Dalton Transactions

RSC Publishing

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Cite this: *Dalton Trans.*, 2013, **42**, 4052

Activation of Si–Si and Si–H bonds at Pt: a catalytic hydrogenolysis of silicon–silicon bonds†

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Received 23rd October 2012,
Accepted 9th January 2013

DOI: 10.1039/c3dt32530j

www.rsc.org/dalton

The activation of $Ph_2HSiSiHPh_2$ and $Me_3SiSiMe_3$ at $[Pt(PEt_3)_3]$ (**1**) yielded the products of oxidative addition. The formation of $[Pt(SiHPh_2)_2(PEt_3)_2]$ (**2**) as a mixture of the *cis* and *trans* isomers appears to proceed quantitatively, whereas a conversion to give *cis*-$[Pt(SiMe_3)_2(PEt_3)_2]$ (**3**) was not complete. Treatment of **1** with one equivalent of H_2SiPh_2 led to *cis*-and *trans*-$[Pt(H)(SiHPh_2)(PEt_3)_2]$ (***cis*-4**, ***trans*-4**) together with the dinuclear complex $[(Et_3P)_2(H)Pt(\mu\text{-}SiPh_2)(\mu\text{–}\eta^2\text{-}HSiPh_2)Pt(PEt_3)]$ (**5**). In contrast, $HSiMe_3$ reacts with $[Pt(PEt_3)_3]$ to yield *cis*-$[Pt(H)(SiMe_3)(PEt_3)_2]$ (**7**) exclusively. Catalytic reactions of dihydrogen with the disilanes $Ph_2HSiSiHPh_2$ or $Me_3SiSiMe_3$ in the presence of catalytic amounts of $[Pt(PEt_3)_3]$ (**1**) led to the products of hydrogenolysis, H_2SiPh_2 and $HSiMe_3$. The conversion of $Me_3SiSiMe_3$ is much slower and needs higher temperature to proceed.

Introduction

The cleavage of Si–H and Si–Si bonds by transition metal complexes[1,2] can be considered as one of the key steps in various catalytic reactions like hydrosilylations[3,4] or disilylations[5] of unsaturated compounds. The catalytic dehydrogenative coupling of silanes is a well recognized process.[6] Thus, the coupling of primary or secondary silanes can be applied for the synthesis of polysilanes.[7] However, the reverse reaction, catalytic hydrogenolysis of disilanes with H_2, still represents a major challenge. The reaction usually proceeds under harsh reaction conditions such as high pressure or high temperature and with low selectivities. Most of the procedures are covered by patent specifications.[8] In 1972 Atwell *et al.* described a catalytic process with palladium on charcoal as a catalyst at 3.8 bar hydrogen pressure to produce $HSiMe_3$ with a turnover number of 16.[9] Note that to the best of our knowledge only one catalytic process in a homogeneous phase which proceeds under moderate pressure and temperature conditions was published by Rosenberg *et al.*[10] They described the catalytic conversion of $Ph_2HSiSiHPh_2$ and H_2 to yield H_2SiPh_2 within one week by using 0.8 mol% $[Rh(Cl)(PPh_3)_3]$ as a catalyst.

An example for the conversion of a disilane to give one equivalent of the corresponding tertiary silane is represented by the reaction of $(OEt)_3SiSi(OEt)_3$ with $[Pt(PEt_3)_3]$ (**1**) in the presence of H_2 to give the hydrido–silyl complexes *cis*-$[Pt(H)\{Si(OEt)_3\}(PEt_3)_2]$ and *trans*-$[Pt(H)\{Si(OEt)_3\}(PEt_3)_2]$ as well as $HSi(OEt)_3$. However, no subsequent reaction of the Pt complexes with dihydrogen was observed.[11] Previously, we also reported a cyclic process for the reaction of $ClMe_2SiSiMe_2Cl$ with dihydrogen to yield $HSiMe_2Cl$.[12] Treatment of the bissilyl complex *cis*-$[Pt(SiMe_2Cl)_2(PEt_3)_2]$ with dihydrogen gave *trans*-$[Pt(H)_2(PEt_3)_2]$ and two equivalents of $HSiMe_2Cl$. In the presence of H_2 complex *trans*-$[Pt(H)_2(PEt_3)_2]$ does not react with $Me_2ClSiSiClMe_2$ to give again the activation product *cis*-$[Pt(SiMe_2Cl)_2(PEt_3)_2]$. This inhibition reaction by dihydrogen hampered a catalytic conversion. However, by adding PEt_3 and a subsequent removal of H_2 *in vacuo* it is possible to regain the complex $[Pt(PEt_3)_3]$, which then reacts again with $ClMe_2SiSiMe_2Cl$ to give $[Pt(SiMe_2Cl)_2(PEt_3)_2]$.

