si2	93.58(7)
Pt1–P2	2.3406(17)	P2–Pt1–Si1	94.00(6)
		P2–Pt1–Si2	175.22(7)
		Si1–Pt1–Si2	88.36(7)

As mentioned above, NMR spectroscopic investigations revealed the formation of $[\mathrm{Pt(H)(SiMeCl_2)(dcpe)}]$ (**10**) as an intermediate (Scheme 1). An independent reaction of the dihydrido complex **1** with one equivalent of dichloromethylsilane also yielded the complex **10**. Addition of another equivalent of dichloromethylsilane to **10** gave the bis(silyl) complex **9**. Both reactions might occur *via* σ-bond metathesis steps or *via* an oxidative addition of the Si–H bond of the silane and the reductive elimination of dihydrogen from an intermediate platinum(IV) complex.

The $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of **10** displays two doublets with $^{195}\mathrm{Pt}$ satellites at $\delta = 84.6$ ppm ($^{1}J_{\mathrm{P,Pt}} = 1546$ Hz) and $\delta = 70.7$ ppm ($^{1}J_{\mathrm{P,Pt}} = 1924$ Hz). The P–Pt coupling constants varies because of the strong *trans* influence of the silyl ligand.[36] The hydrido ligand gives rise to a doublet of doublets with $^{195}\mathrm{Pt}$ satellites in the $^{1}\mathrm{H}$ NMR spectrum at $\delta = 0.26$ ppm. The chemical shift is in an unusual range compared to the data for comparable complexes.[23,44–46] The complex *cis*-$[\mathrm{Pt(H)(SiMeCl_2)(PCy_3)_2}]$, synthesized by reaction of $[\mathrm{Pt(PCy_3)_2}]$ with dichloromethylsilane at 260 K, exhibits in the $^{1}\mathrm{H}$ NMR spectrum for the hydrido ligand a doublet of doublets at $\delta = -4.5$ ppm.[23] The hydrido ligand of *trans*-$[\mathrm{Pt(H)(SiMeCl_2)(PEt_3)_2}]$ gives rise to a signal in the $^{1}\mathrm{H}$ NMR spectrum at $\delta = -3.32$ ppm.[44] The $^{1}\mathrm{H}$, $^{29}\mathrm{Si}$ HMBC NMR spectrum of **10** displays cross-peaks between the signal for the silicon atoms and the signals for the hydrido ligands as well as for the methyl groups.

Platinum-mediated hydrodechlorination reactions of the chloro silyl ligands were not observed. Neither the reaction of an excess of dichloromethylsilane with the complex **1** nor with the complex **9**, even by heating up the reaction solution to 70 °C over several days, did result in any rearrangement reactions (Scheme 1). We also did not observe any formation of platinum chlorido complexes by Si–Cl bond activation.[44,47–50] The complex **9** is very stable, even in solution and at higher temperatures. However, rearrangement reactions of silyl chloro ligands are known.[4] Berry *et al.* reported the thermic isomerization of $[\mathrm{W(SiMe_3)(SiR_2Cl)(Cp)_2}]$ to give $[\mathrm{W(SiMe_2Cl)(SiR_2Me)(Cp)_2}]$ which includes a migration of Cl^{-}.[37] Note that treatment of $[\mathrm{Ru(H)_2(\eta^2\text{-}H_2)_2(PCy_3)_2}]$ with ten equivalents of $\mathrm{HSiMeCl_2}$ results in the formation of the three ruthenium silyl complexes $[\mathrm{Ru(H)_2(\eta^2\text{-}H_2)(\eta^2\text{-}HSiMeCl_2)(PCy_3)_2}]$, $[\mathrm{Ru(H)_2(\eta^2\text{-}HSiMeCl_2)(PCy_3)_2}]$ and $[\mathrm{Ru(Cl)(SiMeCl_2)(\eta^2\text{-}H_2)(PCy_3)_2}]$, which are stabilised by SISHA interactions (SISHA = Secondary Interactions between Silicon and Hydrogen Atoms).[45,46,51]

Reactivity of the complexes 2 and 3 towards iodomethane

After the successful synthesis of $[\mathrm{Pt(SiH_3)_2(dcpe)}]$ (**2**)[18] and $[\mathrm{Pt(SiH_2Me)_2(dcpe)}]$ (**3**) we focused on their reactivity towards a possible cleavage of the Pt–Si bonds. The reaction of complex **3** with hydrochloric acid led to a protonation of the Pt–Si bond and gave SiH_3Me and $[Pt(Cl)_2(dcpe)]$ (**4**). Complex **2** showed a similar reactivity.[18] Treatment of the complexes **2** and **3** with iodomethane led to the transfer of the silyl groups to the carbon atom by formation of Si–C bonds. Methylsilane or dimethylsilane, respectively, and the platinum diiodo complex $[Pt(I)_2(dcpe)]$ (**11**) were identified as main products (Scheme 4). Small amounts of methane were also detected. The ratio of methylsilane to methane is approximately 10 : 1. Methylsilane[52] and dimethylsilane[53,54] were identified by comparison with literature NMR data. To support the observed transfer of the SiH_3 moiety to the methyl group of iodomethane, the complex **2** was treated with ^{13}C-labelled iodomethane and deuterated iodomethane which resulted in the formation of $SiH_3{}^{13}CH_3$ or SiH_3CD_3, respectively, and the diiodo complex **11** (Scheme 4).

