Towards a catalytic hydrogenolysis of silicon-silicon bonds: Formation of Si–H bonds from disilanes and H_2 at platinum

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Reactions of the disilanes Cl₂MeSiSiMeCl₂, ClMe₂SiSiMe₂Cl and Me₃SiSiMe₃ led to the products of oxidative addition *cis*-[Pt(SiMeCl₂)₂(PEt₃)₂] (**2**), *cis*-[Pt(SiMe₂Cl)₂(PEt₃)₂] (**3**) and *cis*-[Pt(SiMe₃)₂(PEt₃)₂] (**4**). Complex *cis*-[Pt(SiMe₂Cl)₂(PEt₃)₂] (**3**) converts in the presence of dihydrogen into two equivalents HSiMe₂Cl and complex *trans*-[PtH₂(PEt₃)₂] (**10**). NMR investigations reveal the initial formation of *trans*-[PtH(SiMe₂Cl)(PEt₃)₂] (**5**) and one equivalent HSiMe₂Cl.

Introduction

Silicon–hydrogen bond cleavage can be considered as a key step in a variety of transition-metal mediated reactions including hydrosilylations, dehydrogenative silylations and polysilane formation.¹ Important elementary steps of catalytic cycles are the oxidative addition of a Si–H bond, σ -bond metathesis reactions or the addition of a Si–H bond at a silylene ligand.¹⁻⁵

We became interested in a transition-metal catalyzed "hydrogenolysis" of a Si–Si bond of disilanes using dihydrogen as a second substrate. Such a reaction route is of considerable importance, because it opens up new opportunities to access higher-value silanes which can be applied for further synthesis.¹ It should also be thermodynamically conceivable because a Si–H bond with a bond dissociation energy of 380–420 kJ mol⁻¹ is more stable than a Si–Si bond (310–330 kJ mol⁻¹), whereas the bond dissociation energy of H₂ is 436 kJ mol^{-1.6} The reverse reaction, a dihydrogenative coupling of silanes, can be catalyzed by early transition metal complexes.^{16,7} Late transition metal complexes typically exhibit competing catalytic activities for both dehydrocoupling and substituent redistribution reactions of hydrosilanes.^{15,8}

Catalytic processes, which involve a hydrogenolysis of disilanes are rare and have been covered by patent specifications. Chlorinated disilanes can be converted into silanes in the presence of dihydrogen and metal salts such as NiCl₂, CuCl₂, AlCl₃ or FeCl₂. The transformations can be heterogeneous or homogeneous and proceed with low selectivity usually under drastic reaction conditions such as high pressure and higher temperatures.⁹ No mechanistic investigations on elementary steps of a putative catalytic cycle have been carried out.

In this paper, we report on a selective transformation of Si–Si bonds with H_2 into Si–H bonds in a homogeneous phase. Studies of elementary steps led to the development of a cyclic process for the hydrogenolysis of disilanes, which proceeds under mild conditions. The reaction cascade can be repeated several times, but the "catalyst" has to be regained after each cycle.

Results

Si-Si activation of disilanes at Pt(0)

Treatment of a solution of $[Pt(PEt_3)_3]$ (1) in THF with Cl₂MeSiSiMeCl₂ affords the silvl complex *cis*-[Pt(SiMeCl₂)₂- $(PEt_3)_2$] (2) as well as of $[PtCl(PEt_3)_3]Cl$ und $MeSi(SiMeCl_2)_3$. The latter compounds have been identified by comparison of their NMR data with the literature.10 Their formation can be explained by redistribution reactions via metal silvlene species starting from 2.^{1,11} However, a reaction at 0 °C leads spontaneously to a selective generation of 2 (Scheme 1). A conversion of 1 with ClMe₂SiSiMe₂Cl to give cis-[Pt(SiMe₂Cl)₂(PEt₃)₂] (3) has been described before and proceeds at room temperature within 30 min.¹² We found that a reaction of 1 with Me₃SiSiMe₃ is very slow and the generation of cis-[Pt(SiMe₃)₂(PEt₃)₂] (4) with approximately 50% conversion within 3 weeks was observed at room temperature (Scheme 1). The facilitated oxidative addition with electronegative substituents at silicon is consistent with literature data.12,13



Scheme 1 Si–Si oxidative addition of disilanes at 1.