In this paper we describe Si–Si activation reactions of $Ph_2HSiSiHPh_2$ and $Me_3SiSiMe_3$ at $[Pt(PEt_3)_3]$ (**1**). In addition, the reactivity of the bissilyl complexes *cis*-$[Pt(SiHPh_2)_2(PEt_3)_2]$ (***cis*-2**) and *trans*-$[Pt(SiHPh_2)_2(PEt_3)_2]$ (***trans*-2**) towards dihydrogen was investigated. The reactivity of the hydrido silyl complexes *cis*-$[Pt(H)(SiHPh_2)(PEt_3)_2]$ (***cis*-4**) and *trans*-$[Pt(H)(SiHPh_2)(PEt_3)_2]$ (***trans*-4**) and *cis*-$[Pt(H)(SiMe_3)(PEt_3)_2]$ (**7**), which are possible intermediates in a catalytic process, was also studied. These investigations led to the development of a catalytic process for the hydrogenolysis of $Ph_2HSiSiHPh_2$ and $Me_3SiSiMe_3$.

Results

Si–Si activation at $[Pt(PEt_3)_3]$ (1)

A mixture of the bissilyl complexes *cis*-$[Pt(SiHPh_2)_2(PEt_3)_2]$ (***cis*-2**) and *trans*-$[Pt(SiHPh_2)_2(PEt_3)_2]$ (***trans*-2**) was synthesized

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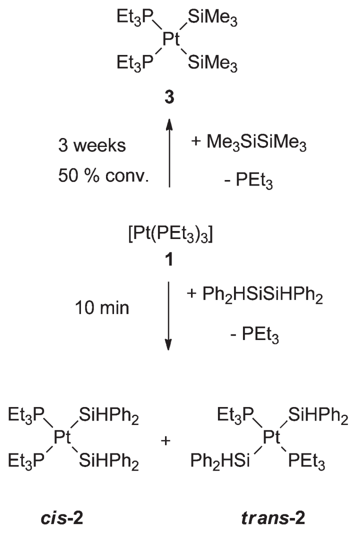
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3dt32530j



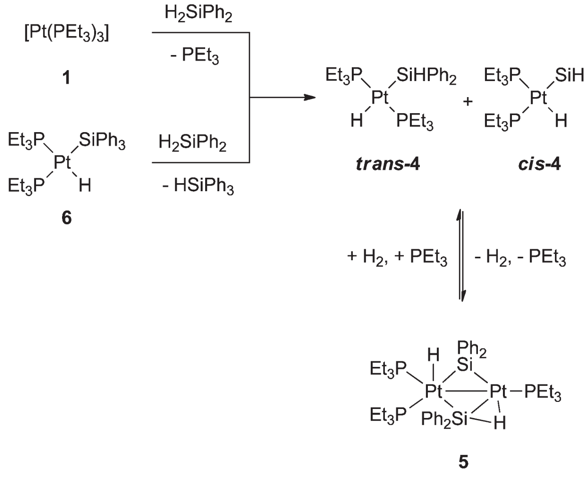
Scheme 1 Formation of the bissilyl complexes ***cis*-2**, ***trans*-2** and **3**.

by the oxidative addition of $Ph_2HSiSiHPh_2$ at $[Pt(PEt_3)_3]$ (**1**) (Scheme 1). The reaction proceeds at room temperature, in benzene and is completed after 10 minutes. The ratio for ***cis*-2 : *trans*-2** is 1 : 0.27. The $^{31}P\{^1H\}$ NMR spectrum for ***cis*-2** shows a singlet with ^{195}Pt satellites at δ 15.3 ppm ($^1J_{PtP}$ = 1706 Hz). The coupling constant is in a typical range of *cis*-substituted platinum phosphine bissilyl complexes.[11–13] In contrast, the resonance for complex ***trans*-2** at δ 6.80 ppm in the $^{31}P\{^1H\}$ NMR spectrum shows a much larger phosphorus–platinum coupling of $^1J_{PtP}$ = 2436 Hz, because of the weaker *trans*-influence of the phosphine ligands compared to the silyl groups.[14]

The ^1H NMR spectrum of ***cis*-2** displays a virtual triplet with platinum satellites at δ 5.82 ppm ($J_{PH,apparent}$ = 15.7 Hz) for the silicon-bound hydrogen atoms. ^{31}P decoupling experiments reveal the $^2J_{PtH}$ coupling constant to be 68.8 Hz. A triplet at δ 5.54 ppm with platinum satellites ($^2J_{PtH}$ = 23.6 Hz and $^3J_{PH}$ = 10.9 Hz) for the silicon bound hydrogen atoms reveals the presence of ***trans*-2**. Note that Lee *et al.* prepared the same complexes by treatment of $[Pt(PEt_3)_4]$ with 2 equivalents of H_2SiPh_2 followed by drying the reaction mixture *in vacuo*.[15]

It was described before that the oxidative addition of $Me_3SiSiMe_3$ at $[Pt(PEt_3)_3]$ (**1**) leads to the bissilyl complex *cis*-$[Pt(SiMe_3)_2(PEt_3)_2]$ (**3**) (Scheme 1).[12] In contrast to the reactivity of **1** towards $Ph_2HSiSiHPh_2$, the reaction with $Me_3SiSiMe_3$ is much slower. After 3 weeks at room temperature we observed approximately 50% conversion to give the bissilyl complex **3**.

