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# Si-H and Si-Si activation at Pt: synthesis and reactivity of neutral and cationic silyl complexes

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Reactions of  $[Pt(PEt_3)_3]$  (1) with the silanes HSiPh<sub>3</sub>, HSiPh<sub>2</sub>Me and HSi(OEt)<sub>3</sub> led to the products of oxidative addition, *cis*- $[Pt(H)(SiPh_3)(PEt_3)_2]$  (2), *cis*- $[Pt(H)(SiPh_2Me)(PEt_3)_2]$  (3), *cis*- $[Pt(H){Si(OEt)_3}-(PEt_3)_2]$  (*cis*-4) and *trans*- $[Pt(H){Si(OEt)_3}(PEt_3)_2]$  (*trans*-4). The complexes *cis*-4 and *trans*-4 can also be generated by hydrogenolysis of  $(EtO)_3SiSi(OEt)_3$  in the presence of 1. Furthermore, the silyl compounds *cis*-4 and *trans*-4 react with  $B(C_6F_5)_3$  and  $CH_3CN$  by hydride abstraction to give the cationic silyl complex *trans*- $[Pt{Si(OEt)_3}(NCCH_3)(PEt_3)_2][HB(C_6F_5)_3]$  (8). In addition, the reactivity of the complexes *cis*-4, *trans*-4 and 8 towards alkenes and CO was studied using NMR experiments.

# Introduction

The cleavage of Si-H and Si-Si bonds by transition metal complexes can be considered as one of the key steps in various reactions like hydrosilylations,1,2 disilylations3,4 or the dehydrocoupling of hydrosilanes.<sup>5</sup> In particular, the formation of hydrido silvl platinum complexes by Si-H activation reactions at Pt(0) species is well known.<sup>6,7</sup> For instance, the reactions of [Pt(PCy<sub>3</sub>)<sub>2</sub>] with tertiary silanes, such as HSiEt<sub>3</sub>, HSiMe<sub>2</sub>Et or H<sub>2</sub>SiEt<sub>2</sub>, led to the formation of cis-[Pt(H)(SiR<sub>2</sub>R')(PCy<sub>3</sub>)<sub>2</sub>] (R = R' = Et; R = Me, R' = Et; R = Et, R' = H).<sup>7</sup> Osakada and Yamamoto reported that a reaction of  $[Pt(PEt_3)_4]$  with the rhodium hydrido silyl complex [Rh(Cl)(H)(SiPh<sub>3</sub>)(PiPr<sub>3</sub>)<sub>2</sub>] gives the Pt(II) complex  $[Pt(H)(SiPh_3)(PEt_3)_2]$ , as well as  $[Rh(Cl)(PEt_3)_3]$  as the major rhodium-containing product.8 The reaction pathway presumably involves a reductive elimination of the silane HSiPh<sub>3</sub> at rhodium, followed by an oxidative addition at platinum. Examples for the activation of Si-Si bonds at platinum complexes and the formation of disilyl complexes have also been described before.4,9,10 Thus, Goto *et al.* showed that  $[Pt(PEt_3)_3]$  (1) reacts at -30 °C in pentane with HMe<sub>2</sub>SiSiMe<sub>2</sub>H to yield the silyl compound *cis*- $[Pt(SiMe_2H)_2(PEt_3)_2].^{10}$ 

The hydrogenolysis of disilanes with H<sub>2</sub> still represents a major challenge. Catalytic processes, which involve such a conversion are rare. Most of them are covered by patent specifications.<sup>11</sup> The reactions normally proceed under harsh reaction conditions such as high pressure or high temperature, but with low selectivities. Previously, we reported on a cyclic process for the reaction of ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl with hydrogen to yield HSiMe<sub>2</sub>Cl.<sup>9</sup> Treatment of the disilyl complex *cis*-[Pt(SiMe<sub>2</sub>Cl)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>], which is available from ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl, with dihydrogen gave *trans*-[Pt(H)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] and two equivalents of HSiMe<sub>2</sub>Cl. Complex *trans*-[Pt(H)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] reacted subsequently with ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl to give again the

Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Str. 2, 12489 Berlin, Germany. E-mail: thomas.braun@chemie.hu-berlin.de activation product *cis*-[Pt(SiMe<sub>2</sub>Cl)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>], but not in the presence of  $H_2$ . Thus, inhibition by dihydrogen hampered a catalytic conversion.

In this paper we describe Si–H activation reactions as well as the stoichiometric hydrogenolysis of  $(EtO)_3SiSi(OEt)_3$  by Si–Si activation. The reaction of  $(EtO)_3SiSi(OEt)_3$  with  $[Pt(PEt_3)_3]$  in the presence of H<sub>2</sub> led to the formation of the hydrido silyl complexes *cis*-[Pt(H){Si(OEt)\_3}(PEt\_3)\_2] (*cis*-4), *trans*-[Pt(H){Si(OEt)\_3}(PEt\_3)\_2] (*trans*-4) and the silane HSi(OEt)\_3. In addition, we report on the generation of an unprecedented cationic silyl complex *trans*-[Pt{Si(OEt)\_3}(NCCH\_3)(PEt\_3)\_2][HB(C<sub>6</sub>F<sub>5</sub>)\_3] (8), which can be synthesized by hydride abstraction from the hydrido silyl complexes *cis*-[Pt(H){Si(OEt)\_3}(PEt\_3)\_2] (*cis*-4) and *trans*-[Pt(H){Si(OEt)\_3}(PEt\_3)\_2] (*trans*-4).