Selected NMR data of **2–4** are given in Table 1. The ²⁹Si $\{^{1}H\}$ NMR spectra show virtual triplets for the silicon atoms with couplings to the phosphorus atoms. The ³¹P $\{^{1}H\}$ NMR spectra

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Complex	¹ H NMR ^{<i>a</i>}		${}^{31}P{1H} NMR$			²⁹ Si{ ¹ H} NMR	
	δ /ppm	$^{3}J_{\mathrm{H,Pt}}/\mathrm{Hz}$	δ /ppm	$^{1}J_{\mathrm{P,Pt}}/\mathrm{Hz}$	$^{2}J_{\mathrm{P,Si}}/\mathrm{Hz}$	δ/ppm	$^{1}J_{\mathrm{Si,Pt}}/\mathrm{Hz}$
2	1.51	15.6	13.1	1872	98	46	1622
3	1.02	21.0	14.2	1751	76	45	1438
4	0.35	24.5	16.5	1586	60	3.3	1175

 Table 1
 Selected NMR data of 2-4

display a singlet for the phosphines in the mutually *cis* position. The platinum–phosphorus coupling constants are characteristic for Pt(II) compounds with a phosphine in the *trans* position to a silyl group.^{12,14} Note that the increasing size of ${}^{1}J_{P,Pt}$, ${}^{2}J_{P,Si}$, and ${}^{1}J_{Si,Pt}$ coupling constants mirror the decreasing *trans*-influence of the silyl group with an increasing number of chlorine substituents.

Reactivity of the silyl complexes

Treatment of complex cis-[Pt(SiMeCl₂)₂(PEt₃)₂] (2) with H₂ at 1 atm leads to the formation of small amounts of HSiMeCl₂. In contrast, the reaction of $cis-[Pt(SiMe_2Cl)_2(PEt_3)_2]$ (3) with H₂ at 1 atm gave the silane HSiMe₂Cl and complex trans- $[PtH(SiMe_2Cl)(PEt_3)_2]$ (5) as well as considerable amounts of the platinum compounds trans-[PtCl(SiMe₂Cl)(PEt₃)₂] (6), trans- $[PtHCl(PEt_3)_2]$ (7) and *trans*- $[PtCl_2(PEt_3)_2]$ (8) in a ratio of 63 : 18:10:9 according to the ³¹P NMR spectrum. The ¹H NMR spectrum reveals the presence of complex 6, HSiMe₂Cl and HMe₂SiOSiMe₂H in a ratio of approximately 10 : 4 : 1. The generation of siloxane and the chloro complexes indicates the presence of adventitious water which converts HSiMe₂Cl into HCl and the siloxane. Independent experiments on the reactivities of [Pt(PEt₃)₃] (1) and cis-[Pt(SiMe₂Cl)₂(PEt₃)₂] (3) support this assumption (Scheme 2). Thus, treatment of 3 with HCl results in the formation of the chloro complex *trans*- $[PtCl(SiMe_2Cl)(PEt_3)_2]$ (6) and $HSiMe_2Cl$, whereas 1 reacts with one equivalent HCl to furnish *trans*-[PtHCl(PEt₃)₂] (7). More HCl leads to the generation of *trans*- $[PtCl_2(PEt_3)_2]$ (8). For the formation of 7 and siloxane a hydrolysis of the Pt-Si in 6 is also conceivable.¹⁵ The chloro complexes 6-8 have been described before.16



Scheme 2 Formation of platinum chloro complexes.

Note that for the synthesis of the starting compound 1 water has been used in the work-up process.¹⁷ We therefore recrystallised 1 in the presence of PEt₃ at 193 K yielding colourless crystals of $[Pt(PEt_3)_4]$ (9), which are free of water. Complex 9 is only stable at low temperature and can be transformed into 1 at 333 K and 2 Torr within 2 h.¹⁸ If this batch of 1 is used for the synthesis of the silyl complex **3**, the latter subsequently converts in the presence of dihydrogen into two equivalents $HSiMe_2Cl$ and complex *trans*-[PtH₂(PEt₃)₂] (**10**). NMR investigations reveal the initial formation of *trans*-[PtH(SiMe₂Cl)(PEt₃)₂] (**5**) and one equivalent $HSiMe_2Cl$ (Scheme 3). The conversion is very selective and no platinum chloro complexes are formed. The silyl complex **5** was also prepared *via* an alternative reaction pathway by treatment of **1** with $HSiMe_2Cl$ (Scheme 3).



Scheme 3 Reactivity of the disilyl complex 3.