The NMR data of **11** are comparable to literature data.[55,56] The LIFDI data reveal a peak at m/z = 871 which can be assigned to the molecular ion $[M]^+$ and a peak at m/z = 744 which corresponds to the fragment ion $[M - I]^+$. Furthermore the molecular structure of **11** was determined by single-crystal X-ray analysis (Fig. 4). Selected bond lengths and angles are summarized in Table 3. The structure shows a distorted square-planar arrangement of the two *cis*-orientated iodine ligands and the chelating phosphine ligand. The platinum–iodine bond lengths of 2.6306(5) Å and 2.6647(5) Å are comparable to those of the complex $[Pt(I)_2(dppe)]$ [2.6533(9) Å, 2.6684(9) Å; dppe = 1,2-bis(diphenylphosphino)ethane].[57,58] The Pt–P bonds of 2.2463(11) Å and 2.2431(11) Å are comparable with those of $[Pt(I)_2(dppe)]$ [2.240(3) Å, 2.246(3) Å].

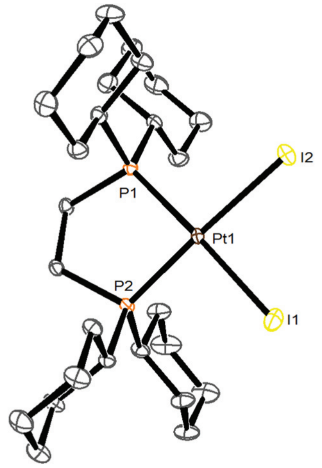
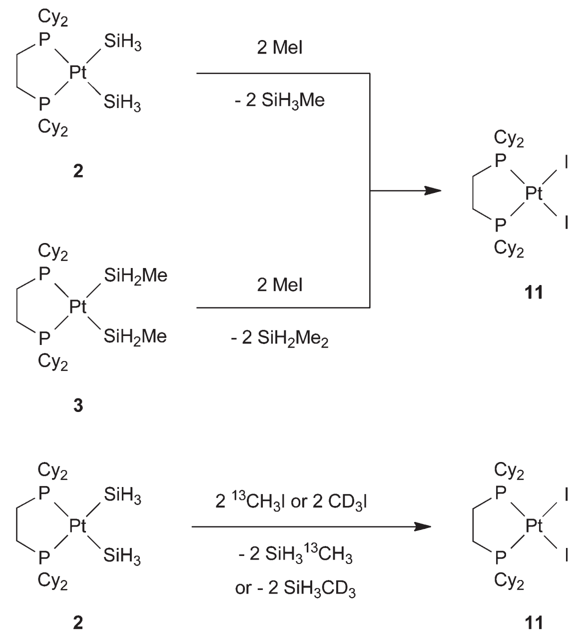


Fig. 4 An ORTEP diagram of $\mathbf{11}\cdot C_6H_6$. The ellipsoids are drawn to 50% probability level. The hydrogen atoms are omitted for clarity.

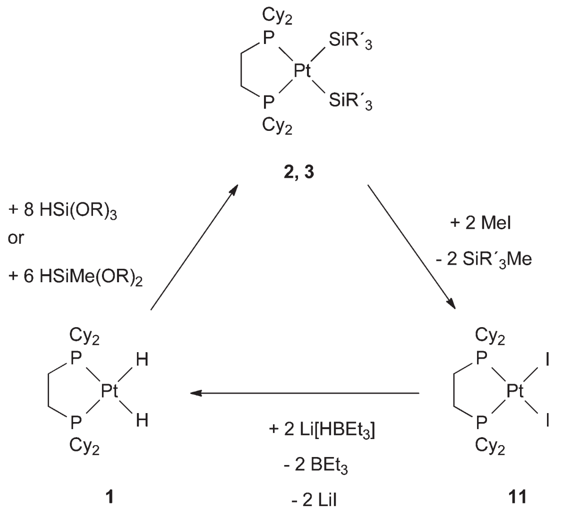
Table 3 Selected bond lengths (Å) and angles (°) for **11** with estimated standard deviations in parentheses

Bond lengths [Å]		Bond angles [°]	
I1–Pt1	2.6306(5)	P1–Pt1–I1	174.65(3)
I2–Pt1	2.6647(5)	P1–Pt1–I2	92.42(3)
P1–Pt1	2.2463(11)	P2–Pt1–I1	90.62(3)
P2–Pt1	2.2431(11)	P2–Pt1–I2	173.36(3)
		P1–Pt1–P2	87.85(4)
		I1–Pt1–I2	89.694(16)

To the best of our knowledge there might be only one example for a metal-mediated transfer of a SiH_3 ligand onto a carbon atom.[59] Reaction of the samarium complex $[Cp^*{}_2Sm(SiH_3)(OPPh_3)]$ with iodomethane leads to $[Cp^*{}_2Sm(I)(OPPh_3)]$ and methylsilane.[59] The formation of the latter was only postulated without any spectroscopic evidence.