# Results

### Si-Si and Si-H activation at [Pt(PEt<sub>3</sub>)<sub>3</sub>]

The hydrido silyl complexes cis-[Pt(H)(SiPh<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (2), cis-[Pt(H)(SiPh<sub>2</sub>Me)(PEt<sub>3</sub>)<sub>2</sub>] (3) cis-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (cis-4) and trans-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (trans-4) were synthesized by oxidative addition of silanes at [Pt(PEt<sub>3</sub>)<sub>3</sub>] (1) (Scheme 1). Thus, reactions of HSiPh<sub>3</sub> or HSiPh<sub>2</sub>Me with [Pt(PEt<sub>3</sub>)<sub>3</sub>] (1) yielded the complexes cis-[Pt(H)(SiPh<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (2) or cis-[Pt(H)(SiPh<sub>2</sub>Me)(PEt<sub>3</sub>)<sub>2</sub>] (3), respectively (Scheme 1). Note that other routes to furnish hydrido silyl complexes include the treatment of [Pt(Cl)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] with LiSiPh<sub>3</sub> followed by an alcoholysis reaction with methanol to give cis-[Pt(SiPh<sub>3</sub>)(H)(PEt<sub>3</sub>)<sub>2</sub>].<sup>12</sup>

Single crystals of **2**, which were suitable for X-ray analysis, were grown from a benzene/*n*-hexane solution at room temperature. Comparison of the unit cell and results of the X-ray crystallographic analysis with the literature data revealed the presence of **2**. Complex **3** was characterized by its NMR spectroscopic data. The  ${}^{31}P{}^{1}H{}$  NMR spectrum shows two mutually coupled resonances,



Scheme 1 Formation of hydrido silvl complexes at platinum.

each with <sup>195</sup>Pt satellites at  $\delta$  23.7 ppm ( $J_{PPt}$  = 1552.6 Hz) and at  $\delta$  22.7 ppm ( $J_{PPt}$  = 2382.8 Hz). The signal with the smaller P–Pt coupling corresponds to the PEt<sub>3</sub> group in the trans position to the silvl ligand, which has a larger trans influence than the hydride ligand.<sup>13</sup> The <sup>1</sup>H NMR spectrum of **3** displays a signal at  $\delta$  –2.3 ppm with a platinum-hydrogen coupling of 908.8 Hz, which can be assigned to the metal bound hydrogen nucleus. The signal appears as a doublet of doublets with  $J_{\text{HP}(trans)} = 147.0$  Hz and  $J_{\text{HP}(cis)} =$ 21.5 Hz. A 1H, 29Si HMBC NMR spectrum shows a resonance at  $\delta 0.2$  ppm in the <sup>29</sup>Si domain, which correlates with the resonances for the hydrido ligand and for the SiPh<sub>2</sub>Me group. The platinumsilyl coupling is 1100 Hz. The infrared spectrum of 3 displays an absorption band at  $v = 2031 \text{ cm}^{-1}$  for the Pt–H vibration.

A reaction of  $[Pt(PEt_3)_3]$  with  $HSi(OEt)_3$  afforded the isomeric compounds cis-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (cis-4) and trans- $[Pt(H){Si(OEt)_3}(PEt_3)_2]$  (trans-4) in approximately a ratio of 10:1 (Scheme 1). Notably, the same complexes cis-4 and trans-4 as well as  $HSi(OEt)_3$  were obtained in a similar ratio by reaction of 1 and (EtO)<sub>3</sub>SiSi(OEt)<sub>3</sub> in the presence of hydrogen (Scheme 1). After irradiation of a mixture of cis-4 and trans-4 for 5 h, the cis: trans ratio changed from 10:1 to 5:1. Storage of the reaction mixture at room temperature led to the original distribution. It is known that complexes of the type cis-[Pt(H)(SiR<sub>2</sub>R')(PCy<sub>3</sub>)<sub>2</sub>] undergo quantitative cis-trans isomerization when irradiated by a UV source.7,14

The <sup>31</sup>P NMR spectrum of *cis*-4 displays two doublets with platinum satellites for the non-equivalent phosphines at  $\delta$  23.5 ppm ( $J_{PPt} = 1546.2 \text{ Hz}$ , PEt<sub>3</sub> in the *trans*-position to the silyl ligand) and  $\delta$  22.7 ppm ( $J_{PPt} = 2341.7$  Hz, PEt<sub>3</sub> in the *cis*-position to the silyl ligand). A singlet at  $\delta$  23.3 ppm with platinum satellites ( $J_{PPt}$  = 2590 Hz) reveals the presence of trans-4. The <sup>1</sup>H NMR spectrum of cis-4 and trans-4 shows two signals for the hydrido ligands. A doublet of doublets with <sup>195</sup>Pt satellites ( $J_{HPt} = 926.5$  Hz) at  $\delta$ -2.6 ppm can be assigned to cis-4. For trans-4 a triplet with <sup>195</sup>Pt satellites ( $J_{\rm HPt}$  = 678.8 Hz) appears at  $\delta$  0.7 ppm.