Complex **5** was characterized by its NMR spectroscopic data. The ¹H NMR spectrum displays a signal at δ –3.32 ppm with a platinum–hydrogen coupling of 910 Hz, which can be assigned to the metal bound hydrogen nucleus. A resonance at δ 1.01 ppm with a ³*J*_{H,Pt} coupling constant of 28.0 Hz reveals the SiMe₂Cl ligand. The data are consistent with those of other Pt(II) silyl hydrido species.^{3,18} A singlet in the ³¹P NMR spectrum at δ 21.9 ppm with platinum satellites (¹*J*_{P,Pt} = 2836 Hz) indicates the presence of phosphines in a mutual *trans* position.¹⁹ A ¹H,²⁹Si-HMBC NMR spectrum shows a signal at δ 50.1 ppm in the ²⁹Si domain which correlates with the resonances for the hydrido ligand and the SiMe₂Cl groups. The silicon–platinum coupling constant is 1314 Hz.

Development of a cyclic process for the formation of HSiMe₂Cl

After the successful formation of HSiMe₂Cl starting from the disilane ClMe₂SiSiMe₂Cl, we studied the reactivity of the

dihydride *trans*- $[PtH_2(PEt_3)_2]$ (10) towards further activation reactions. Indeed, an NMR experiment reveals that treatment of complex 10 with ClMe₂SiSiMe₂Cl furnishes the activation product cis-[Pt(SiMe₂Cl)₂(PEt₃)₂] (3) within one day, but the starting compound 10 is still present. Encouraged by these results, we turned our attention to a possible catalytic hydrogenolysis of ClMe₂SiSiMe₂Cl. The formation of HSiMe₂Cl with H₂ in the presence of ClMe₂SiSiMe₂Cl and cis-[Pt(SiMe₂Cl)₂(PEt₃)₂](3) was investigated. Small amounts of Et₃N have been added to trap adventitious HCl. After several hours reaction time at atmospheric pressure the stoichiometric generation of HSiMe₂Cl and only compound 10 was observed. Apparently, there is no catalytic conversion of the Si-Si bond in the presence of free hydrogen. If the oxidative addition of ClMe₂SiSiMe₂Cl proceeds at $\{Pt(PEt_3)_2\}$, the generation of the latter, and therefore also of 3, might be hampered by free H_2 , which is with {Pt(PEt_3)_2} in equilibrium with trans- $[PtH_2(PEt_3)_2]$ (10). Additional phosphine also does not lead to catalytic turnovers. However, addition of PEt₃ to a solution of trans-[PtH₂(PEt₃)₂] (10) gives the trisphosphine complex trans- $[PtH_2(PEt_3)_3]$ (11) (Scheme 2). After one hour reaction time, the generation of $[Pt(PEt_3)_3]$ (1) and $[Pt(PEt_3)_4]$ (9) is observed by reductive elimination of H₂. Complex 9 does also react with ClMe₂SiSiMe₂Cl to yield 3, but the reaction is slower than with 1 as starting compound and the conversion is not complete.

Based on these observations, which are described above it is possible to draft a cyclic process for the hydrogenolysis of $ClMe_2SiSiMe_2Cl$ (Scheme 4). After activation of $ClMe_2SiSiMe_2Cl$ at $[Pt(PEt_3)_3]$ (1) the disilyl complex *cis*- $[Pt(SiMe_2Cl)_2(PEt_3)_2]$ (3) is furnished. Treatment of **3** with H₂ gives the dihydride *trans*- $[PtH_2(PEt_3)_2]$ (10) and HSiMe_2Cl. The addition of phosphine gives *trans*- $[PtH_2(PEt_3)_3]$ (11), which is in equilibrium with 1. The reductive elimination of H₂ is then facilitated and by Si–Si bond cleavage a cyclic process is completed.

[Pt(PEt₃)₄]

Scheme 4 Cyclic process for the transformation of $ClMe_2SiSiMe_2Cl$ into $HSiMe_2Cl$.

To facilitate the reductive elimination of H_2 from 10 or 11 we treated a solution consisting of 3, PEt₃, NEt₃ and an excess of ClMe₂SiSiMe₂Cl by turns with argon and H₂. However, the generation of HSiMe₂Cl was still stoichiometric. Yet, a regeneration of 1 is possible by application of a vacuum at 11. Thus, HSiMe₂Cl can be separated from the platinum compounds by trap-to-trap distillation. Subsequent addition of PEt₃ and the application of the next batch of ClMe₂SiSiMe₂Cl and its conversion into HSiMe₂Cl. This reaction cascade can be performed several times to yield two equivalents of HSiMe₂Cl from ClMe₂SiSiMe₂Cl and H₂ in each cycle.

