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Rate and Mechanism of the Oxidative Addition of a Silylborane to Pt^0 Complexes – Mechanism for the Pt-Catalyzed Silaboration of 1,3-Cyclohexadiene

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The chemical reduction of $Pt(acac)_2$ by DIBALH in the presence of phosphanes, which is used to generate active Pt^0 complexes in the Pt-catalyzed silaboration of cyclohexadiene by 2-(dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**) leading to the 1,4-silaborated product, was mimicked by the electrochemical reduction of $Pt(acac)_2$ in the presence of 2 equiv. of PR_3 (R = Ph, *n*Bu). The electrochemical reduction generates free acac anions and neutral $Pt^0(PR_3)_2$ complexes. The kinetics of the oxidative addition of bromobenzene (used first as a model molecule) and silylborane **1** to the Pt^0 complexes was investigated and the rate constants determined. $Pt^0(PnBu_3)_2$ is much more reactive than $Pt^0(PPh_3)_2$ towards **1**. From the electrochemical study, it emerges that the acac anions released in the reduction of $Pt(acac)_2$ do not coordinate to the $Pt^0(PR_3)_2$ complexes. Consequently, the rate of the oxidative addition of **1** to $Pt^0(PR_3)_2$, generated either by the electrochemical reduction or by the chemical reduction by DIBALH, is not affected by the acac anions and a posteriori not by aluminum cations. The oxidative addition and the further step of the catalytic cycle [insertion of the diene into the Pt–B bond of the Si–Pt–B complex generated in the oxidative addition, with formation of the (η^3-allyl)Pt–Si complex] were monitored by NMR spectroscopy. Pt^0 and Pt^{II} complexes involved in the catalytic cycle were characterized. The oxidative addition is faster when the ligand is PMe_2Ph relative to that obtained with PPh_3, in agreement with the electrochemical data. No reductive elimination within the (η^3-allyl)Pt–Si complex is observed when the ligand is PMe_2Ph, whereas reactions in the presence of PPh_3 proceeded to give the final product. As a consequence, PPh_3 is a better ligand than PMe_2Ph for the catalytic reaction, as observed experimentally.
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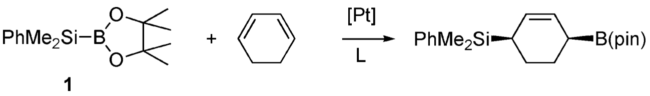
Introduction

Additions of element–element linkages to unsaturated substrates catalyzed by the platinum group metals constitutes a synthetically versatile process whereby compounds containing two equal or different reactive groups are obtained.[1] Among the additions studied, silaborations are particularly interesting, as they provide adducts containing both silicon and boron functionalities,[2] which serve as powerful synthetic intermediates.[3] The silaboration of 1,3-dienes was studied by Ito, Suginome, and coworkers, who, using a nickel catalyst, found conditions for selective formation of 1,4-functionalized *Z* adducts from linear dienes and *cis*-1,4 adducts from cyclic dienes [Equation (1)].[4] We later found that Pt^0 in combination with chiral phosphoramidite ligands catalyzed enantioselective silaborations of 1,3-cyclohexadiene.[5] In order to be able to further develop this type of processes, detailed knowledge about the reaction mechanism is essential.



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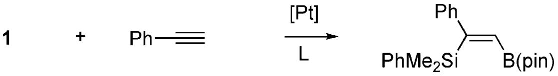
(1)

The mechanism of the related silaboration of alkynes [Equation (2)] has been investigated by Ozawa et al. by means of NMR spectroscopy.[6]



(2)

The reaction was shown to follow the generally accepted catalytic cycle proceeding by three main steps: (i) oxidative addition of the silylborane to a Pt^0 complex leading to *cis*-silyl–Pt^{II}–boryl complexes, (ii) insertion of the acetylene into the Pt–B bond of the silyl–Pt^{II}–boryl complex, and (iii) reductive elimination. Although the carbopalladation and reductive elimination steps were investigated in full detail, including the determination of the rate constants of each