Mechanistically, the reaction of 1 with disilane and hydrogen might proceed via  $[Pt{Si(OEt)_3}_2(PEt_3)_2]$ . It has been reported before that cis-[Pt(SiMePh<sub>2</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] reacts with hydrogen to yield trans-[Pt(H)(SiMePh<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>] and HSiMePh<sub>2</sub>.<sup>15</sup> However cis-[Pt(SiMe<sub>2</sub>Cl)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] gives with dihydrogen two equiva-

lents of HSiMe<sub>2</sub>Cl and complex trans-[Pt(H)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>].<sup>9</sup> Initially, the complex *trans*-[Pt(H)(SiMe<sub>2</sub>Cl)(PEt<sub>3</sub>)<sub>2</sub>] and one molecule of HSiMe<sub>2</sub>Cl was formed, but in contrast to the behaviour of *cis*-4 and *trans*-4 (see also below), *trans*-[Pt(H)(SiMe<sub>2</sub>Cl)(PEt<sub>3</sub>)<sub>2</sub>] reacts further with H<sub>2</sub> to generate another molecule of HSiMe<sub>2</sub>Cl. Note that Trogler *et al.* synthesized *cis*-[Pt(SiEt<sub>3</sub>)(H)(PEt<sub>3</sub>)<sub>2</sub>] by reacting cis-/trans- $[Pt(H_2)(PEt_3)_2]$  with HSiEt<sub>3</sub>.<sup>16</sup> The conversion is accompanied by hydrogen elimination.

### Reactivity of cis-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (cis-4) and trans-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (trans-4)

To gain some information on the reactivity of cis-4 and trans-4, they were treated with alkenes, CO and H<sub>2</sub>. Thus, a reaction of *cis*-4 and *trans*-4 with CO at 1 atm led immediately to the formation of [Pt(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] (5) and HSi(OEt)<sub>3</sub> (Scheme 2). Complex 5 was characterized by comparison of its NMR data with those in the literature.<sup>16</sup> Treatment of *cis*-4 and *trans*-4 with ethene or norbornene did not lead to hydrosilylation of the olefins.<sup>17</sup> Instead, the formation of the olefin complexes  $[Pt(C_7H_{10})(PEt_2)_2]$  (6) and  $[Pt(C_2H_4)(PEt_2)_2]$  (7) was observed, as well as the generation of HSi(OEt)<sub>3</sub> (Scheme 2). Note that [(Cp\*)Rh(H)<sub>2</sub>(SiEt<sub>3</sub>)<sub>2</sub>] also reacts with ethene to yield free silane and  $[(Cp^*)Rh(H)(SiEt_3)(C_2H_4)]^{.18}$ The complexes 6 and 7 were identified by comparison of their NMR spectroscopic data with the literature.<sup>19,20</sup>



Scheme 2 Reactivity of cis-4 and trans-4.

The treatment of a mixture of cis-4 and trans-4 with H<sub>2</sub> in toluene did not lead to the formation of HSi(OEt)<sub>3</sub>, even at high pressure (5 atm) or high temperature (80 °C). This observation is in contrast to the behaviour of trans-[Pt(H)(SiMe<sub>2</sub>Cl)(PEt<sub>3</sub>)<sub>2</sub>] which gave, with H<sub>2</sub>, the silane HSiMe<sub>2</sub>Cl and the dihydrido complex trans- $[Pt(H)_2(PEt_3)_2]$ .

#### Synthesis of cationic silyl complexes

The reaction of cis-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (cis-4) and trans- $[Pt(H){Si(OEt)_3}(PEt_3)_2]$  (trans-4) with one equivalent of the Lewis acid  $B(C_6F_5)_3$  in 1,2 diffuorobenzene at -30 °C yielded, after subsequent addition of acetonitrile, the cationic silvl compounds trans-[Pt{Si(OEt)<sub>3</sub>}(NCCH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (8) and trans- $[Pt{Si(OEt)_3}(NCCH_3)(PEt_3)_2][HOB(C_6F_5)_3]$  (9) which exhibit two different anions. We presume that 9 was generated by traces of adventitious water. However, on treatment of the reaction mixture of **8** and **9** with an excess of HSi(OEt)<sub>3</sub>, complex **8** was furnished only (Scheme 3). The formation of siloxanes was detected by GC-MS and NMR measurements. Mechanistically, we assume that HSi(OEt<sub>3</sub>)<sub>3</sub> reacts in an initial step with HOB( $C_6F_5$ )<sub>3</sub><sup>-</sup> to give HOSi(OEt)<sub>3</sub> and HB( $C_6F_5$ )<sub>3</sub><sup>-</sup>. The silanol HOSi(OEt)<sub>3</sub> reacts then with itself to give the siloxane (OEt)<sub>3</sub>SiOSi(OEt)<sub>3</sub> and H<sub>2</sub>O. Alternatively, HOSi(OEt)<sub>3</sub> might react with HSi(OEt)<sub>3</sub> to yield H<sub>2</sub> and the siloxane (OEt)<sub>3</sub>SiOSi(OEt)<sub>3</sub>. Examples for a comparable conversion of a B–O bond into a B–H bond are very rare. Parvez *et al.* found that a reaction of 2,2,6,6-tetramethylpiperidine (TMPH) with B( $C_6F_5$ )<sub>3</sub> and CO<sub>2</sub> yields [TMPH<sub>2</sub>][(TMP)C(O)OB( $C_6F_5$ )<sub>3</sub>]. Treatment of the latter with HSiEt<sub>3</sub> led to a cleavage of the B–O bond and the compounds [TMPH<sub>2</sub>][HB( $C_6F_5$ )<sub>3</sub>] and [(TMP)C(O)OSiEt<sub>3</sub>] were formed.<sup>21</sup>



Scheme 3 Formation and reactivity of 8.