Scheme 4 Reactivity of the complex **2** towards iodomethane, ^{13}C-labelled iodomethane and deuterated iodomethane and the reactivity of complex **3** towards iodomethane.



Scheme 5 Cyclic process for the formation of SiH_3Me or SiH_2Me_2 from $HSi(OR)_3$ or $HSiMe(OR)_2$ (R = Me, Et; **2**: $SiR'_3 = SiH_3$, with $HSi(OR)_3$; **3**: $SiR'_3 = SiH_2Me$, with $HSiMe(OR)_2$).

The conversion of **2** or **3** into the complex **11** completes a cyclic process for the formation of SiH_3Me or SiH_2Me_2 from $HSi(OR)_3$ or $HSiMe(OR)_2$, respectively (Scheme 5), since the complex **11** can be converted into the dihydrido complex **1** by treatment with lithium triethylborohydride.[60] A catalytic conversion is not possible due to interferences between the reagents. However, the used platinum complex can be recovered because each individual reaction can be performed in high yield.

Conclusions

In conclusion, treatment of $[Pt(H)_2(dcpe)]$ (**1**) with an excess of dialkoxymethylsilanes $HSiMe(OR)_2$ (R = Me, Et) at room temperature leads to hydrodealkoxylation reactions and gives the bis(silyl) complex $[Pt(SiH_2Me)_2(dcpe)]$ (**3**) and trialkoxymethylsilane. The stepwise exchange of alkoxy moieties to silicon-bound hydrogen atoms at the silyl ligands by Si–O bond activation was monitored by NMR spectroscopy and three intermediates were detected. We did not observe any migration of the methyl groups. For the synthesis of the bis(silyl) complex $[Pt(SiMeCl_2)_2(dcpe)]$ (**9**) by Si–H bond activation of $HSiMeCl_2$ at complex **1** the intermediate hydrido silyl complex $[Pt(H)(SiMeCl_2)(dcpe)]$ (**10**) was identified. Moreover, treatment of the complex **3** and $[Pt(SiH_3)_2(dcpe)]$ (**2**) with iodomethane leads to the transfer of the SiH_3 or SiH_2Me ligands onto the methyl group and the formation of methylsilane and dimethylsilane, respectively, as well as $[Pt(I)_2(dcpe)]$ (**11**).

Experimental

The synthetic work was carried out on a Schlenk line or in a glove box under an atmosphere of argon. Toluene, hexane, benzene-d_6 and tetrahydrofuran-d_8 were purified by distillation from Na/K and stored under argon over molecular sieves. The NMR spectra were recorded on a Bruker DPX 300, a Bruker Avance 300 or a Bruker Avance 400 spectrometer. ^1H NMR chemical shifts were referenced to residual C_6D_5H at δ = 7.15 ppm or C_4D_7HO at δ = 3.58 ppm. The $^{31}P\{^1H\}$ NMR and $^{29}Si\{^1H\}$ NMR spectra were referenced externally to H_3PO_4 at δ = 0.0 ppm and to $SiMe_4$ at δ = 0.0 ppm, respectively. Microanalyses were performed with a HEKAtech Euro EA Elemental Analyzer. Mass spectra were recorded on a Micromass Q-Tof-2 instrument equipped with a Linden LIFDI source (Linden CMS GmbH). GC-MS mass spectra were recorded with an Agilent 6890N gas chromatograph and an Agilent 5973 Network mass selective detector. The compounds $[Pt(Cl)_2(cod)]$[61] and $[Pt(Cl)_2(dcpe)]$ (**4**)[55] were prepared according to the literature. The platinum dihydrido complex $[Pt(H)_2(dcpe)]$ (**1**) was synthesized from $[Pt(Cl)_2(dcpe)]$ (**4**) and lithium triethylborohydride.[18] The complex **1** was prepared *in situ* for the further conversions to prevent the formation of the binuclear complex $[Pt_2(H)_3(dcpe)_2]^+$.[62]

Synthesis of $[Pt(SiH_2Me)_2(dcpe)]$ (3)

(a) A toluene solution (2 mL) of *in situ* prepared $[Pt(H)_2(dcpe)]$ (**1**) (0.19 mmol) was treated with dimethoxymethylsilane (0.14 mL, 1.14 mmol) at room temperature. After stirring for an hour the solution was filtered through a cannula and all volatile compounds were removed *in vacuo*. The residue was washed twice with hexane (3 mL) and was dried *in vacuo*. Yield: 107 mg (0.15 mmol, 79%). Colourless crystals were grown from a concentrated benzene solution at 298 K.