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step, the mechanism and rate of the oxidative addition of silylborane **1** to Pt^0 complexes were not investigated due to too fast reactions which could not be followed by NMR spectroscopy. In the catalytic reactions of **1**, transient Pt^0 complexes were generated in situ by reduction of $Pt(acac)_2$ with DIBALH in the presence of the appropriate phosphane ligands.[5] Some questions arise. What is the structure of the reactive Pt^0 complex? Do the acac anions stabilize the Pt^0 moiety by forming anionic complexes? Do aluminum cations delivered by the chemical reductant DIBALH play a role in the oxidative addition? Because electrochemistry can easily mimic chemical reduction processes, Pt^0 complexes can be generated by the electrochemical reduction of $Pt(acac)_2$ in the presence of phosphanes, and the oxidative addition of the electrogenerated Pt^0 complexes can be followed by electrochemical techniques.[7] We report herein data on the rate and mechanism of the oxidative addition of bromobenzene (used first as a model molecule) and that of a silylborane, 2-(dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**), to Pt^0 complexes ligated by phosphane ligands (PPh_3 or $PnBu_3$). The oxidative addition and insertion steps of the catalytic cycle were also followed by ^1H and ^{31}P NMR spectroscopy starting from Pt^0 prepared in situ by reduction of $Pt(acac)_2$ with DIBALH.

Results and Discussion

Structure and Reactivity of Pt^0 Complexes Generated in the Electrochemical Reduction of $Pt(acac)_2$ in the Presence of PR_3 (R = Ph, *n*Bu)

The electrochemical properties of $Pt(acac)_2$ (2 mM) were first investigated in DMF containing nBu_4NBF_4 (0.3 M). $Pt(acac)_2$ exhibited a reduction peak at $E^p{}_{R1} = -2.05$ V vs. SCE at a gold disk electrode (Figure 1a). Only one tiny oxidation peak was detected on the reverse scan, close to the oxidation peak of acac anions, establishing that the Pt^0 complex generated in the reduction of $Pt(acac)_2$ was not stable or made aggregates that could not be detected on the reverse scan.

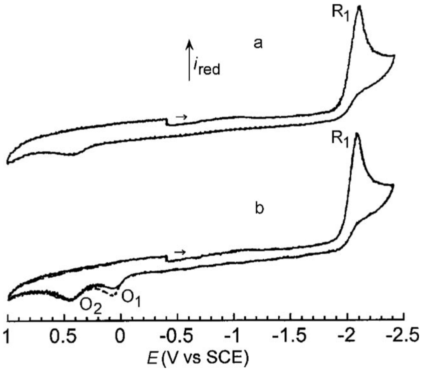
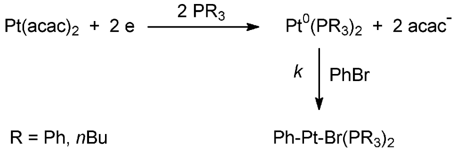


Figure 1. (a) Reduction of $Pt(acac)_2$ (2 mM) in DMF (containing nBu_4NBF_4, 0.3 M) at a steady gold disk electrode (d = 1 mm) with a scan rate $v = 0.5\ V\,s^{-1}$, at 27 °C; (b) reduction of $Pt(acac)_2$ (2 mM) in the presence of PPh_3 (——) 2 mM; (- - -) 4 mM, under the same conditions as in (a).

When cyclic voltammetry (CV) was performed in the presence of 1 equiv. of PPh_3, the reduction peak current and potential of $Pt(acac)_2$ were not affected, but a new oxidation peak was detected on the reverse scan at $E^p{}_{O1}$ = +0.04 V vs. SCE (Figure 1b). No oxidation peak was observed when the cyclic voltammetry was first performed towards oxidation potentials. The oxidation peak current at O_1 doubled in the presence of a second equivalent of PPh_3, whereas R_1 remained unaffected. Consequently, $Pt(acac)_2$ did not coordinate to PPh_3 at room temperature, because its reduction peak did not change in the presence of PPh_3 (1 or 2 equiv.). This was confirmed by ^{31}P NMR spectroscopy performed on a mixture of $Pt(acac)_2$ and 2 equiv. of PPh_3 in DMF; only the singlet from free PPh_3 was observed at $\delta = -5.35$ ppm.