Other examples for the activation of Si–Si bonds at platinum complexes and the formation of bissilyl complexes were reported before.[2] For instance, Goto *et al.* showed that $[Pt(PEt_3)_3]$ (**1**) reacts with $HMe_2SiSiMe_2H$ at 243 K in pentane to yield the bissilyl compound *cis*-$[Pt(SiMe_2H)_2(PEt_3)_3]$.[16] Ito *et al.* reported that the reaction of $[Pt_3(CNAd)_6]$ (Ad = 1-adamantyl) with $Me_3SiSiMe_3$ at 353 K yields the bissilyl complex $[Pt(SiMe_3)_2(CNAd)_2]$ in nearly quantitative yields.[17] Note that the activation of $Ph_2HSiSiHPh_2$ might proceed *via* an initial Si–H activation step and is therefore more facile.[18]



Scheme 2 Formation of ***cis*-4**, ***trans*-4** and **5**.

Reactions of H_2SiPh_2 and $HSiMe_3$ with $[Pt(PEt_3)_3]$ (1)

Treatment of **1** with one equivalent of H_2SiPh_2 at room temperature led instantly to a reaction. However, the products are highly dynamic in solution on the NMR time-scale. At room temperature a very broad feature from 5 ppm to 22 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum (121.5 MHz). In the ^1H NMR spectrum a broad resonance at δ −1.8 ppm with a coupling constant of $^1J_{PtH}$ = 932 Hz was observed. The low temperature (190 K) $^{31}P\{^1H\}$, ^1H, and $^1H,^{29}Si$ HMBC NMR spectra indicate the presence of the three complexes *cis*-$[Pt(H)(SiHPh_2)(PEt_3)_2]$ (***cis*-4**), *trans*-$[Pt(H)(SiHPh_2)(PEt_3)_2]$ (***trans*-4**) and the dinuclear compound $[(Et_3P)_2(H)Pt(\mu\text{-}SiPh_2)(\mu\text{–}\eta^2\text{-}HSiPh_2)Pt(PEt_3)]$ (**5**) as well as of hydrogen and PEt_3 in the reaction mixture (Scheme 2), the ratio ***cis*-4 : *trans*-4 : 5** is approximately 2 : 0.58 : 3.2. At low temperature, the signals of ***trans*-4** and **5** sharpened whereas the resonances of ***cis*-4** remained broad. The generation of **5** can be explained by the elimination of H_2 and PEt_3 from 2 equivalents of ***cis*-4**/***trans*-4**. Nevertheless, free H_2 might induce an isomerisation between ***cis*-4** and ***trans*-4** *via* a Pt(IV) compound. Reductive elimination processes of tertiary silanes at Pt(II) are also known.[19] In addition, a photochemical isomerization of Pt(II) hydrido–silyl complexes was reported.[19,20]

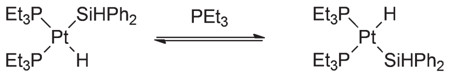
Note that even by evaporation of the volatiles and drying of the reaction mixture for 24 hours in a high vacuum it was not possible to achieve a quantitative formation of **5**. To verify the identity of ***cis*-4** and ***trans*-4**, we synthesised the complexes by an alternative route which involves a replacement of the silyl group in *cis*-$[Pt(H)(SiPh_3)(PEt_3)_2]$ (**6**). Thus, the reaction of **6** with one equivalent of H_2SiPh_2 resulted at room temperature in broad signals in the $^{31}P\{^1H\}$ NMR spectrum in a ratio of 1 : 0.22 for ***cis*-4** and ***trans*-4**. Free $HSiPh_3$ was also observed (Scheme 2).

At 190 K a resonance at δ 18.0 ppm with a coupling constant of $^1J_{PtP}$ = 2536 Hz was found for complex ***trans*-4** in the $^{31}P\{^1H\}$ NMR spectrum. As mentioned above, the resonances for the complex ***cis*-4** are broad even at low temperature and appear at δ 22.5 ppm and δ 16.6 ppm. The signals exhibit coupling constants of $^1J_{PPt} \sim 2260$ Hz (*cis* to a silyl ligand) and $^1J_{PPt} \sim 1700$ Hz (*trans* to a silyl ligand). The latter value is in a typical range for complexes in which the metal bound silyl group exerts a strong *trans* influence.[14,19] The ^{1}H,^{29}Si HMBC NMR spectrum reveals cross resonances at δ 6 ppm in the ^{29}Si domain for ***cis*-4** and at δ −3 ppm for ***trans*-4**.