Compound 8 was characterised by its NMR and IR spectroscopic data as well as by mass spectrometric studies. The <sup>31</sup>P NMR spectrum of 8 displays a singlet at  $\delta$  22.6 ppm with <sup>195</sup>Pt satellites and a platinum-phosphorus coupling constant of 2600 Hz. The <sup>1</sup>H,<sup>29</sup>Si HMBC NMR spectrum shows a cross peak between a signal in the <sup>29</sup>Si domain at  $\delta$  –56 ppm and the resonances for the OCH<sub>2</sub> groups of the silvl group at  $\delta({}^{1}\text{H})$  4 ppm. The  ${}^{1}J_{\text{siPt}}$  coupling constant is 2150 Hz. The <sup>31</sup>P,<sup>29</sup>Si HMBC shows a cross peak at  $\delta^{(29}\text{Si})$  –56 ppm and  $\delta^{(31}\text{P})$  23 ppm. The IR spectrum of 8 displays an absorption band for the CN stretching vibration at v = 2294 $cm^{-1}$  and a band for the B–H vibration at  $v = 2376 cm^{-1}$ . The former is in good agreement with literature values for other platinum cationic complexes, such as [Pt(Ph)(NCCH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub>.<sup>22</sup> The anion  $[HB(C_6F_5)_3]^-$  was identified by comparison of the <sup>11</sup>B and <sup>19</sup>F NMR spectroscopic data with the literature.<sup>23</sup> Conductivity measurements of a solution of 8 in CH<sub>3</sub>CN are also in accordance with the presence of an ionic compound.<sup>24</sup>

In contrast to the observations which are described above, the trityl cation  $Ph_3C^+$  did not induce any hydride abstraction as it was observed with  $B(C_6F_5)_3$ . Instead it acts as an oxidation agent. Hence, a reaction of *cis*-[Pt(H){Si(OEt)\_3}(PEt\_3)\_2] (*cis*-4) and *trans*-[Pt(H){Si(OEt)\_3}(PEt\_3)\_2] (*trans*-4) with  $Ph_3CPF_6$  in acetonitrile gave the cationic complex *trans*-[Pt{Si(OEt)\_3}-(NCCH\_3)(PEt\_3)\_2][PF\_6] (10) together with Gomberg's dimer  $(C_{38}H_{30}; Ph_2C=C_6H_5CPh_3)^{25}$  as the organic product. We could also identify *trans*-[Pt(H)(NCCH\_3)(PEt\_3)\_2][PF\_6] (11) in the reaction solution (ratio 10:11 = 1:0.5). The latter has been

described before.<sup>26</sup> An analogous reaction was observed by Bullock *et al.* with molybdenum hydrido complexes.<sup>27</sup> Formation of Gomberg's dimer implies the generation of a Ph<sub>3</sub>C<sup>•</sup> radical by a one-electron oxidation of *cis-4/trans-4* to yield the radical cation [Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (Scheme 4). Two equivalents of Ph<sub>3</sub>C<sup>•</sup> recombine to give Gomberg's dimer.<sup>28</sup> Protonation of *cis-4/trans-4* by [Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> might furnish H<sub>2</sub> as well as [Pt{Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [Pt{Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> or, as an alternative, HSi(OEt)<sub>3</sub> as well as [Pt(H)(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [Pt{Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>]<sup>-</sup>. The latter can again be oxidized by a trityl cation to give [Pt{Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. Finally, [Pt{Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [Pt(H)(PEt<sub>3</sub>)<sub>2</sub>]<sup>+</sup> convert in the presence of acetonitrile into **10** and **11**, respectively.

Treatment of *trans*-[Pt{Si(OEt)<sub>3</sub>}(NCCH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (8) with CO at 1 atm led to the formation of *trans*-[Pt{Si(OEt)<sub>3</sub>}(CO)(PEt<sub>3</sub>)<sub>2</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (12) (Scheme 3). One singlet in the <sup>31</sup>P NMR spectrum with <sup>195</sup>Pt satellites at  $\delta$  24.8 ppm ( $J_{PPt} = 2263$  Hz) reveals the presence of two phosphine ligands in a mutual *trans* position. The <sup>31</sup>P NMR spectrum of [Pt{Si(OEt)<sub>3</sub>}(<sup>13</sup>CO)(PEt<sub>3</sub>)<sub>2</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] shows an additional doublet coupling of  $J_{PC} = 8$  Hz. The coupling constant for the carbon–phosphorus coupling is in a good agreement with a *cis* configuration of CO and PEt<sub>3</sub>. The IR spectrum of 12 displays an absorption band for the CO stretching vibration of v = 2029cm<sup>-1</sup>. The value is unexpected low compared with other cationic platinum carbonyl complexes.<sup>29</sup> One possible explanation could be the high *trans*-influence of the Si(OEt)<sub>3</sub> ligand.<sup>13</sup>