The oxidation peak at O_1 disappeared in the presence of an excess amount of PhBr, attesting that a Pt^0 complex, oxidized at O_1, was generated in the electrochemical reduction of $Pt(acac)_2$ performed in the presence of PPh_3. This Pt^0 complex was stabilized by two PPh_3 as in $Pt^0(PPh_3)_2$,[8a] as its oxidation peak current at O_1 doubled upon the addition of a second equivalent of PPh_3 (Figure 1b, Scheme 1). Further addition of PPh_3 (1 equiv.) did not modify the oxidation peak potential significantly. However, the peak was slightly broader, suggesting the formation of different Pt^0 species, as $Pt^0(PPh_3)_3$ and $Pt^0(PPh_3)_2$ in equilibrium with the ligand.[8] Because the $Pt^0(PPh_3)_2$ complex is reported to be unstable at long times[8a] (it is transiently generated in cyclic voltammetry at short times, $t < 5.5$ s), an exhaustive electrolysis of a solution of $Pt(acac)_2$ (0.02 mmol) was performed in DMF (12 mL) in the presence of 3 equiv. of PPh_3 at a potential of –2 V (divided cell equipped with a 4-cm^2 gold grid cathode). The electroreduction consumed two electrons per mol. At the end of the electrolysis, the reduction peak of $Pt(acac)_2$ was no longer observed when the cyclic voltammetry was performed towards reduction potentials (from –0.4 to –2.5 V). An oxidation peak was observed at E^p = +0.04 V when the CV was performed towards oxidation potentials first (from –0.4 to +0.3 V), that is, at the same oxidation potential as that of O_1 observed by CV when $Pt(acac)_2$ was reduced in the presence of PPh_3 (3 equiv.). Consequently, $Pt(acac)_2$ was reduced by two electrons in the electrolysis and its reduction performed in the presence of 3 equiv. of PPh_3 provided the same complex as the one observed by cyclic voltammetry when $Pt(acac)_2$ was reduced in the presence of PPh_3 (3 equiv.), that is, $Pt^0(PPh_3)_3$.[8b]



Scheme 1.

A second oxidation peak was observed on the reverse scan at $E^p{}_{O2}$ = +0.42 V vs. SCE when $Pt(acac)_2$ was reduced in the presence of 2 equiv. of PPh_3 (Figure 1b). The oxidation peak O_2 was assigned to the oxidation of the acac anions released in the reduction process by comparison with the oxidation peak potential of $Zn(acac)_2$, observed independently under the same conditions. The oxidation peak current of the acac anion released in the reduction process was not modified when $Pt(acac)_2$ was reduced in the presence of 1 or 2 equiv. of PPh_3 (see O_2 in Figure 1b). It is then established that the two acac anions of $Pt(acac)_2$ were quantitatively released in the two-electron reduction of $Pt(acac)_2$. Consequently, the electrogenerated $Pt^0(PPh_3)_2$ is a neutral complex that is not ligated by the acac anions (Scheme 1).