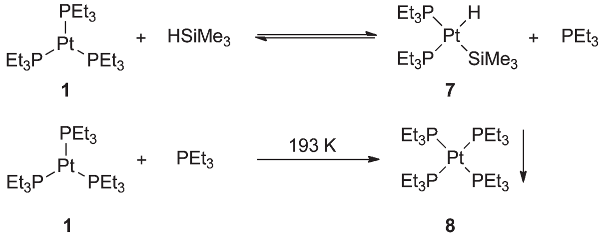
The $^{31}P\{^1H\}$ NMR spectrum of **5** at 190 K shows two resonances for the inequivalent phosphine ligands; a triplet at δ 13.3 ppm ($^1J_{PPt} = 3874$ Hz, $^2J_{PPt} = 258$ Hz) and a doublet at δ −1.15 ppm ($^1J_{PPt} = 3500$ Hz, $^2J_{PPt} = 105$ Hz). The phosphorus–phosphorus coupling constant is $^3J_{PP} = 23$ Hz. The ^{1}H NMR spectrum displays a triplet resonance at δ −7.4 ppm with coupling constants of $^1J_{HPt} = 537$ Hz, $^2J_{HPt} = 79$ Hz, and $^2J_{HP} = 13$ Hz for the non-bridging hydrido ligand. The signal for the bridging hydrogen atom is covered by the resonances of the ethyl groups, but the ^{1}H,^{29}Si HMBC NMR spectrum reveals a correlation at δ 1.2 ppm in the ^{1}H domain. The ^{1}H,^{29}Si HMBC NMR spectrum also shows a large downfield shift of the resonances at δ 179 ppm and δ 178 ppm in the ^{29}Si domain for the silicon containing groups compared to the signals ***cis*-4**/***trans*-4**. Equilibrium reactions between hydrido–silyl complexes and unsymmetric binuclear platinum silyl complexes (Scheme 2) were described before by Braddock-Wilking *et al.*[21] and by Mochida *et al.*[22] The ^{31}P, ^{1}H, and ^{29}Si NMR data for **5** are in good agreement with the reported literature data.

The observation of the broad resonances in the ^{31}P NMR spectrum of ***cis*-4** even at 190 K indicates a further equilibrium. VT NMR studies revealed no significant change of the chemical shift of the signals. We suggest a dynamic behaviour which is characterized by an intramolecular exchange of the hydrido and silyl ligands that involves free triethylphosphine (Scheme 3). The latter is always present in the solution, because of the equilibrium with **5** (see above). A similar broadening in the $^{31}P\{^1H\}$ and ^{1}H NMR spectra for the signals of triethylphosphine hydrido–silyl complexes can be observed after treatment of $[Pt(PEt_3)_3]$ (**1**) with other silanes such as $HSiMe_2Cl$,[12] $HSiEt_3$,[23] $HSiPh_3$,[24] $HSiMePh_2$,[11] and $HSi(OEt)_3$[11] as long as residual PEt_3 is still present in the reaction mixture. The NMR resonances are broadened also by adding PEt_3 to solutions of the *cis*-$[Pt(H)(SiR_3)(PEt_3)_2]$ ($R_3 = Me_2Cl$, Et_3, Ph_3, Me_3, $MePh_2$, OEt_3, Ph_2H) complexes. Intramolecular phosphine exchange on platinum hydrido silyl complexes was reported before.[19]

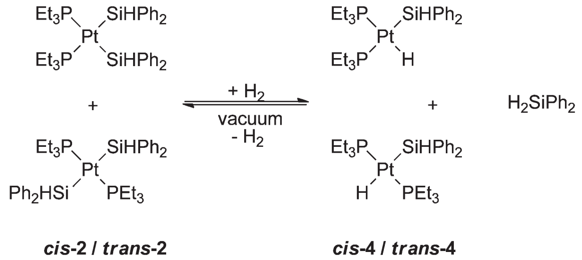
NMR studies of a reaction of **1** with $HSiMe_3$ at room temperature revealed after work-up 5% conversion to yield *cis*-$[Pt(H)(SiMe_3)(PEt_3)_2]$ (**7**) (Scheme 4).[25] However, at 193 K free phosphine reacts with complex **1** to form $[Pt(PEt_3)_4]$ (**8**), which precipitates. Repeating this procedure yielded 50% conversion of **1** into **7**. Complex **7** can be isolated as a dark red oil. Note that Trogler *et al.* synthesized **7** by reaction of $[Pt(C_2F_4)(PEt_3)_2]$ with an excess of $HSiMe_3$ at room temperature.[26]



Scheme 3 Fluxionality in complex ***cis*-4**.



Scheme 4 Reactivity of **1** with $HSiMe_3$.



Scheme 5 Reactivity of ***cis*-2** and ***trans*-2** towards dihydrogen.

Reactivity of *cis*-$[Pt(SiHPh_2)_2(PEt_3)_2]$ (*cis*-2) and *trans*-$[Pt(SiHPh_2)_2(PEt_3)_2]$ (*trans*-2) towards dihydrogen