Discussion

Oxidative addition reactions of disilanes are depicted in Scheme 1. The reactivity of the disilanes increases in the row Me₃SiSiMe₃ << Me₂ClSiSiClMe₂ < MeCl₂SiSiCl₂Me. Comparable trends have been observed in palladium or platinum catalysed bissilylation reactions with disilanes.^{12,13} Note that electronegative substituents at silicon lead to a Si–Si bond with a σ^* -orbital, which is lower in energy. This facilitates a concerted oxidative addition at electron rich metal centres.^{12,20} Ito *et al.* showed that hexamethyldisilane reacts with [Pt₃(CNAd)₆] (Ad = Adamantyl) to yield [Pt(SiMe₃)₂(CNAd)₂].²¹ Si–Si bond cleavage reactions at disilanes with Si–H functionalities are thought to be initiated by a Si–H activation.^{22–24}

The disilyl complex cis-[Pt(SiMe₂Cl)₂(PEt₃)₂] (3) reacts with dihydrogen to give trans-[PtH₂(PEt₃)₂] (10) and two equivalents of HSiMe₂Cl. The hydrido silyl species *trans*-[PtH(SiMe₂Cl)(PEt₃)₂] (5) has been identified as intermediate. This reaction sequence is unique. It has been reported that *cis*-[Pt(SiMePh₂)₂(PMe₂Ph)₂] reacts with H₂ at 1.5 bar in a reversible reaction to yield trans-[PtH(SiMePh₂)(PMe₂Ph)₂] and HSiMePh₂, but the bissilyl complex was synthesised from cis-[PtCl₂(PMe₂Ph)₂] and MePh₂SiLi.²⁵ No formation of a platinum dihydride was observed. In contrast, the triphenylphosphine complex cis-[PtH(SiHPh₂)(PPh₃)₂] is not susceptible to a reductive elimination step. Instead the dimer $[Pt(\mu-\eta^2(Si,H)-SiHPh_2)(PPh_3)]_2$ is generated upon heating.²⁶ Mechanistically, the reactions of 3 or 5 with H₂ might proceed via a Pt(IV) species, which give after reductive elimination 5 or 10, respectively.²⁷ As an alternative σ -bond metathesis pathways are also conceivable.⁴ Note that *trans*-[PtH₃(SiH₂Cl)(PCy₃)₃] reacts above 193 K to give H₂ and *trans*-[PtH(SiH₂Cl)(PCy₃)₂], but no silane formation has been observed.¹⁸ Complex 5 can be synthesised via an alternative reaction pathway by oxidative addition of HSiMe₂Cl starting from the platinum(0) compound 1. Perutz et al. demonstrated that [Pt(PCy₃)₂] reacts with HSiMe₂Cl or HSiMeCl₂ at 200 K to give initially the cis oxidative addition products which rearrange to the trans isomers at room temperature.³

Complex *trans*-[PtH₂(PEt₃)₂] (**10**) reacts with Me₂ClSiSiClMe₂ to give the activation product *cis*-[Pt(SiMe₂Cl)₂(PEt₃)₂] (**3**). Mechanistically, the reaction might proceed *via* Pt(IV) or Pt(0) species.¹⁶ We favour the latter reaction pathway, because the presence of free H₂ inhibits the oxidative addition of the disilane. This observation is in accordance with our studies on the stoichiometric conversion of **10** into **3**, which proceeds only in the absence of dihydrogen.



Conclusions

A cyclic process for the hydrogenolysis of $ClMe_2SiSiMe_2Cl$ has been developed (Scheme 4). All of the elementary steps of a putative catalytic cycle have been realised including the oxidative addition of a Si–Si- bond and the hydrogenolysis of the new metal– silicon bonds by H₂ (Scheme 4). The reaction cascade is close to being catalytic, but a regeneration step to remove excess of H₂ hampers a smooth catalysis.