(b) To a benzene-d_6 solution (0.5 mL) of *in situ* prepared $[Pt(H)_2(dcpe)]$ (**1**) (0.12 mmol) diethoxymethylsilane (0.12 mL, 0.72 mmol) was added at room temperature. NMR spectra reveal the intermediate formation of $[Pt(H)\{SiMe(OEt)_2\}(dcpe)]$ (**5**), $[Pt\{SiMe(OEt)_2\}_2(dcpe)]$ (**6**) and $[Pt\{SiHMe(OEt)\}_2(dcpe)]$ (**7**). After 24 h the solution was filtered through a cannula and all volatile compounds were removed *in vacuo*. The residue was washed twice with hexane (2 mL) and was dried *in vacuo*. Yield: 61 mg (86 μmol, 72%).

Analytical data for $[Pt(SiH_2Me)_2(dcpe)]$ (3). Elemental analysis (%) for $C_{28}H_{58}P_2PtSi_2\cdot C_4H_8O$ (780.08): calcd C 49.27, H 8.53; found C 49.02, H 8.57. The sample for the elemental analysis was obtained by recrystallization in THF. **^1H NMR** (300.1 MHz, THF-d_8): δ = 4.04 (m + satellites, q + satellites in the $^1H\{^{31}P\}$ NMR spectrum, $^1J_{H,Si}$ = 161 Hz, $^2J_{H,Pt}$ = 46 Hz, $^3J_{H,H}$ = 4.5 Hz, 4H, SiH; the coupling constants were determined from the $^1H\{^{31}P\}$ NMR spectrum), 1.8–1.0 (m, 48H, CH_2, CH), 0.31 ppm (m + satellites, t + satellites in the $^1H\{^{31}P\}$ NMR spectrum, $^3J_{H,H}$ = 4.5 Hz, $^3J_{H,Pt}$ = 33 Hz, 6H, $SiCH_3$; the coupling constants were determined from the $^1H\{^{31}P\}$ NMR spectrum). **^1H NMR** (300.1 MHz, C_6D_6): δ = 4.91 (m + satellites, q + satellites in the $^1H\{^{31}P\}$ NMR spectrum, $^1J_{H,Si}$ = 161 Hz, $^2J_{H,Pt}$ = 46 Hz, $^3J_{H,H}$ = 4.5 Hz, 4H, SiH; the coupling constants were determined from the $^1H\{^{31}P\}$ NMR spectrum), 1.8–1.0 (m, 48H, CH_2, CH), 0.58 ppm (m + satellites, t + satellites in the $^1H\{^{31}P\}$ NMR spectrum, $^3J_{H,H}$ = 4.5 Hz, $^3J_{H,Pt}$ = 32 Hz, 6H, $SiCH_3$; the coupling constants were determined from the $^1H\{^{31}P\}$ NMR spectrum). **$^{31}P\{^1H\}$ NMR** (121.5 MHz, THF-d_8): δ = 73.8 ppm (s + satellites, $^1J_{P,Pt}$ = 1558 Hz). **$^{31}P\{^1H\}$ NMR** (121.5 MHz, C_6D_6): δ = 75.1 ppm (s + satellites, $^1J_{P,Pt}$ = 1542 Hz). **^1H, ^{31}P HMBC NMR** (400.1/162.0 MHz, C_6D_6): δ = 4.9/75.1, 1.8/75.1, 1.5/75.1, 1.1/75.1, 0.6/75.1 ppm. **$^{29}Si\{^1H\}$ NMR** (59.6 MHz, C_6D_6): δ = −40.1 ppm (dd, $^2J_{Si,P\text{-}trans}$ = 152 Hz, $^2J_{Si,P\text{-}cis}$ = 14 Hz; ^{195}Pt satellites were not observed). **^1H, ^{29}Si HMBC NMR** (300.1/59.6 MHz, THF-d_8): δ = 4.0/−40.6 (d/d, $^1J_{H,Si}$ = 161 Hz, $^2J_{Si,P\text{-}trans}$ = 152 Hz, SiH), 0.3/−40.6 ppm (s + satellites/d + satellites, $^1J_{Si,Pt}$ = 1172 Hz, $^2J_{Si,P\text{-}trans}$ = 152 Hz, $^3J_{H,Pt}$ = 33 Hz, $SiCH_3$). **LIFDI-TOF-MS:** calcd for $C_{28}H_{58}P_2PtSi_2$ $[M]^+$: m/z = 707, found 707; calcd for $C_{27}H_{53}P_2PtSi$ $[M - \{SiH_2Me\}]^+$: m/z = 662, found 662.