It should be mentioned that square-planar cationic platinum silyl complexes are rare. The occurrence of  $[Pt(SiH_2Cl)(PEt_3)_3][BPh_4]$  was suggested, but the compound was never isolated.<sup>30</sup> Tilley *et al.* observed the complex *cis*-[Pt{Si(S'Bu)\_2H}(NCCH\_3)(PEt\_3)\_2][OTf] by NMR spectroscopy.<sup>31</sup> In addition, there are a number of cationic silyl complexes which exhibit a silyl entity as part of a multidentate chelating ligand. Examples of such ligands are the pincer ligands bis(8-quinolyl)methylsilyl<sup>32</sup> or  $(2-R_2PC_6H_4)_2$ SiMe.<sup>33</sup>

### Conclusions

In conclusion, we reported on the syntheses of the hydrido silyl complexes cis-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (cis-4), trans-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (trans-4), cis-[Pt(H)(SiPh<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (2) and cis-[Pt(H)(SiPh<sub>2</sub>Me)(PEt<sub>3</sub>)<sub>2</sub>] (3) by oxidative addition reactions of Si–H bonds. The activation of a Si–Si bond in the presence of H<sub>2</sub> has also been achieved. The conversion involves an unusual hydrogenolysis of the Si–Si bond to give cis-4 and trans-4 as well as HSi(OEt)<sub>3</sub>. On treatment of cis-4 and trans-4 with norbornene, ethylene or CO, a second equivalent of silane was formed. Furthermore, unique cationic silyl complexes such as trans-[Pt{Si(OEt)<sub>3</sub>}(NCCH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] were characterized.

#### Experimental

#### General considerations

The synthetic work was carried out on a Schlenk line or a glovebox. Toluene and pentane were purified by distillation from Na/K and stored under argon over molecular sieves. Acetonitrile was freshly



Scheme 4 Proposed mechanism of the reaction of *cis*-4 with Ph<sub>3</sub>CPF<sub>6</sub>; *trans*-4 will react in a similar fashion; D represents a free coordination site.

distilled at Sicapent from CaH<sub>2</sub>. Then it was distilled again and stored over a molecular sieve.

NMR spectra were acquired on a Bruker AV 400 spectrometer. <sup>1</sup>H NMR spectra were referenced to residual C<sub>6</sub>D<sub>5</sub>H at  $\delta$  7.15 ppm. <sup>11</sup>B NMR spectra were referenced to external BF<sub>3</sub>·OEt<sub>3</sub> at  $\delta$  0 ppm. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were referenced externally using 85% H<sub>3</sub>PO<sub>4</sub> at  $\delta$  0 ppm. <sup>19</sup>F NMR spectra were referenced to C<sub>6</sub>F<sub>6</sub> at  $\delta$  –162.9 ppm. Infrared spectra were recorded on a Bruker Vektor 22 spectrometer which was equipped with a diamond ATR unit. X-ray data for compound **3** were collected with a Stoe IPDS 2T diffractometer. [Pt(PEt<sub>3</sub>)<sub>3</sub>] was prepared according to the literature.<sup>34</sup>

# Synthesis of cis-[Pt(H)(SiPh<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (2)

A red solution of  $[Pt(PEt_3)_3]$  (1) (800 mg, 1.46 mmol) in 6 ml n-pentane was treated with 379 mg (1.5 mmol) HSiPh<sub>3</sub>. After stirring for 1 h, the colour of the solution turned yellow. The reaction mixture was then evaporated to dryness. The colourless solid was dissolved in a 1:1 mixture of benzene/n-hexane (5 ml). Slow evaporation of the solvent at room temperature led, after 2 weeks, to the formation of colourless crystals. Yield: 0.99 g (98%). (Found C, 52.76; H, 6.69%. C<sub>30</sub>H<sub>46</sub>P<sub>2</sub>PtSi requires C, 52.08, H, 6.70%); v (ATR, diamond)/cm<sup>-1</sup>: 2048 (PtH); <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -2.4 (1 H, dd + satellites,  $J_{HPt}$  = 873.4 Hz,  $J_{HP}$  = 150.4 Hz,  $J_{HP} = 20.4$  Hz, PtH), 0.8 (9 H, m, t in the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum,  $J_{HH} = 7.6$  Hz, CH<sub>3</sub>), 1.0 (9 H, m, t in the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum,  $J_{\rm HH} = 7.7$  Hz, CH<sub>3</sub>), 1.3 (6 H, m, q in the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum,  $J_{\rm HH}$  = 7.6, PCH<sub>2</sub>), 1.5 (6 H, m, q in the <sup>1</sup>H{<sup>31</sup>P} NMR,  $J_{\rm HH} = 7.7$  Hz, PCH<sub>2</sub>), 7.3 (3 H, t,  $J_{\rm HH} = 7.3$  Hz,  $H_{para}$ ), 7.4 (6 H, m,  $H_{meta}$ ), 8.2 (6 H, m,  $H_{ortho}$ ); <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 23.2 (1 P, d + satellites,  $J_{PPt} = 1617.2$  Hz,  $J_{PSi} = 162.2$  Hz,  $J_{PP} = 15.8$ Hz, trans to Si), 19.6 (1 P, d + satellites,  $J_{PPt} = 2413.8$  Hz,  $J_{PSi} =$ 16 Hz,  $J_{PP}$  = 15.8 Hz, *cis* to Si); <sup>1</sup>H, <sup>29</sup>Si HMBC NMR (400.1/79.5 MHz,  $C_6D_6$ ):  $\delta - 2/6$  (s + satellites,  $J_{SiPt} = 1300$  Hz, HPtSi).