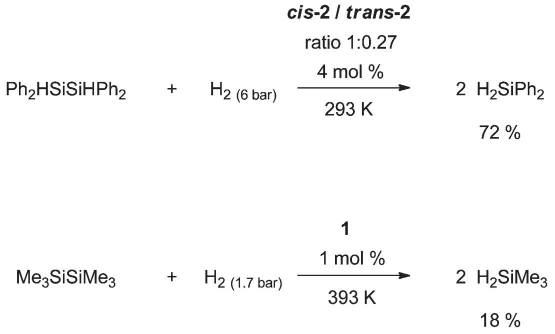
The reaction of ***cis*-2** and ***trans*-2** with H_2 under ambient conditions led to the formation of *cis*-$[Pt(H)(SiHPh_2)(PEt_3)_2]$ (***cis*-4**) and *trans*-$[Pt(H)(SiHPh_2)(PEt_3)_2]$ (***trans*-4**) in a ratio of 1 : 0.1 as well as of H_2SiPh_2 (Scheme 5). After one hour 80% of the starting material was converted according to the ^{1}H NMR spectrum. The *trans* isomer ***trans*-2** could not be detected anymore which indicates a higher reactivity of ***trans*-2**, which might be caused by the strong *trans* influence of the silyl groups. In contrast, ***cis*-2** does not convert completely even at higher dihydrogen pressure. After removal of the volatiles *in vacuo* the bissilyl complexes ***cis*-2** and ***trans*-2** (ratio 1 : 0.2) were regenerated by elimination of dihydrogen and consumption of the free silane (Scheme 5).

Development of catalytic processes for the formation of H_2SiPh_2 and $HSiMe_3$

Based on the stoichiometric reactions described above, we studied the reactivity of ***cis*-2** and ***trans*-2** (ratio 1 : 0.27) towards a possible catalytic hydrogenolysis of $Ph_2HSiSiHPh_2$ for producing H_2SiPh_2. The reaction of ***cis*-2** and ***trans*-2** with 10 equiv. of $Ph_2HSiSiHPh_2$ was carried out at different temperatures and dihydrogen pressures (Table 1). The progress of the reactions was monitored by NMR spectroscopy and GC-MS analysis. Note that the formation of H_2SiPh_2 at room temperature and one atmosphere of dihydrogen is very slow. After 12 hours only one equivalent of $Ph_2HSiSiHPh_2$ was converted. By increasing the temperature the reaction accelerated at 1.7 bar hydrogen pressure, but more products of a redistribution

Table 1 Silane products (mol%) after a reaction of $Ph_2HSiSiHPh_2$ with hydrogen in the presence of ***cis*-2** and ***trans*-2** (10 mol%) after 2 h

Pressure	Temp.	Consumption of disilane	$HSiPh_3$	H_2SiPh_2	H_3SiPh	Others
1 bar	298 K	10% (after 12 h)	1.5	97	1.5	—
1.7 bar	298 K	2%	0.7	98.6	0.7	—
1.7 bar	323 K	6%	50	42	8	—
1.7 bar	353 K	33%	49	45	5	$PhH_2SiSiPh_3$
6 bar	298 K	36%	0.9	98.2	0.9	—



Scheme 6 Catalytic formation of H_2SiPh_2 and $HSiMe_3$.

of the phenyl groups at the silane such as $HSiPh_3$, $PhH_2SiSiPh_3$ and H_3SiPh were formed (Table 1).

For a catalytic conversion, the reaction was finally performed at 6 bar dihydrogen pressure in an autoclave at room temperature with 25 equiv. of disilane. According to the GC-MS and ^1H NMR spectroscopic data, a turnover number of 18 was achieved after 50 hours, based on the disilane consumption (Scheme 6). In addition to the product H_2SiPh_2 less than 2% of $HSiPh_3$ and H_3SiPh were present as impurities. Notably, the amount of redistribution products is very low, although such reactions were observed frequently at transition metal centres.[10,27] The ^1H and ^{31}P NMR spectroscopic data of the resulting reaction mixture also showed the presence of the complexes ***cis*-2** and ***trans*-2** in a ratio of 1 : 0.27.

Rosenberg *et al.* estimated an equilibrium constant of $K_c = 10^4$ at room temperature for the reaction of $Ph_2HSiSiHPh_2$ with dihydrogen to form two equivalents of H_2SiPh_2 with $[Rh(Cl)(PPh_3)_3]$ as a catalyst.[10] This shows that the hydrogenolysis of $Ph_2HSiSiHPh_2$ is an exergonic process. For comparison, DFT calculations for the analogous reaction of $Me_3SiSiMe_3$ with dihydrogen at the B3LYP/cc-pVTZ level[28–30] suggest that the hydrogenolysis yielding $HSiMe_3$ is also exergonic with an equilibrium constant of approximately $K = 10^9$ ($\Delta G = -54.0$ kJ mol^{-1}) at 293 K. However, a reaction of $Me_3SiSiMe_3$ with dihydrogen in the presence of **1** at room temperature and 6 bar H_2 yielded only small amounts of $HSiMe_3$, but by increasing the temperature to 392 K a catalytic reaction was achieved. The conversion was monitored by NMR spectroscopy and GC-MS analysis. In a reaction of **1** with 100 equivalents of $Me_3SiSiMe_3$ at 393 K and a dihydrogen pressure of 1.7 bar a turnover number of 18, based on the disilane consumption, was achieved after 90 hours (Scheme 6). Monitoring the reaction by NMR spectroscopy revealed that after adding dihydrogen to the solution of **1** and disilane the NMR signals became very broad, and it was not possible to identify any platinum compounds. On cooling to 213 K only signals for $[Pt(H)_2(PEt_3)_3]$ (**9**) were observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.[31] After removal of the solvent and the excess silane under vacuum only complex **1** was present. Note that there are very few examples for the hydrogenolysis of $Me_3SiSiMe_3$ reported in the literature.[9]