Experimental

 $[D_6]$ benzene was dried by stirring over potassium and then distilled under vacuum. The silanes were obtained from Aldrich or the Wacker AG and distilled before use. $[Pt(PEt_3)_3]$ (1) was prepared according to the literature.¹⁷

The NMR spectra were recorded on a Bruker DRX 500 or Bruker Avance 600 spectrometer at 300 K. The ¹H NMR chemical shifts were referenced to residual C₆D₅H at $\delta = 7.15$ ppm. The ³¹P{¹H} NMR spectra were referenced externally to H₃PO₄ at δ 0.0 ppm. Infrared spectra were recorded on a Bruker Vector 22 spectrometer. Abbreviation: $N = {}^{2}J_{PSi,cis} + {}^{2}J_{PSi,trans}$.

Synthesis of cis-[Pt(SiMeCl₂)₂(PEt₃)₂] (2)

A solution of 1 (97 mg, 0.18 mmol) in 5 mL THF was treated with MeCl₂SiSiCl₂Me (162 µL, 0.90 mmol) at 0 °C. The solution turned from red to yellow within a few minutes. After 10 min, the reaction mixture was warmed to room temperature and the volatiles were removed *in vacuo*. The residue was dissolved in 10 mL hexane and the solution was filtered. The filtrate was concentrated to 3 mL and stored at 243 K. Yellow crystals precipitated after one day. The crystals were filtered off and dried *in vacuo*. Yield 110 mg (93%). ¹H-NMR (500 MHz, C₆D₆) δ /ppm: 0.83 (dt, 18 H, $J_{H,P}$ = 15.8 Hz, $J_{H,H}$ = 7.5 Hz, PCH₂CH₃), 1.51 (s + satellites, 6 H, $J_{H,P1}$ = 15.6 Hz, SiCH₃), 1.74 (apparent quint, 12 H, $J_{H,H}$ = $J_{P,H}$ = 7.5 Hz, PCH₂CH₃). ³¹P{¹H}-NMR (202.4 MHz, C₆D₆) δ /ppm: 13.1 (s + satellites, $J_{P,P1}$ = 1872 Hz, $J_{P,Si}$ = 98 Hz). ²⁹Si{¹H}-NMR (C₆D₆, 99.4 MHz) δ /ppm: 45.8 (vt + satellites, $J_{Si,P1}$ = 1622 Hz, N = 196 Hz).

Formation of cis-[Pt(SiMe₃)₂(PEt₃)₂] (4)

A solution of **1** (38 mg, 0.07 mmol) and Me₃SiSiMe₃ (0.6 mL, 2.88 mmol) in 0.5 mL C₆D₆ was transferred into an NMR tube. According to the NMR data, the solution contained **1** and **4** in a ratio of 1 : 1 after 3 weeks. Analytical data for **4**: ¹H-NMR (C₆D₆, 300 MHz) δ /ppm: 0.35 (s + satellites, 18 H, J_{H,Pt} = 24.5 Hz, SiCH₃), 1.09 (dt, 18 H, J_{H,P} = 15.8, J_{H,H} = 7.5 Hz, PCH₂CH₃), 1.75 (apparent quint, 12 H, J_{H,H} = J_{PH} = 7.5 Hz, PCH₂CH₃). ³¹P{¹H}-NMR (C₆D₆, 121.5 MHz) δ /ppm: 16.5 (s + satellites, J_{P,Pt} = 1586 Hz, J_{P,Si} = 60 Hz). ²⁹Si{¹H}-NMR (C₆D₆, 99.4 MHz) δ /ppm: 3.3 (vt + satellites, J_{Si,Pt} = 1175 Hz, N = 120 Hz).

Synthesis of trans-[PtH(SiMe₂Cl)(PEt₃)₂] (5)

An orange solution of **1** (132 mg, 0.24 mmol) in 5 mL THF was treated with HSiMe₂Cl (26 μ L, 0.24 mmol). The solution turned light yellow within several minutes. The volatiles were removed *in vacuo* and the residue was washed with hexane (1 mL) and then

dried *in vacuo* to obtain **5** as yellow oil. Found: C 32.40, H 7.21. $C_{14}H_{37}CIPtP_2Si$ requires C 31.97, H 7.09). Yield 90 mg (73%). $\tilde{v}(ATR)/cm^{-1}$ 1971 (PtH). ¹H-NMR (500 MHz, C₆D₆) δ /ppm: -3.32 (br, s + satellites, $\Delta v_{\frac{1}{2}} = 27$ Hz, 1H, $J_{H,Pt} = 910$ Hz, PtH), 0.90–0.93 (m, 18 H, PCH₂CH₃), 1.01 (br, s + satellites, 6 H, $J_{H,Pt} = 28.0$ Hz, SiCH₃), 1.56–1.60 (m, 12 H, PCH₂CH₃). ³¹P{¹H}-NMR (202.4 MHz, C₆D₆) δ /ppm: 21.9 (s + satellites, $J_{P,Pt} = 2836$ Hz). ²⁹Si{¹H}-NMR (C₆D₆, 99.4 MHz) δ /ppm: 50.1 (s + satellites, $J_{Si,Pt} = 1314$ Hz).