# Synthesis of cis-[Pt(H)(SiPh<sub>2</sub>Me)(PEt<sub>3</sub>)<sub>2</sub>] (3)

[Pt(PEt<sub>3</sub>)<sub>3</sub>] (1) (80 mg, 0.15 mmol) was dissolved in toluene to give a red solution. Then 32 μl (0.17 mmol) HSiPh<sub>2</sub>Me was added. After stirring for 15 min the solution turned orange–red, and colourless after 12 h. The solvent was then removed in vacuum to yield **3** as a colourless oily solid. Yield: 0.085 g (93%). *v* (ATR, diamond)/cm<sup>-1</sup>: 2031 (PtH); <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –2.3 (1 H, dd + satellites, *J*<sub>HPt</sub> = 908.8 Hz, *J*<sub>HP</sub> = 153.0 Hz, *J*<sub>HP</sub> = 22.0 Hz, PtH), 0.73–0.99 (18 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 1.2 (3 H, d + satellites, *J*<sub>HPt</sub> = 32.4 Hz, *J*<sub>HP</sub> = 2.6 Hz, SiCH<sub>3</sub>), 1.3–1.6 (12 H, m, PCH<sub>2</sub>), 7.3 (2 H, t, *J*<sub>HH</sub> = 7.5 Hz, H<sub>para</sub>), 7.2 (4 H, m, H<sub>meta</sub>), 7.9 (4 H, m, H<sub>ortho</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  23.7 (1 P, d + satellites, *J*<sub>PPt</sub> = 1552.6 Hz, *J*<sub>PSi</sub> = 161 Hz, *J*<sub>PP</sub> = 15.7 Hz, *trans* to Si), 22.7 (1 P, d + satellites, *J*<sub>PPt</sub> = 2382.8 Hz, *J*<sub>PP</sub> = 15.7 Hz, *cis* to Si); <sup>1</sup>H, <sup>29</sup>Si HMBC NMR (400.1 MHz/79.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –2/0 (s + satellites, *J*<sub>SiPt</sub> = 1100 Hz, HPtSi), 1/0 (s, PtSiCH<sub>3</sub>), 8/0 (s, Si/H<sub>ortho</sub>).

# $\label{eq:synthesis of cis-[Pt(H){Si(OEt)_3}(PEt_3)_2] (cis-4) and trans-[Pt(H){Si(OEt)_3}(PEt_3)_2] (trans-4)$

(a) A red solution of  $[Pt(PEt_3)_3]$  (1) (448 mg, 0.82 mmol) in 4 ml *n*pentane was treated with 180 µl (0.8 mmol) HSi(OEt)\_3. The colour of the solution changed rapidly to pale yellow. After stirring for 15 min, the volatiles were removed *in vacuo*. A pale yellow highly viscous oil was obtained. Yield: 476 mg (98%). Ratio *cis-4*: *trans-*4 = 10: 1.

(b) 320 mg (0.58 mmol)  $[Pt(PEt_3)_3]$  (1) was dissolved in 5 ml pentane. 200 µl (0.6 mmol)  $(EtO)_3SiSi(OEt)_3$  was added. After refluxing for 3 days, H<sub>2</sub> gas was bubbled for 5 min into the bright red solution until it turned pale yellow. The volatiles were removed *in vacuo*. A pale yellow, highly viscous oil was obtained. Ratio: *cis*-4 : *trans*-4 = 10 : 1.

Analytical data: (found: C, 36.73; H, 7.68%.  $C_{18}H_{46}O_3P_2PtSi$  requires C, 36.29; H, 7.78%); v (ATR, diamond)/cm<sup>-1</sup> 2024 (PtH, *cis-4*), 1851 (PtH, *trans-4*); selected NMR data of *cis-4*: <sup>1</sup>H NMR