Conclusions

Catalytic processes for the hydrogenolysis of $Ph_2HSiSiHPh_2$ and $Me_3SiSiMe_3$ were developed. Conceivable intermediates of the catalytic process were synthesised and identified by NMR spectroscopy. We consider the use of dihydrogen as a hydrogen source as superior to alternative methods for the transformation of silicon–silicon bonds into hydrogen–silicon bonds, which often include the reaction of disilanes with HCl at high temperature and high pressure resulting in a mixture of chloro and hydrido silanes.[32] The development of a reaction route for the hydrogenolysis of disilanes is of certain importance, because it opens up new opportunities to access higher-value silanes which can be applied for further synthesis.[12,33] Note that in the Müller–Rochow process chlorinated disilanes and polysilanes are produced, which might be converted into monosilanes by hydrogenolysis.[34] Other catalytic reactions which involve the activation of the Si–Si bond in $Me_3SiSiMe_3$ include the bissilylation of double bonds,[35] triple bonds,[36] or α,α-diketones.[37] The Si–Si bond in $Me_3SiSiMe_3$ can also be cleaved stoichiometrically on using for instance Br_2, B_2H_6, MeLi or KOMe.[38]

Experimental

The synthetic work was carried out on a Schlenk line or in a glovebox. Toluene and pentane were purified by distillation from Na/K and stored under argon over molecular sieves (3 Å). High pressure experiments were performed in an autoclave HR-100 with a PTFE insert (Berghof instruments). NMR high pressure tubes were purchased from Wilmad Lab glass. NMR spectra were acquired on a Bruker DPX 300 or a Bruker AV 400 spectrometer. ^1H NMR spectra were referenced to residual C_6D_5H at δ 7.15 ppm. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 at δ 0 ppm, respectively. ^{19}F NMR spectra were referenced to C_6F_6 at δ −162.9 ppm. GC-MS data were obtained at an Agilent Technologies GC 6890N which was equipped with a 5973 mass spectrometer as a detector. [Pt(PEt$_3$)$_3$] (**1**) was prepared according to the literature.[39] Hexamethyldisilane and tetraphenyldisilane were purchased from ABCR.

Synthesis of *cis*-[Pt(SiHPh$_2$)$_2$(PEt$_3$)$_2$] (*cis*-2) and *trans*-[Pt(SiHPh$_2$)$_2$(PEt$_3$)$_2$] (*trans*-2)

A red solution of [Pt(PEt$_3$)$_3$] (**1**) (400 mg, 0.73 mmol) in benzene (5 ml) was treated with 267 mg (0.73 mmol) Ph$_2$HSiSiHPh$_2$. After stirring for 10 min the colour of the solution turned yellow. The reaction mixture was then evaporated to dryness. A pale yellow highly viscous oil was obtained. Yield: 565 mg (97%). Ratio: ***cis*-2** : ***trans*-2** = 1 : 0.27 (Found C, 54.38; H, 6.55. C$_{36}$H$_{52}$P$_2$PtSi$_2$ requires C, 54.18; H, 6.57%). NMR data for ***cis*-2**: ^{1}H NMR (400.1 MHz, C$_6$D$_6$): δ 0.91 (18 H, m, t in the ^{1}H{^{31}P} NMR spectrum, J_{HH} = 7.6 Hz, PCH$_2$*CH*$_3$), 1.73 (12 H, m, q in the ^{1}H{^{31}P} NMR spectrum, J_{HH} = 7.6 Hz, P*CH*$_2$CH$_3$), 5.82 (2 H, vt + ^{195}Pt satellites, $J_{\mathrm{PH,apparent}}$ = 15.7 Hz, J_{PtH} = 68.8 Hz, SiH), 7.25 (12 H, m, *meta* and *para* Ar), 7.87 (8 H, m, *ortho* Ar); ^{31}P{^{1}H} NMR (161.9 MHz, C$_6$D$_6$): δ 15.3 (s + satellites, J_{PPt} = 1706 Hz), ^{1}H,^{29}Si HMBC NMR (400.1 MHz/79.5 MHz, C$_6$D$_6$): δ 7.8/−11 (s + ^{195}Pt satellites, $^1J_{\mathrm{SiPt}}$ = 1330 Hz, *ortho* Ar), 5.8/−11 (s, SiH). NMR data for ***trans*-2**: ^{1}H NMR (400.1 MHz, C$_6$D$_6$): δ 0.83 (18 H, m, t in the ^{1}H{^{31}P} NMR spectrum, J_{HH} = 7.4 Hz, PCH$_2$*CH*$_3$), 1.99 (12 H, m, q in the ^{1}H{^{31}P} NMR spectrum, J_{HH} = 7.4 Hz, P*CH*$_2$CH$_3$), 5.54 (2 H, t + ^{195}Pt satellites, J_{PH} = 10.9 Hz, J_{PtH} = 23.6 Hz, SiH), 7.20 (4 H, m, *para* Ar), 7.37 (8 H, m, *meta* Ar), 8.04 (8 H, m, *ortho* Ar); ^{31}P{^{1}H} NMR (161.9 MHz, C$_6$D$_6$): δ 6.80 (s + ^{195}Pt satellites, J_{PPt} = 2436 Hz); ^{1}H,^{29}Si HMBC NMR (400.1 MHz/79.5 MHz, C$_6$D$_6$): δ 8.0/5 (s + ^{195}Pt satellites, J_{SiPt} = 875 Hz, *ortho* Ar), 5.5/5 (s, SiH).