Reaction of cis-[Pt(SiMe₂Cl)₂(PEt₃)₂] (3) with HCl

A solution of *cis*-[Pt(SiMe₂Cl)₂(PEt₃)₂] (**3**) (115 mg, 0.19 mmol) in benzene (5 mL) was treated with a solution of HCl (95 μ L, 0.19 mmol) in ether. The reactions mixture was stirred for 10 min at room temperature and the volatiles were removed *in vacuo*. The resulting yellow oil was washed with hexane (1 mL) and dried *in vacuo*. The NMR data confirm the presence of *trans*-[PtCl(SiMe₂Cl)(PEt₃)₂] (**6**).¹⁶ Yield 86 mg (81%).²⁹Si{¹H}-NMR (C₆D₆, 99.4 MHz) δ /ppm: 22.4 (s + satellites, $J_{Si,Pt} = 1564$ Hz).

Reaction of [Pt(PEt₃)₃] (1) with HCl

A solution of $[Pt(PEt_3)_3]$ (1) (82 mg, 0.15 mmol) in benzene (5 mL) was treated with solution of HCl (75 μ L, 0.15 mmol) in ether. The volatiles were removed *in vacuo* and the colourless residue was washed twice with hexane (2 mL). The colourless residue was dried under vacuum. The NMR data confirm the presence of *trans*-[PtHCl(PEt_3)_2] (7).¹⁶ Yield 66 mg (97%).

Reaction of cis-[Pt(SiMe₂Cl)₂(PEt₃)₂] (3) with H₂

 H_2 gas was bubbled for 20 min into a yellow solution of **3** (124 mg, 0.20 mmol) in THF (5 mL) until the solution turned colourless. The ¹H, ²⁹Si and ³¹P NMR spectroscopic data reveal the initial formation of *trans*-[PtH(SiMe₂Cl)(PEt₃)₂] (**5**) after 10 min. Complex *trans*-[PtH₂(PEt₃)₂] (**10**) and HSiMe₂Cl were furnished after 30 min reaction time.¹⁰

Reaction of cis-[Pt(SiMeCl₂)₂(PEt₃)₂] (2) with H₂

 H_2 gas was bubbled for 1 h into a yellow solution of **2** (90 mg, 0.14 mmol) in 5 mL THF (5 mL) until the solution turned colourless. The ¹H and ³¹P NMR spectroscopic data reveal the presence of **2** and HSiMeCl₂ in a ratio of 10 : 2.

Reaction of trans-[PtH(SiMe₂Cl)(PEt₃)₂] (5) with H₂

 H_2 gas was bubbled for a few seconds into a yellow solution of **5** (74 mg, 0.14 mmol) in benzene (5 mL) until the solution turned colourless. The ¹H and ³¹P NMR spectroscopic data reveal the formation of *trans*-[PtH₂(PEt₃)₂] (**10**) and HSiMe₂Cl.¹⁰

Stepwise treatment of cis-[Pt(SiMe₂Cl)₂(PEt₃)₂] (3) with H₂ and ClMe₂SiSiMe₂Cl under recovery of [Pt(PEt₃)₃] (1)

Hydrogen was bubbled into a solution of *cis*-[Pt(SiMe₂Cl)₂(PEt₃)₂] (3) (193 mg, 0.31 mmol) and Et₃N (132 μ L, 0.94 mmol) in THF (5 mL) for 20 min. The reaction mixture was distilled by trapto-trap distillation. The NMR spectroscopic data of the distillate confirmed the presence of two equivalents HSiMe₂Cl (integration

on an external standard). The residue was treated with PEt₃ (44 μ L, 0.31 mmol) to give, after application of vacuum, complex [Pt(PEt₃)₃] (1). Yield 163 mg (96%).

Complex 1 can again be used for a Si–Si activation of ClMe₂SiSiMe₂Cl. The reaction cycle was performed three times and 2.7 equivalents of ClMe₂SiSiMe₂Cl (based on the amount of **3**) were transformed into HSiMe₂Cl.