Because PhBr is well known to undergo oxidative addition to M^0 complexes,[9] it was selected as a model substrate to test the reactivity of the electrogenerated $Pt^0(PPh_3)_2$. The oxidation peak current at O_1 of the electrogenerated $Pt^0(PPh_3)_2$ (2 mM) was lower when the cyclic voltammetry was performed in the presence of PhBr (10 equiv.) (scan rate, $v = 0.5\ \mathrm{V\,s^{-1}}$) due to oxidative addition (rate constant k in Scheme 1). This reaction took place within the time elapsed between the generation of $Pt^0(PPh_3)_2$ at R_1 and its oxidation at O_1 ($\delta t = 4.8$ s at a scan rate of $0.5\ \mathrm{V\,s^{-1}}$). When the scan rate v was increased, the oxidation peak current of O_1 increased, because the time scale for the oxidative addition was shortened. Because the oxidation peak current of $Pt^0(PPh_3)_2$ is proportional to its concentration, the molar fraction x of $Pt^0(PPh_3)_2$ was determined for different scan rates as $x = i/i_0$ [i: oxidation peak current of $Pt^0(PPh_3)_2$ at O_1 in the presence of PhBr (in the range 0.02–0.4 M); i_0: oxidation peak current of $Pt^0(PPh_3)_2$ in the absence of PhBr, at the same scan rate v]. The plot of x against $\log([PhBr]_0/v)$ shown in Figure 2, attests to a first-order reaction for PhBr and $Pt^0(PPh_3)_2$.[7] The kinetic law for the oxidative addition is: $\ln(x) = -k[PhBr]_0t$. When $x = 0.5$, $\ln(0.5) = -k[PhBr]_0t_{1/2} = -k[PhBr]_0(\Delta E)/v_{1/2}$ with $\Delta E = (|E_{inv}| - |E^p_{R1}|) + (|E_{inv}| - |E^p_{O1}|) = 2.33$ V (E_{inv}: inversion potential of the scan). The rate constant k for the oxidative addition was then determined from the value of $[PhBr]_0/v_{1/2}$ corresponding to the half reaction, as indicated in Figure 2 (Table 1). The reaction was slower in the presence of an extra equivalent of PPh_3. $Pt^0(PPh_3)_2$ is thus in equilibrium with PPh_3 and $Pt^0(PPh_3)_3$, but $Pt^0(PPh_3)_2$ remains the reactive complex in the oxidative addition.[8]

The behavior of the more electron-donating ligand $PnBu_3$ was very similar. No detectable Pt^{II} phosphane complex was formed by treating $Pt(acac)_2$ with 2 equiv. of $PnBu_3$. The electrochemical reduction of $Pt(acac)_2$ in the presence of 2 equiv. of $PnBu_3$ delivered a Pt^0 complex ligated by two $PnBu_3$ and oxidized at E^p_{O3} (Figure 3, Scheme 1). $Pt^0(PnBu_3)_2$ was more easily oxidized than $Pt^0(PPh_3)_2$, as could be expected, because it is more electron rich (Table 1). A second oxidation peak was also observed at $E^p_{O2} = +0.42$ V, characteristic of free acac ions released in the reduction of $Pt(acac)_2$ (Figure 3, Scheme 1).

Kinetic data on the reactivity of the electrogenerated $Pt^0(PnBu_3)_2$ with PhBr were obtained by performing cyclic voltammetry at various scan rates, as done for PPh_3 (see above and Figure S1 in Supporting Information). As expected, the more electron-rich $Pt^0(PnBu_3)_2$ is more reactive (by a factor of 17) towards PhBr than $Pt^0(PPh_3)_2$ (Table 1).

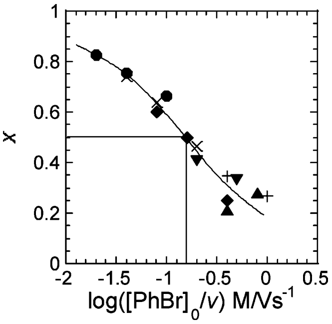


Figure 2. Kinetics of the oxidative addition of PhBr (●: 0.02 M; ×: 0.04 M; ♦: 0.08 M; ▼: 0.1 M; +: 0.2 M; ▲: 0.4 M) to $Pt^0(PPh_3)_2$ (2 mM) generated by the electrochemical reduction of $Pt(acac)_2$ (2 mM) in the presence of 2 equiv. of PPh_3 in DMF at 27 °C. Plot of the molar fraction x of $Pt^0(PPh_3)_2$ vs. $\log([PhBr]_0/v)$. $x = i/i_0$ i: oxidation peak current of $Pt^0(PPh_3)_2$ at O_1 in the presence of PhBr (in the range 0.02–0.4 M); i_0: oxidation peak current of $Pt^0(PPh_3)_2$ in the absence of PhBr, at the same scan rate v. Oxidation current intensities were measured after a fivefold amplification.