Reaction of [Pt(PEt$_3$)$_3$] (1) with H$_2$SiPh$_2$

A red solution of 48.6 mg (0.09 mmol) **1** in 1 ml benzene was treated with 16.3 μl (0.09 mmol) H$_2$SiPh$_2$. The colour of the solution changed rapidly to pale yellow. After stirring for 30 min all volatiles were removed *in vacuo*. A yellow highly viscous oil was obtained. Yield: 49 mg (90%). Selected NMR data (in the ^{1}H NMR spectrum the signals for the PEt$_3$ ligands at ***cis*-4**, ***trans*-4** and **5** overlap). NMR data for ***cis*-4**: ^{1}H NMR (300.1 MHz, toluene-d^8, 190 K): δ −1.81 (1 H, br, d + ^{195}Pt satellites, $^1J_{\mathrm{PtH}}$ = 925 Hz, $^2J_{\mathrm{PH}(trans)}$ = 132 Hz, PtH), 5.41 (1 H, m + ^{195}Pt satellites, $^1J_{\mathrm{SiH}}$ = 155 Hz, $^2J_{\mathrm{PtH}}$ = 25 Hz, SiH), 7.14 (2 H, m, *para* Ar), 7.31 (4 H, *meta* Ar), 8.11 (4 H, m, *ortho* Ar); ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d^8, 190 K): δ 16.6 (s, br, + ^{195}Pt satellites, J_{PPt} = 2260 Hz, P *cis* to Si), 22.5 (s, br, + ^{195}Pt satellites, $^1J_{\mathrm{PPt}}$ = 1700 Hz, P *trans* to Si); ^{1}H,^{29}Si HMBC NMR (300.1 MHz/59.6 MHz, toluene-d^8, 190 K): δ 8.1/6 (s + ^{195}Pt satellites, $^1J_{\mathrm{PtSi}}$ = 1140 Hz, *ortho* Ar), 7.3/6 (s + ^{195}Pt satellites, $^1J_{\mathrm{PtSi}}$ = 1140 Hz, *meta* Ar), 5.4/6 (s + ^{195}Pt satellites, $^1J_{\mathrm{PtSi}}$ = 1140 Hz, SiH). NMR data for ***trans*-4**: ^{1}H NMR (300.1 MHz, toluene-d^8, 190 K): δ 0.45 (1 H, t + ^{195}Pt satellites, $^1J_{\mathrm{PtH}}$ = 750 Hz, $^2J_{\mathrm{PH}}$ = 18 Hz, PtH), 5.52 (1 H, m + ^{195}Pt satellites, $^2J_{\mathrm{PtH}}$ = 27 Hz, ^{29}Si satellites not observed, SiH), 7.20–7.30 (6 H, m, *meta* and *para* Ar), 7.91 (4 H, m, *ortho* Ar); ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d^8, 190 K): δ 18.0 (s + ^{195}Pt satellites, J_{PPt} = 2536 Hz); ^{1}H,^{29}Si HMBC NMR (300.1 MHz/59.6 MHz, toluene-d^8, 190 K): δ 7.9/−3 (s + ^{195}Pt satellites, $^1J_{\mathrm{PtSi}}$ = 995 Hz, *ortho* Ar), 5.3/−3 (s, SiH). NMR data for **5**: ^{1}H NMR (300.1 MHz, toluene-d^8, 190 K): −7.41 (1 H, t + ^{195}Pt satellites, $^1J_{\mathrm{PtH}}$ = 536 Hz, $^2J_{\mathrm{PtH}}$ = 79 Hz, $^2J_{\mathrm{PH}}$ = 13 Hz, PtH), 8.07 (4 H, m, *ortho* Ar, PtHSi), 8.16 (4 H, m, *ortho* Ar), the signal for PtHSi hydrogen is covered by resonances of the Et groups; ^{31}P{^{1}H} NMR (121.5 MHz, toluene-d^8, 190 K): δ −1.2 (d + ^{195}Pt satellites, $^1J_{\mathrm{PPt}}$ = 3500 Hz, $^2J_{\mathrm{PPt}}$ = 105 Hz, $^4J_{\mathrm{PP}}$ = 23 Hz, Pt(*P*Et$_3$)$_2$), 13.3 (t + ^{195}Pt satellites, $^1J_{\mathrm{PPt}}$ = 3874 Hz, $^2J_{\mathrm{PPt}}$ = 258 Hz, $^3J_{\mathrm{PP}}$ = 23 Hz, Pt(*P*Et$_3$); ^{1}H,^{29}Si HMBC NMR (300.1 MHz/59.6 MHz, toluene-d^8, 190 K): δ −7.4/179 (s, PtH), 8.2/179 (s, *ortho* Ar), −7.4/178 (s, PtH), 1.2/178 (s, Pt–H–Si), 8.1/178 (s, *ortho* Ar).