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References

- G. W. Parshall and S. D. Ittel, Homogeneous Catalysts: The Applications and Chemistry of Catalysts by Transition Metal Complexes, Wiley, New York, 1992; D. Karshtedt, A. T. Bell and T. D. Tilley, Organometallics, 2006, 25, 4471-4482; T. J. Clark, K. Lee and I. Manners, Chem.– Eur. J., 2006, 12, 8634-8648; K. A. Horn, Chem. Rev., 1995, 95, 1317-1350; M. Wright and B. B. Cochran, Organometallics, 1996, 15, 317-324; I. Matsuda, Y. Fukuta, T. Tsuchihashi and H. Nagashima, Organometallics, 1997, 16, 4327-4345; T. Braun, F. Wehmeier and K. Altenhöner, Angew. Chem., 2007, 119, 5415-5418; T. Braun, F. Wehmeier and K. Altenhöner, Angew. Chem., Int. Ed., 2007, 46, 5321-5324; J. A. Reichl and D. H. Berry, Adv. Organomet. Chem., 1999, 43, 197-265; F. Gauvin, J. F. Harrod and W. G. Woo, Adv. Organomet. Chem., 1998, 42, 363-405.
- 2 T. D. Tilley, *Comments Inorg. Chem.*, 1990, **10**, 37–51; R. Waterman, P. G. Hayes and T. Don Tilley, *Acc. Chem. Res.*, 2007, **40**, 712–719.
- 3 D. Chan, S. B. Duckett, S. L. Heath, I. G. Khazal, R. N. Perutz, S. Sabo-Etienne and P. L. Timmins, *Organometallics*, 2004, **23**, 5744–5756.
- 4 R. N. Perutz and S. Sabo-Etienne, Angew. Chem., Int. Ed., 2007, 46, 2578–2592; R. N. Perutz and S. Sabo-Etienne, Angew. Chem., 2007, 119, 2630–2645; T. D. Tilley, Acc. Chem. Res., 1993, 26, 22–29.
- 5 S. Deeken, S. Proch, E. Casini, H. F. Braun, C. Mechtler, C. Marschner, G. Motz and R. Kempe, *Inorg. Chem.*, 2006, 45, 1871–1879.
- 6 M. A. Brook, Silicon in Organic, Organometallic and Polymer Chemistry, Wiley, New York, 2000, p. 30.
- 7 See for example: V. K. Dioumaev and J. F. Harrod, *Organometallics*, 1994, **13**, 1548–1550; T. Imori and T. D. Tilley, *Polyhedron*, 1994, **13**, 2231–2243; V. K. Dioumaev and J. F. Harrod, *J. Organomet. Chem.*, 1996, **521**, 133–143.
- 8 See for example: L. Rosenberg and D. N. Kobus, J. Organomet. Chem., 2003, 685, 107–112; F.-G. Fontaine, T. Kadkhodazadeh and D. Zargarian, Chem. Commun., 1998, 1253–1254; B. P. S. Chauhan, T. Shimiziu and M. Tanaka, Chem. Lett., 1997, 785–786; M. D. Fryzuk, L. Rosenberg and S. J. Rettig, Inorg. Chim. Acta, 1994, 222, 345–364; B. J. Grimmond and J. Y. Corey, Organometallics, 1999, 18, 2223–2229; B. J. Grimmond and J. Y. Corey, Organometallics, 2000, 19, 3776–3783; V.K. Dioumaev, K. Rahimian, F. Gauvin and J. F. Harrod, Organometallics, 1999, 19, 2249–2255.
- 9 Dow Corning Co., US 3 639 105, 1972; Union Carbide Co., US 4079 071, 1978; Dow Corning Co., US 5 175 329, 1992; Rhône Poulene, FR 2 342 981A1, 1977; Rhodia Chimie, FR 2 777 006 B1, 1999; Rhodia Chemie, EP 1 070 073 B1; Union Carbide Co., US 2 606 811, 1952; Dow

Corning Co., US 5326896, 1994; Dow Corning Co., US 6013235, 2000; Dow Corning Co., US 5430168, 1995.