Table 1. Oxidation peak potential E^p_{ox} of $Pt^0(PR_3)_2$ complexes generated in the reduction of $Pt(acac)_2$ in the presence of 2 equiv. of PR_3 and rate constant k of the oxidative addition of PhBr and Si–B derivative **1**[a] as followed by fast cyclic voltammetry, in DMF at 27 °C (Scheme 1, Scheme 2).

$Pt^0(PR_3)_2$	E^p_{Ox} (V vs. SCE)[b]	k [$M^{-1}s^{-1}$]	
		PhBr	Si–B **1**
$Pt^0(PPh_3)_2$	+0.04	1.9 ± 0.2	<0.2
$Pt^0(PnBu_3)_2$	–0.48	32 ± 1	384 ± 1

[a] $Pt^0(PR_3)_2$ was first generated by the electrochemical reduction of $Pt(acac)_2$ in the presence of 2 equiv. of PR_3 and then in the presence of PhBr or **1**. [b] Potentials were determined at a gold disk electrode (d = 1 mm) with a scan rate of $0.5\ \mathrm{V\,s^{-1}}$.

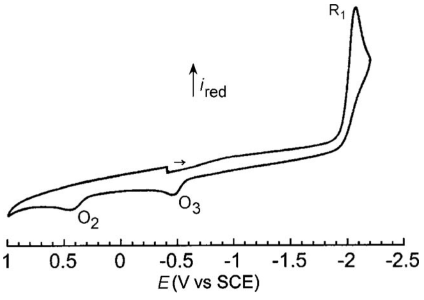
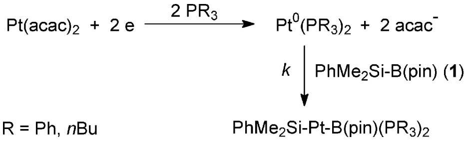


Figure 3. Reduction of $Pt(acac)_2$ (2 mM) in DMF (containing nBu_4NBF_4, 0.3 M) in the presence of $PnBu_3$ (4 mM) at a steady gold disk electrode (d = 1 mm) with a scan rate $v = 0.5\ \mathrm{V\,s^{-1}}$, at 27 °C.

Reactivity of $Pt^0(PR_3)_2$ (R = Ph, *n*Bu) in the Oxidative Addition of 2-(Dimethylphenylsilyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1) in DMF

The reactivity of **1** towards $Pt(PnBu_3)_2$ and $Pt(PPh_3)_2$ was investigated by cyclic voltammetry as done for PhBr.

From the value of their respective rate constants (Scheme 2, Table 1, Figure S2 in Supporting Information), it is clear that the reaction of **1** with Pt(P*n*Bu$_3$)$_2$ is much faster than that with Pt(PPh$_3$)$_2$ (by a factor of at least 1500, Table 1).

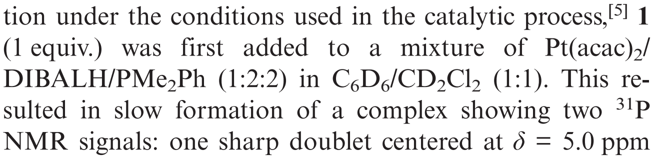


Scheme 2.

As illustrated above, electrochemical techniques can provide kinetic data, and the rate constants of oxidative additions of PhBr and **1** with Pt^0 complexes were obtained for the first time. However, electrochemical techniques cannot provide any structural information. Consequently, the complexes formed in the oxidative addition and in the following steps were investigated by NMR spectroscopy.