Reaction of *cis*-[Pt(SiHPh$_2$)$_2$(PEt$_3$)$_2$] (*cis*-2) and *trans*-[Pt(SiHPh$_2$)$_2$(PEt$_3$)$_2$] (*trans*-2) with H$_2$

Hydrogen gas was bubbled into a bright yellow solution of *cis*-[Pt(SiHPh$_2$)$_2$(PEt$_3$)$_2$] (***cis*-2**) and *trans*-[Pt(SiHPh$_2$)$_2$(PEt$_3$)$_2$] (***trans*-2**) (48 mg, 0.06 mmol) in C$_6$D$_6$. Within one hour the solution turned colourless. The NMR spectrum shows the presence of *cis*-[Pt(H)(SiHPh$_2$)(PEt$_3$)$_2$] (***cis*-4**) and ***trans*-4** in a ratio of 1 : 0.1 as well as of H$_2$SiPh$_2$.

Reaction of *cis*-[Pt(H)(SiPh$_3$)(PEt$_3$)$_2$] (6) with H$_2$SiPh$_2$

112 mg (0.16 mmol) **6** were suspended in 3 ml C$_6$D$_6$ and 30 μl (0.16 mmol) H$_2$SiPh$_2$ were added at room temperature. The reaction mixture became clear. The ^{1}H, ^{31}P and ^{1}H,^{29}Si HMBC NMR spectroscopic data of the solution revealed the presence of the complexes ***cis*-4** and ***trans*-4** as well as of HSiPh$_3$. Ratio: ***cis*-4** : ***trans*-4** = 1 : 0.22.

Reaction of [Pt(PEt$_3$)$_3$] (1) with HSiMe$_3$

A red solution of [Pt(PEt$_3$)$_3$] (**1**) (125 mg, 0.23 mmol) in toluene (3 ml) was cooled to −80 °C and an excess of HSiMe$_3$ was condensed to the solution. The resulting suspension was filtered and the filtrate was treated a second time with HSiMe$_3$ and filtered again. After removing the solvent from the filtrate a dark red oil was obtained. The ^{1}H and ^{31}P NMR spectroscopic data reveal the formation of *cis*-[Pt(H)(SiMe$_3$)(PEt$_3$)$_2$] (**7**).[26]

Catalytic formation of H$_2$SiPh$_2$ by reaction of Ph$_2$HSiSiHPh$_2$ with dihydrogen in the presence of *cis*-2 and *trans*-2

87 mg (0.11 mmol) of a mixture of ***cis*-2** and ***trans*-2** in a ratio of 1 : 0.27 were dissolved in C$_6$D$_6$ (3 ml). The resulting yellow solution was combined with 1 g (2.75 mmol) Ph$_2$HSiSiHPh$_2$ in 20 ml C$_6$D$_6$ and the mixture was then transferred into an autoclave. 6 bar dihydrogen were fed. The reaction was monitored by NMR spectroscopy and GC-MS measurements. After 50 hours the reaction was interrupted, the mixture dried in a vacuum and the resulting oily solid was dissolved in C$_6$D$_6$ and investigated by NMR spectroscopy. The GC-MS and ^{1}H NMR spectroscopic data revealed the formation of H$_2$SiPh$_2$ (TON = 18, based on the disilane consumption, 36 equiv. silane H$_2$SiPh$_2$ with respect to the amount of a catalyst). The ^{1}H and ^{31}P NMR spectroscopic data of the residue showed the

presence of the complexes ***cis*-2** and ***trans*-2** (ratio ***cis*-2** : ***trans*-2** = 1 : 0.20).

Catalytic formation of $HSiMe_3$ by reaction of $Me_3SiSiMe_3$ with dihydrogen

A mixture of 10 mg (0.018 mmol) of **1** in toluene (0.7 ml) and 0.036 ml (1.8 mmol) $Me_3SiSiMe_3$ in C_6D_6 (0.1 ml) was transferred into an NMR pressure tube. 1.7 bar hydrogen pressure was then applied. The NMR tube was heated to 120 °C. After 90 hours the solution was investigated by ^1H NMR spectroscopy and by GC-MS. The spectroscopic data reveal the formation of $HSiMe_3$ (TON 18, based on the disilane consumption, 36 equiv. silane $HSiMe_3$ with respect to the amount of catalyst). After evaporating the volatiles and drying the solution in a vacuum the residue was dissolved in C_6D_6, and complex $[Pt(PEt_3)_3]$ (**1**) was observed in the NMR spectrum.

Acknowledgements

We would like to acknowledge the Deutsche Forschungsgemeinschaft for financial support. We also thank the BASF SE for a gift of solvents.

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