(400.1 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -2.6 (1 H, dd + satellites,  $J_{HPt}$  = 926.5 Hz,  $J_{\rm HP} = 147.0$  Hz,  $J_{\rm HP} = 21.5$  Hz, PtH)), 1.4 (9 H, t + satellites,  $J_{\rm HH} =$ 7.2 Hz,  $J_{\text{HPt}} = 1.8$  Hz, OCH<sub>2</sub>CH<sub>3</sub>), 1.6 (6 H, m, q in the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum,  $J_{HH} = 7.7$  Hz, PCH<sub>2</sub>CH<sub>3</sub>), 2.0 (6 H, m, q in the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum,  $J_{\rm HH} = 7.7$  Hz, PCH<sub>2</sub>CH<sub>3</sub>), 4.2 (6 H, q + Pt satellites,  $J_{\text{HH}} = 7.7 \text{ Hz}$ ,  $J_{\text{HPt}} = 4.3 \text{ Hz}$ , OCH<sub>2</sub>) one resonance for the methyl groups is covered by signals of *trans*-4; <sup>31</sup>P{<sup>1</sup>H} NMR  $(161.9 \text{ MHz}, C_6 D_6): \delta 23.5 (1 \text{ P}, \text{d} + \text{satellites}, J_{\text{PPt}} = 1546.2 \text{ Hz}, J_{\text{PSi}} =$ 239.2 Hz,  $J_{PP} = 17.9$  Hz, *trans* to Si), 22.7 (1 P, d + satellites,  $J_{PPt} =$ 2341.7 Hz,  $J_{PSi} = 21.8$  Hz, *cis* to Si); <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz,  $C_6D_6$ ):  $\delta - 2.3$  (dd + satellites,  $J_{SiPt} = 1844$  Hz,  $J_{SiP} = 239.2$  Hz,  $J_{SiP} =$ 21.8 Hz); selected NMR data of trans-4: 1H NMR (400.1 MHz,  $C_6 D_6$ ):  $\delta$  0.7 (1 H, t + satellites,  $J_{HPt} = 678.8$  Hz,  $J_{HP} = 19.5$  Hz, PtH), 1.9 (12 H, m, q in the  ${}^{1}H{}^{31}P{}$  NMR spectrum,  $J_{HH} = 7.5$  Hz,  $PCH_2CH_3$ ), 4.0 (6 H, q,  $J_{HH}$  = 6.8 Hz,  $OCH_2$ ), the resonances for the methyl groups are covered by signals of *cis*-4;  ${}^{31}P{}^{1}H{}$  NMR (161.9 MHz,  $C_6 D_6$ ):  $\delta$  23.3 (s + satellites,  $J_{PPt} = 2590$  Hz,  $J_{PSi} =$ 18.9 Hz); <sup>29</sup>Si{<sup>1</sup>H} NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  11.5 (t,  $J_{SiP} = 19$ Hz, Pt satellites were not observed, because of the low intensity of the signal).

# Reaction of *cis*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*cis*-4) and *trans*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*trans*-4) with CO

CO gas was bubbled into a bright yellow solution of *cis*- $[Pt(H){Si(OEt)_3}(PEt_3)_2]$  (*cis*-4)/*trans*- $[Pt(H){Si(OEt)_3}(PEt_3)_2]$  (*trans*-4) (40 mg, 0.075 mmol) in 0.5 ml 1,2-difluorobenzene until the solution turned orange. The <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy data reveal the formation of *trans*- $[Pt(CO)_2(PEt_3)_2]^{16}$  (5) and HSi(OEt)<sub>3</sub>.

#### Reaction of *cis*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*cis*-4) and *trans*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*trans*-4) with norbornene

50 mg (0.091 mmol) 4 *cis*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*cis*-4)/*trans*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*trans*-4) in 0.6 ml 1,2-difluorobenzene was treated with 8.5 mg (0.091 mmol) norbornene. The solution was transferred into an NMR tube and the mixture was heated to 80 °C for 4 days. The <sup>1</sup>H and <sup>31</sup>P NMR spectroscopic data reveal the presence of 4 and [Pt(norbornene)(PEt<sub>3</sub>)<sub>2</sub>]<sup>19</sup> (6) in a 1:1 ratio as well as of HSi(OEt)<sub>3</sub>.

# Reaction of cis-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (cis-4) and trans-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (trans-4) with ethene

Ethene was bubbled for 10 min into a solution of 130 mg (23 mmol) *cis*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*cis*-4)/*trans*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*trans*-4) in acetonitrile/ $C_6D_6$  (5:1). After 20 min at room temperature only traces of [Pt(ethene)(PEt<sub>3</sub>)<sub>2</sub>]<sup>20</sup> (7) were formed. After 5 days at room temperature the <sup>1</sup>H and <sup>31</sup>P NMR spectroscopic and GC-MS data revealed the presence of **2** and **7** (1:1) as well as of HSi(OEt)<sub>3</sub>.

# $\label{eq:stars-product} Formation of {\it trans-[Pt{Si(OEt)_3}(NCCH_3)(PEt_3)_2][HB(C_6F_5)_3]} (8) and {\it trans-[Pt{Si(OEt)_3}(NCCH_3)(PEt_3)_2][HOB(C_6F_5)_3]} (9)$

(a) A solution of *cis*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*cis*-4) and *trans*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*trans*-4) (90 mg, 0.17 mmol) in 3 ml 1,2difluorobenzene was treated with 85 mg (0.17 mmol) B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at -30 °C. The solution was stored for 3 days at -30 °C. Afterwards all volatiles were removed at room temperature *in vacuo*. The residue was washed twice with 5 ml hexane, and 3 ml  $CH_3CN$  was added. The spectroscopic data revealed the presence of **8** and **9** in a ratio of 1:0.6.

(b) 100 mg (0.17 mmol) of *cis*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*cis*-4) and *trans*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*trans*-4) were dissolved in 3 ml CH<sub>3</sub>CN and the solution was cooled to -30 °C. The solution was then treated with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (86 mg, 0.17 mmol in 2 ml CH<sub>3</sub>CN) at -30 °C. After stirring for 16 h at room temperature, the volatiles were removed *in vacuo*. The residue was extracted with CD<sub>3</sub>CN. 100 µl (0.56 mmol) HSi(OEt)<sub>3</sub> was then added and the solution was stirred again for 1 day at room temperature. The residue was dried in vacuum and washed with pentane. The <sup>1</sup>H, <sup>11</sup>B, <sup>19</sup>F and <sup>31</sup>P NMR spectroscopic data reveal the presence of **8**.