NMR Spectroscopic Investigations of the Reactions of 1,3-Cyclohexadiene with Silylborane 1

Two ligands were investigated: PPh$_3$, which was known to be efficient for the catalytic reaction depicted in Equation (1), and PMe$_2$Ph. In order to study the reactivity of silylborane **1** towards Pt^0 generated in a stoichiometric reaction under the conditions used in the catalytic process,[5] **1** (1 equiv.) was first added to a mixture of Pt(acac)$_2$/DIBALH/PMe$_2$Ph (1:2:2) in C$_6$D$_6$/CD$_2$Cl$_2$ (1:1). This resulted in slow formation of a complex showing two ^{31}P NMR signals: one sharp doublet centered at δ = 5.0 ppm with ^{195}Pt satellites ($J_{P,Pt}$ = 1400 Hz, $J_{P,P}$ = 29 Hz) and a broad signal at δ = 5.7 ppm characteristic of a phosphorus atom *trans* to a boron atom ($J_{P,Pt}$ = 1404 Hz). In the ^{1}H NMR spectrum the signal from the methyl protons of the silylborane at δ = 0.20 ppm decreased in intensity and a new singlet with Pt satellites at δ = 0.47 ppm ($J_{H,Pt}$ = 32 Hz) appeared. The complex could be isolated in pure form from the reaction mixture (see Experimental Section). Comparison of the spectra (in CD$_2$Cl$_2$) with those reported by Ozawa for the product obtained by oxidative addition of **1** to the Pt^0 complex generated from Pt^0(cod)$_2$ and PMe$_2$Ph,[6] confirmed that the same product **2** was obtained under our conditions (Scheme 3). Thus, in accordance to what was shown in the electrochemical studies, the complex does not contain the anion (acac) or any Al species.



Scheme 3.

The reaction between **1** and Pt^0(PMe$_2$Ph)$_2$, generated by reduction of Pt(acac)$_2$ with DIBALH in the presence of the phosphane, was also followed by recording the ^{1}H NMR spectra every 30 min at room temperature. In order to achieve full conversion of **1** an excess amount of Pt was employed (Pt/**1**, 2:1; C$_6$D$_6$/CD$_2$Cl$_2$, 1:1; 0.1 M in Pt). Under such conditions, the half-life time of the oxidative addition was estimated to $t_{1/2}$ = 200 min.

A second complex **3** was slowly formed in reactions between **1** and Pt^0. After 3 d at room temperature, the ratio **1/2/3** was ca. 2:4:1 when a 1:1 ratio of Pt/**1** was used. Complex **3** could be isolated and separated from **2** by precipitation from CH$_2$Cl$_2$ with diethyl ether. According to NMR spectroscopic analysis, it contained one phosphane for each silyl group, and showed a single ^{31}P NMR signal at δ = 4.20 ppm ($J_{Pt,P}$ = 1519 Hz, $J_{P,Si}$ = 68 Hz) and a singlet with Pt satellites at δ = 0.56 ($^1J_{H,Pt}$ = 27 Hz) in the ^{1}H NMR spectrum. Comparison with literature NMR spectroscopic data[10] (CD$_2$Cl$_2$) suggests that the compound is bis[(dimethylphenyl)phosphane]bis[(dimethylphenyl)silyl]platinum(II) (**3**). In reactions using a Pt/**1** ratio of 2:1 merely ca. 2% of this complex was observed, suggesting that it is formed from **2** and silylborane **1** rather than by metathesis of **2**. This hypothesis was later contradicted: when 1,3-cyclohexadiene was added to complex **2**, isolated in pure form, large amounts of complex **3** were still formed, without any noticeable amount of silylborane being present.[11]