- 10 R. S. Paonessa, A. L. Prignano and W. C. Trogler, *Organometallics*, 1985, 4, 647–657; U. Herzog, R. Richter, E. Brendler and G. Roewer, *J. Organomet. Chem.*, 1996, 507, 221–228.
- 11 M. D. Curtis and P. S. Epstein, Adv. Organomet. Chem., 1981, 19, 213– 255.
- 12 H. Yamashita, T. Kobayashi and M. Tanaka, *Chem. Lett.*, 1990, **8**, 1447–1450.
- 13 T. Hayashi, T.-a. Kobayashi, A. M. Kawamoto, H. Yamashita and M. Tanaka, *Organometallics*, 1990, 9, 280–281; K. Tamao, T. Hayashi and M. Kumada, *J. Organomet. Chem.*, 1976, 114, C19–C22; H. Matsumoto, K. Shono, A. Wada, I. Matsubara, H. Watanabe and Y. Nagai, *J. Organomet. Chem.*, 1980, 199, 185–193.
- 14 H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1992, 11, 3227–3232; T. Kobayashi, T. Hayashi, H. Yamashita and M. Tanaka, *Chem. Lett.*, 1988, 1411–1414.
- 15 F. Glockling and K. A. Hooton, J. Chem. Soc. A, 1967, 1066–1075; F. Glockling and K. A. Hooton, Chem. Commun., 1966, 218–219.
- 16 H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1997, 16, 4696–4704; S. O. Grim, R. L. Keiter and W. McFarlane, *Inorg. Chem.*, 1967, 6, 1133–1137; R. Romeo, G. Alibrandi and L. M. Scolaro, *Inorg. Chem.*, 1993, 32, 4688–4694.
- 17 T. Yoshida, T. Matsuda and S. Otsuka, *Inorg. Synth.*, 1990, 28, 119–123.
- 18 E. A. V. Ebsworth, V. M. Marganian, F. J. S. Reed and R. O. Gould, *J. Chem. Soc., Dalton Trans.*, 1978, 1167–1170; J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.*, 1999, **99**, 175–292.
- 19 P. S. Pregosin, R. W. Kunz, ³¹P- and ¹³C-NMR of Transition Metal Phosphine Complexes, Springer Verlag, Berlin, 1979; W. Duncan, W. Anderson, E. A. V. Ebsworth and D. W. H. Rankin, J. Chem. Soc., Dalton Trans., 1973, 21, 2370–2373.
- 20 H. K. Sharma and K. H. Pannel, Chem. Rev., 1995, 95, 1351–1374; H. Yamashita, M. Tanaka and M. Goto, Organometallics, 1992, 11, 3227–3232; U. Schubert, Angew. Chem., 1994, 106, 435–437; K. A. Horn, Chem. Rev., 1995, 95, 1317–1350; Y. Tanaka, H. Yamashita and M. Tanaka, Organometallics, 1995, 14, 530–541; M. Murakami, T. Yoshida and Y. Ito, Organometallics, 1994, 13, 2900–2902; Y. Pan, J. T. Mague and M. J. Fink, Organometallics, 1992, 11, 3495–3497; F. Ozawa, M. Sugawara and T. Hayashi, Organometallics, 1994, 13, 3237– 3243; M. Suginome, H. Oike and Y. Ito, Organometallics, 1994, 13, 4148–4150; M. Suginome, H. Oike and Y. Ito, J. Am. Chem. Soc., 1995, 117, 1665–1666.
- 21 M. Suginome, H. Oike, P. H. Shuff and Y. Ito, J. Organomet. Chem., 1996, 521, 405–408.
- 22 S. Sakaki and M. Ieki, J. Am. Chem. Soc., 1993, 115, 2373–2381; E. A. V. Ebsworth, V. M. Marganian, F. J. S. Reed and R. O. Gould, J. Chem. Soc., Dalton Trans., 1978, 1167–1170.
- H. K. Sharma and K. H. Pannel, *Chem. Rev.*, 1995, 95, 1351–1374;
 H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1992, 11, 3227–3232.
- 24 M. J. Michalczyk, C. A. Recatto, J. C. Celabrese and M. J. Fink, J. Am. Chem. Soc., 1992, 114, 7955–7957.
- 25 J. Chatt, C. Eaborn, S. D. Ibekwe and P. N. Kapoor, J. Chem. Soc. A, 1970, 1343–1351.
- 26 J. Braddock-Wilking, J. Y. Corey, K. A. Trankler, H. Xu, L. M. French, N. Praingam, C. White and N. P. Rath, *Organometallics*, 2006, 25, 2859–2871.
- 27 U. Schubert, Adv. Organomet. Chem., 1990, 30, 151–187; F. Delpech, J. Mansas, H. Leuser, S. Sabo-Etienne and B. Chaudret, Organometallics, 2000, 19, 5750–5757.