Analytical data for $[Pt(H)\{SiMe(OEt)_2\}(dcpe)]$ (5). ^1H NMR (300.1 MHz, C_6D_6): δ = 3.66 (q, $^3J_{H,H}$ = 7 Hz, 4H, OCH_2), 1.8–1.0 (m, CH, CH_2; no integration possible because of overlapping signals), 1.06 (t, $^3J_{H,H}$ = 7 Hz, OCH_2CH_3; no integration possible because of overlapping signals), 0.31 (s, 3H, $SiCH_3$), −1.12 ppm (dd + satellites, $^1J_{H,Pt}$ = 1020 Hz, $^2J_{H,P\text{-}trans}$ = 152 Hz, $^2J_{H,P\text{-}cis}$ = 13 Hz, 1H, PtH). **$^{31}P\{^1H\}$ NMR** (121.5 MHz, C_6D_6): δ =

83.3 (d + satellites, $^1J_{\mathrm{P,Pt}}$ = 1403 Hz, $^2J_{\mathrm{P,P}}$ = 2 Hz, 1P, P *trans* to Si), 73.7 ppm (d + satellites, $^1J_{\mathrm{P,Pt}}$ = 2044 Hz, $^2J_{\mathrm{P,P}}$ = 2 Hz, 1P, P *trans* to H).

Analytical data for [Pt{SiMe(OEt)$_2$}$_2$(dcpe)] (6). **^{1}H NMR** (300.1 MHz, C_6D_6): δ = 3.74 (q, $^3J_{\mathrm{H,H}}$ = 7 Hz, 8H, OCH_2), 1.8–1.0 (m, CH, CH_2; no integration possible because of overlapping signals), 1.07 (t, $^3J_{\mathrm{H,H}}$ = 7 Hz, OCH_2CH_3; no integration possible because of overlapping signals), 0.36 ppm (s, 6H, $SiCH_3$). **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): δ = 74.4 ppm (s + satellites, $^1J_{\mathrm{P,Pt}}$ = 1342 Hz). **^{29}Si{^{1}H} NMR** (59.6 MHz, C_6D_6): δ = 36.7 ppm (dd, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 193 Hz, $^2J_{\mathrm{Si,P}\text{-}cis}$ = 16 Hz; ^{195}Pt satellites were not observed). **^{1}H, ^{29}Si HMBC NMR** (300.1/59.6 MHz, C_6D_6): δ = 3.7/36.7 (s/d + satellites, $^1J_{\mathrm{Si,Pt}}$ = 1577 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 193 Hz, $SiOCH_2$), 0.4/36.7 ppm (s + satellites/d + satellites, $^1J_{\mathrm{Si,Pt}}$ = 1578 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 193 Hz, $^3J_{\mathrm{H,Pt}}$ = 17 Hz, $SiCH_3$). **^{31}P, ^{29}Si HMBC NMR** (162.0/79.5 MHz): δ = 74.4/36.7 ppm (d + satellites/s + satellites, $^1J_{\mathrm{P,Pt}}$ = 1342 Hz, $^2J_{\mathrm{P,Si}\text{-}trans}$ = 193 Hz, $^1J_{\mathrm{Si,Pt}}$ = 1577 Hz).

Analytical data for the diastereomeric mixture of [Pt{SiHMe(OEt)}$_2$(dcpe)] (7). **^{1}H NMR** (300.1 MHz, C_6D_6): δ = 6.05 (m + satellites, q + satellites in the ^{1}H{^{31}P} NMR spectrum, $^1J_{\mathrm{H,Si}}$ = 202 Hz, $^2J_{\mathrm{H,Pt}}$ = 58 Hz, $^3J_{\mathrm{H,H}}$ = 4 Hz, 2H, SiH; the coupling constants were determined from the ^{1}H{^{31}P} NMR spectrum), 3.72 (q, $^3J_{\mathrm{H,H}}$ = 7 Hz, 4H, OCH_2), 1.8–1.0 (m, CH, CH_2; no integration possible because of overlapping signals), 1.14 (t, $^3J_{\mathrm{H,H}}$ = 7 Hz, OCH_2CH_3; no integration possible because of overlapping signals), 0.47 ppm (d + satellites, $^3J_{\mathrm{H,H}}$ = 4 Hz, $^3J_{\mathrm{H,Pt}}$ = 27 Hz, 6H, $SiCH_3$). **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): δ = 76.4 (s + satellites, $^1J_{\mathrm{P,Pt}}$ = 1445 Hz), 73.4 ppm (br + satellites, $^1J_{\mathrm{P,Pt}}$ = 1408 Hz). **^{29}Si{^{1}H} NMR** (59.6 MHz, C_6D_6): δ = 39.7 (dd, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 162 Hz, $^2J_{\mathrm{Si,P}\text{-}cis}$ = 16 Hz; ^{195}Pt satellites were not observed), 38.8 ppm (dd, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 172 Hz, $^2J_{\mathrm{Si,P}\text{-}cis}$ = 10 Hz; ^{195}Pt satellites were not observed). **^{1}H, ^{29}Si HMBC NMR** (300.1/59.6 MHz, C_6D_6): δ = 6.0/39 (d/d, $^1J_{\mathrm{H,Si}}$ = 202 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 162 Hz, SiH), 3.7/39 (s/d + satellites, $^1J_{\mathrm{Si,Pt}}$ = 1592 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 177 Hz, $SiOCH_2$), 0.5/39 ppm (s + satellites, d + satellites, $^1J_{\mathrm{Si,Pt}}$ = 1311 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 162 Hz, $^2J_{\mathrm{H,Pt}}$ = 27 Hz, $SiCH_3$).