v (ATR, diamond)/cm<sup>-1</sup> 2294 (CH<sub>3</sub>CN), 2376 (B-H); <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.0–1.1 (18 H, m, PCH<sub>2</sub>CH<sub>3</sub>), 1.16 (9 H, t, J<sub>HH</sub> = 7.0 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 1.9 (3 H, s, CH<sub>3</sub>CN), 2.1 (12 H, m, PCH<sub>2</sub>), 3.6 (1 H, q,  $J_{BH}$  = 91.5 Hz, BH), 3.9 (6 H, q,  $J_{HH}$  = 7.1 Hz, OCH<sub>2</sub>); <sup>11</sup>B NMR (128.3 MHz,  $C_6D_6$ ):  $\delta$  –24.7 (d,  $J_{BH}$  = 91.2 Hz), <sup>19</sup>F NMR (282.4 MHz,  $C_6D_6$ ):  $\delta$ -133.9 (m,  $F_{ortho}$ ), -164.3 (m,  $F_{para}$ ), -167.6 (m,  $F_{meta}$ ); <sup>31</sup>P{<sup>1</sup>H} NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  22.6 (s + satellites,  $J_{PPt} = 2600 \text{ Hz}$ ; <sup>1</sup>H, <sup>29</sup>Si HMBC NMR (400.1 MHz/79.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  4/-56 (s + satellites,  $J_{SiPt}$  = 2150 Hz PtSiOCH<sub>2</sub>); <sup>31</sup>P,<sup>29</sup>Si HMBC NMR (161.9 MHz/79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 23/-57 (s, PPtSi); The data for 9 are similar except for the resonances for the anion: <sup>1</sup>H NMR (400.1 MHz,  $C_6 D_6$ ):  $\delta$  3.2 (1 H, m, BOH), <sup>11</sup>B NMR (128.3 MHz,  $C_6D_6$ ):  $\delta$  –2.2 (s); <sup>19</sup>F NMR (282.4 MHz,  $C_6D_6$ ):  $\delta$  -134.5 (m,  $F_{ortho}$ ), -158.0 (m,  $F_{para}$ ), -163.8 (m,  $F_{meta}$ ); ESI-MS found: m/z 594.222 (M+-CH<sub>3</sub>CN), Requires: m/z 594.226 (M<sup>+</sup>-CH<sub>3</sub>CN). Molar conductivity ( $\Lambda_m$ /S cm<sup>2</sup> mol<sup>-1</sup>) = 36.

# $\label{eq:constraint} \begin{array}{l} Reaction \ of \ cis-[Pt(H) \{ Si(OEt)_3 \} (PEt_3)_2 ] \ (cis-4) \ and \\ \ trans-[Pt(H) \{ Si(OEt)_3 \} (PEt_3)_2 ] \ (trans-4) \ with \ Ph_3 CPF_6: \\ formation \ of \ trans-[Pt \{ Si(OEt)_3 \} (NCCH_3) (PEt_3)_2 ] PF_6 \ (10) \end{array}$

A solution of 76 mg (1.3 mmol) *cis*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*cis*-4) and *trans*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*trans*-4) in acetonitril/C<sub>6</sub>D<sub>6</sub> (2:1) was treated with 54 mg (1.4 mmol) Ph<sub>3</sub>CPF<sub>6</sub> at -30° C. A white solid precipitated. The solution was filtered and all volatiles were removed *in vacuo* from the filtrate. The residue was washed with 5 ml pentane and CH<sub>3</sub>CN was added. The <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P NMR spectroscopy data reveal the presence of **10** and *trans*-[Pt(H)(NCCH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>] (**11**).<sup>26</sup> The white solid was dissolved in C<sub>6</sub>D<sub>6</sub>. The <sup>1</sup>H NMR data confirm the formation of Gomberg's dimer.<sup>35</sup> NMR data for the PF<sub>6</sub><sup>-</sup> anion of **10** and **11**: <sup>19</sup>F NMR (282.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -72.3 (d, *J*<sub>FP</sub> = 706.8 Hz); <sup>31</sup>P{<sup>1</sup>H}NMR (161.9 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -143.2 (septet, *J*<sub>PF</sub> = 706.8 Hz).

# Formation of trans-[Pt{Si(OEt)<sub>3</sub>}(CO)(PEt<sub>3</sub>)<sub>2</sub>][HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (12)

A solution of 47 mg (0.09 mmol)) [*cis*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*cis*-4) and *trans*-[Pt(H){Si(OEt)<sub>3</sub>}(PEt<sub>3</sub>)<sub>2</sub>] (*trans*-4) in acetonitrile was treated with 56 mg (0.1 mmol) B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> at -30 °C. The solution was kept at this temperature for 1 day and then all volatiles were removed *in vacuo*. The oily product was then dissolved in 1,2-diffuorobenzene and the solution was treated with CO at 1 atm. The solution was brought to dryness, 0.1 ml toluene-*d*<sup>8</sup> were added. v (ATR, diamond)/cm<sup>-1</sup> 2029 (CO); <sup>1</sup>H NMR (300.1 MHz,

toluene- $d^8$ ):  $\delta$  0.8–1.1 (27 H, m, PCH<sub>2</sub>CH<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub>), 1.6–1.9 (12 H, m, PCH<sub>2</sub>), 3.9 (6 H, q,  $J_{\rm HH}$  = 6.9 Hz, OCH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (121.5 MHz, toluene- $d^8$ ):  $\delta$  24.8 (s + satellites,  $J_{\rm PPt}$  = 2263 Hz).

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