Formation of [Pt{SiHMe(OMe)}$_2$(dcpe)] (8)

Dimethoxymethylsilane (80 μL, 0.64 mmol) was added to a tetrahydrofuran-d_8 solution (0.5 mL) of *in situ* prepared [Pt(H)$_2$(dcpe)] (**1**) (0.16 mmol) at room temperature. The formation of **8** was confirmed by NMR spectroscopic data and MS data.

Analytical data for [Pt{SiHMe(OMe)}$_2$(dcpe)] (8). **^{1}H NMR** (300.1 MHz, THF-d$_8$): δ = 6.01 (m + satellites, q + satellites in the ^{1}H{^{31}P} NMR spectrum, $^1J_{\mathrm{H,Si}}$ = 310 Hz, $^2J_{\mathrm{H,Pt}}$ = 138 Hz, $^3J_{\mathrm{H,H}}$ = 3.6 Hz, 2H, SiH; the coupling constants were determined from the ^{1}H{^{31}P} NMR spectrum), 3.74 (s, 6H, OCH_3), 1.8–1.0 (m, 48H, CH, CH_2), 0.55 ppm (m + satellites, d + satellites in the ^{1}H{^{31}P} NMR spectrum, $^3J_{\mathrm{H,H}}$ = 3.6 Hz, $^3J_{\mathrm{H,Pt}}$ = 26 Hz, 6H, $SiCH_3$; the coupling constants were determined from the ^{1}H{^{31}P} NMR spectrum). **^{31}P{^{1}H} NMR** (121.5 MHz, THF-d$_8$): δ = 78.5 (s + satellites, $^1J_{\mathrm{P,Pt}}$ = 1413 Hz), 77.7 ppm (s for a second diastereomer, ^{195}Pt satellites were not observed). **^{1}H, ^{29}Si HMBC NMR** (300.1/59.6 MHz, THF-d$_8$): δ = 3.7/41.7 (s/d + satellites, $^1J_{\mathrm{Si,Pt}}$ = 1537 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 179 Hz, $SiOCH_3$), 0.5/41.7 ppm (s + satellites/d + satellites, $^1J_{\mathrm{Si,Pt}}$ = 1537 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 179 Hz, $^3J_{\mathrm{H,Pt}}$ = 26 Hz, $SiCH_3$). **LIFDI-TOF-MS**: calcd for $C_{30}H_{62}O_2P_2PtSi_2$ [M]$^+$: *m*/*z* = 767, found 767; calcd for $C_{28}H_{55}OP_2PtSi$ [M − {SiHMe(OMe)}]$^+$: *m*/*z* = 692, found 692.

Formation of [Pt(SiMeCl$_2$)$_2$(dcpe)] (9)

(a) Dichloromethylsilane (37 μL, 0.36 mmol) was added to a toluene solution (1.5 mL) of *in situ* prepared [Pt(H)$_2$(dcpe)] (**1**) (90 μmol) at room temperature. After 10 min the NMR spectroscopic data of the reaction solution reveal the intermediate formation of [Pt(H)(SiMeCl$_2$)(dcpe)] (**10**). After stirring for 3 h the solution was filtered through a cannula and all volatile compounds were removed *in vacuo*. The residue was washed twice with hexane (2 mL) and was dried *in vacuo*. Yield: 48 mg (57 μmol, 63%). Colourless crystals were grown from a concentrated benzene solution at 298 K.

(b) A benzene-d_6 solution (0.5 mL) of [Pt(H)(SiMeCl$_2$)(dcpe)] (**10**) (70 μmol) was treated with dichloromethylsilane (8 μL, 70 μmol) at room temperature. After 3 h the quantitative formation of **9** was revealed by NMR spectroscopy.

Analytical data for [Pt(SiMeCl$_2$)$_2$(dcpe)] (9). **^{1}H NMR** (300.1 MHz, C_6D_6): δ = 1.8–1.0 (m, CH_2, CH, no integration possible because of overlapping signals), 1.60 ppm (s + satellites, $^3J_{\mathrm{H,Pt}}$ = 14 Hz, $SiCH_3$, no integration possible because of overlapping signals). **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): δ = 68.8 ppm (s + satellites, $^1J_{\mathrm{P,Pt}}$ = 1628 Hz). **^{29}Si{^{1}H} NMR** (59.6 MHz, C_6D_6): δ = 61.3 ppm (dd, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 210 Hz, $^2J_{\mathrm{Si,P}\text{-}cis}$ = 15 Hz; ^{195}Pt satellites were not observed). **^{1}H, ^{29}Si HMBC NMR** (300.1/59.6 MHz, C_6D_6): δ = 1.6/61.3 ppm (s + satellites/d + satellites, $^1J_{\mathrm{Si,Pt}}$ = 1617 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 210 Hz, $^3J_{\mathrm{H,Pt}}$ = 14 Hz, $SiCH_3$). **LIFDI-TOF-MS:** calcd for $C_{27}H_{51}Cl_3P_2PtSi_2$ [M − Cl − CH_3]$^+$: *m*/*z* = 794, found 794.

Formation of [Pt(H)(SiMeCl$_2$)$_2$(dcpe)] (10)

To a benzene-d_6 solution (0.5 mL) of *in situ* prepared [Pt(H)$_2$(dcpe)] (**1**) (70 μmol) dichloromethylsilane (7 μL, 70 μmol) was added at room temperature. After 10 min the quantitative formation of **10** was confirmed by NMR spectroscopy.

Analytical data for [Pt(H)(SiMeCl$_2$)(dcpe)] (10). **^{1}H NMR** (300.1 MHz, C_6D_6): δ = 1.8–1.0 (m, 48H, CH_2, CH), 0.87 (s + satellites, $^3J_{\mathrm{H,Pt}}$ = 14 Hz, 3H, $SiCH_3$), 0.26 ppm (dd + satellites, $^1J_{\mathrm{H,Pt}}$ = 1032 Hz, $^2J_{\mathrm{H,P}\text{-}trans}$ = 163 Hz, $^2J_{\mathrm{H,P}\text{-}cis}$ = 15 Hz, 1H, PtH). **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): δ = 84.6 (d + satellites, $^1J_{\mathrm{P,Pt}}$ = 1546 Hz, $^2J_{\mathrm{P,P}}$ = 3 Hz, 1P, P *trans* to Si), 70.7 ppm (d + satellites, $^1J_{\mathrm{P,Pt}}$ = 1924 Hz, $^2J_{\mathrm{P,P}}$ = 3 Hz, 1P, P *trans* to H). **^{1}H, ^{29}Si HMBC NMR** (300.1 MHz/59.6 MHz, C_6D_6): δ = 0.9/−48.6 (s/d, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 159 Hz, $SiCH_3$), 0.2/−48.6 ppm (dd/d, $^2J_{\mathrm{H,P}\text{-}trans}$ = 163 Hz, $^2J_{\mathrm{H,P}\text{-}cis}$ = 15 Hz, $^2J_{\mathrm{Si,P}\text{-}trans}$ = 159 Hz, PtH).

Treatment of [Pt(SiH$_3$)$_2$(dcpe)] (2) with iodomethane

A Young NMR tube with [Pt(SiH$_3$)$_2$(dcpe)] (**2**) (36 mg, 53 μmol) in a benzene-d_6 solution (0.5 mL) was treated with iodomethane (7 μL, 0.11 mol) at room temperature. After 3 days the NMR spectroscopic data revealed the quantitative formation of [Pt(I)$_2$(dcpe)] (**11**) and SiH_3CH_3. Complex **11**[55,56] and methylsilane[52] were identified by comparison with literature

NMR data. As a minor product methane was detected.[63] The ratio of methylsilane to methane was approximately 10 : 1. Colourless crystals of **11** were grown from a concentrated benzene solution at 298 K.

Analytical data for [Pt(I)$_2$(dcpe)] (**11**): **^{31}P{^{1}H} NMR** (121.5 MHz, C_6D_6): δ = 66.3 ppm (s + satellites, $^1J_{P,Pt}$ = 3350 Hz). **LIFDI-TOF-MS:** calcd for $C_{26}H_{48}I_2P_2Pt$ [M]$^+$: m/z = 871, found 871; calcd for $C_{26}H_{48}IP_2Pt$ [M − I]$^+$: m/z = 744, found 744.

Treatment of [Pt(SiH$_3$)$_2$(dcpe)] (2) with iodomethane-^{13}C

A benzene-d_6 solution of [Pt(SiH$_3$)$_2$(dcpe)] (**2**) (29 mg, 43 µmol) in a Young NMR tube was treated with iodomethane-^{13}C (6 µL, 86 µmol) at room temperature. The NMR spectroscopic data revealed the quantitative formation of [Pt(I)$_2$(dcpe)] (**11**) and $SiH_3{}^{13}CH_3$ after 3 days. Complex **11**[55,56] and methylsilane-^{13}C[52] were identified by comparison with literature NMR data. As a minor product methane-^{13}C was detected.[63] The ratio of methylsilane-^{13}C to methane-^{13}C was approximately 10 : 1.

Treatment of [Pt(SiH$_3$)$_2$(dcpe)] (2) with iodomethane-d_3

A Young NMR tube with [Pt(SiH$_3$)$_2$(dcpe)] (**2**) (53 mg, 78 µmol) in a benzene-d_6 solution (0.5 mL) was treated with deuterated iodomethane (10 µL, 0.16 mmol) at room temperature. After 3 days the NMR spectroscopic data revealed the quantitative formation of [Pt(I)$_2$(dcpe)] (**11**) and SiH_3CD_3. Complex **11**[55,56] and methylsilane[52] were identified by comparison with literature NMR data.

Treatment of [Pt(SiH$_2$Me)$_2$(dcpe)] (3) with iodomethane-^{13}C

A benzene-d_6 solution of [Pt(SiH$_2$Me)$_2$(dcpe)] (**3**) (48 mg, 68 µmol) in a Young NMR tube was treated with iodomethane-^{13}C (9 µL, 0.14 mmol) at room temperature. NMR spectroscopic data revealed the quantitative formation of [Pt(I)$_2$(dcpe)] (**11**) and $SiH_3CH_3{}^{13}CH_3$ after 3 days. Complex **11**[55,56] and dimethylsilane[53,54] were identified by comparison with literature NMR data.

Treatment of [Pt(I)$_2$(dcpe)] (11) with lithium triethylborohydride

To a benzene-d_6 solution of [Pt(I)$_2$(dcpe)] (**11**) (34 mg, 0.04 mmol) lithium triethylborohydride (0.08 ml, 0.08 mmol, 1 M solution in tetrahydrofuran) was added. The reaction proceeds within minutes. [Pt(H)$_2$(dcpe)] (**1**) was identified as product by comparison with literature NMR data.[18–20]

Structure determination of the complexes 3·C$_6$H$_6$, 9·C$_6$H$_6$ and 11·C$_6$H$_6$

Colourless crystals of the complexes **3**·C_6H_6, **9**·C_6H_6 and **11**·C_6H_6 precipitated from concentrated benzene solutions at 298 K. Crystallographic data are listed in Table 4. The crystal of complex **9** contains two independent molecules in the asymmetric unit. In both molecules all silicon-bound methyl groups show substitutional disorder with respect to the chloride substituents. Along with distance restraints, the application of SUMP restraints (SHELX-2013)[64,65] ties the densities of the chlorine atoms bound at each silicon atom into three occupancies. This led to occupancies of 0.74 (Cl2), 0.26 (Cl3), 0.20 (Cl4), 0.80 (Cl6), 0.94 (Cl7), 0.94 (Cl8), 0.12 (Cl9), 0.93 (Cl10), 0.80 (Cl11) and 0.27

Table 4 Crystallographic data

Compound	[Pt(SiH$_2$Me)$_2$(dcpe)] (**3**)·C_6H_6	[Pt(SiMeCl$_2$)$_2$(dcpe)] (**9**)·C_6H_6	[Pt(I)$_2$(dcpe)] (**11**)·C_6H_6
Empirical formula	$C_{28}H_{58}P_2PtSi_2$, C_6H_6	$C_{28}H_{54}Cl_4P_2PtSi_2$, C_6H_6	$C_{26}H_{48}I_2P_2Pt$, C_6H_6
Formula weight	786.06	923.83	949.58
Crystal size (mm^3)	0.16 × 0.06 × 0.04	0.23 × 0.08 × 0.04	0.26 × 0.25 × 0.17
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
a (Å)	11.2140(4)	11.5338(8)	12.1585(17)
b (Å)	14.0280(5)	18.0570(13)	18.428(3)
c (Å)	23.0967(7)	20.1236(14)	15.976(3)
α (°)		85.305(2)	
β (°)		73.897(2)	101.390(12)
γ (°)		83.984(2)	
V (Å^3)	3633.3(2)	3998.3(5)	3509.1(9)
Z	4	4	4
Calculated density (Mg m^{-3})	1.437	1.535	1.797
μ (Mo-Kα) (mm^{-1})	4.037	3.940	5.868
θ range (°)	2.284–26.754	2.248–25.174	3.22–28.00
Reflections collected	20 086	171 341	88 723
Independent reflections	7646	14 241	8448
R_{int}	0.0336	0.0485	0.0531
Goodness-of-fit on F^2	0.998	1.047	0.906
Completeness to max. θ	99.8%	99.9%	99.8%
R_1, ωR_2 on all data	0.0257, 0.0463	0.0620, 0.1297	0.0359, 0.0747
R_1, ωR_2 [$I_0 > 2\sigma(I_0)$]	0.0229, 0.0456	0.0514, 0.1229	0.0265, 0.0731
Reflect. with [$I_0 > 2\sigma(I_0)$]	7258	12 129	6821
Largest diff. peak, hole (e A^{-3})	1.483/−0.608	4.647/−3.000	1.440/−2.227
CCDC	1439201	1439202	1439203

(Cl12). Only for the first independent molecule the occupancies of Cl1 and Cl5 were given full occupancy. All atoms involved in disorder have been isotropically refined.

The diffraction data were obtained with a Bruker D8 Venture or a Stoe IPDS 2 T diffractometer. Multi-scan absorption corrections[66] for **3**·C_6H_6 and **9**·C_6H_6 and numerical corrections[67] for **11**·C_6H_6 were applied to the data. The structures were solved by direct methods (SHELXS-97)[68] or by intrinsic phasing method (SHELXT-2014)[64] and refined by full-matrix least-square procedures based on F^2 with all measured reflections (SHELX-97 and SHELXL-2013)[65,69] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically, except the silicon-bound hydrogen atoms, and were refined by using a riding model.

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