The rate of oxidative addition was not affected by the presence of 1,3-cyclohexadiene. Addition of an excess amount of 1,3-cyclohexadiene (10 equiv.) to **2** generated as above (by using a Pt/**1** ratio of 1:1) caused the formation of a new complex, **4**. At room temperature, the process was very slow, but at 80 °C signals for the new species appeared within 1 h. In the ^{31}P NMR spectrum a singlet flanked by ^{131}Pt satellites ($J_{P,Pt}$ = 3524 Hz) appeared for the new complex at δ = 3.20 ppm, but no new broad signal characteristic of phosphorus *trans* to boron was found. As expected, the η^1 complex obtained by Ozawa by reaction of **2** with phenylacetylene contained two chemically different phosphanes, observed as two doublets in the ^{31}P NMR spectrum with additional splitting due to Pt.[6] The presence of a single ^{31}P resonance from the complex obtained from cyclohexadiene is consistent with the formation of a η^3-allyl complex containing only one phosphane ligand (**4**; Scheme 3). This assumption was supported by the presence of a three-spin system characteristic of a metal-coordinated allyl group, consisting of a doublet at δ = ca. 4.92 ppm (J = 7 Hz), a triplet at δ = 4.54 ppm (J = 7 Hz), and a broad signal at δ = ca. 3.6 ppm in the ^{1}H NMR spectrum of **4** (see Supporting Information). As expected, separate signals were observed for the diastereotopic methyl groups on silicon (δ = 0.23 ppm, $J_{H,Pt}$ = 30 Hz and δ = 0.28 ppm, $J_{H,Pt}$ = 30 Hz). When the formation of **4** was followed by ^{1}H NMR spectroscopy at room temperature by using 1-methoxynaphthalene as an internal standard, it was observed that the amount of **4** increased at the expense of **2**, whereas the amount of bis(silyl) complex **3** was essentially constant.[12] No product **5** from reductive elimination was observed even after prolonged heating of the mixture containing **4** or after the addition of an excess amount of triphenylphosphane (see below). Instead, complex **4** slowly decomposed.[13] In agreement with this observation, no product was isolated from a catalytic reaction employing PMe_2Ph as the ligand. Several attempts were made to isolate complex **4** by crystallization, but the complex was elusive.[14]

In contrast to the situation using PMe_2Ph, the product from silaboration (**5**) is obtained in reactions with PPh_3 as the ligand. In this case, oxidative addition was shown by cyclic voltammetry to be extremely slow at 27 °C ($k < 0.2\ \text{M}^{-1}\,\text{s}^{-1}$), and no product was observed by NMR spectroscopy when **1** (one equiv.) was added to a mixture of PPh_3, Pt(acac)$_2$, and DIBALH (2:1:2), even after heating at 80 °C for 18 h. Even a 10-fold excess of **1** did not lead to any observed product from oxidative addition. When the stoichiometric reaction was repeated in the presence of 1,3-cyclohexadiene and monitored by ^1H NMR spectroscopy by using 1-methoxynaphthalene as an internal standard no products were observed after one day at room temperature. However, after heating overnight at 50 °C, 55% unreacted silylborane **1** remained together with unidentified complexes and 18% of the product from silaboration (**5**). After the same time at 60 °C, 4% of **1** and 58% **5** were observed. At 80 °C, only a trace amount of **1** remained and 95% product was formed. It is interesting to note that whereas 96% of silylborane **1** was consumed after being heated at 60 °C overnight, only 58% of product **5** was formed, but a final 95% yield was recorded. This shows that Si–B containing complexes, leading to product, accumulate before the final reductive elimination to give **5**.

From these results it is clear that the relative rates of oxidative addition, insertion, and reductive elimination are highly dependent on the structure of the phosphane ligand. In accordance with expectations, as well as with previous observations,[6] oxidative addition proceeds faster with the more electron-donating phosphane PMe_2Ph than with PPh_3 as ligand. With the former ligand, the barrier for reductive elimination was too high to allow the formation of the final product. With PMe_2Ph as ligand, oxidative addition was found to be faster than migratory insertion, whereas with PPh_3, oxidative addition was not observed in the absence of 1,3-cyclohexadiene. However, in the presence of the unsaturated substrate the small amount of complex from oxidative addition reacted further to give complexes that accumulated before reductive elimination took place to yield the final product **5**, the same as that obtained in the catalytic reaction.

Conclusions

Silylborane **1** undergoes oxidative addition to neutral Pt^0L_2 (L = monophosphanes) generated from Pt(acac)$_2$ either by electrochemical reduction or by chemical reduction by DIBALH. No coordination of phosphanes to Pt(acac)$_2$ was observed, whereas the rate of oxidative addition to Pt^0L_2 was influenced by the structure of the phosphane ligand. From electrochemical data, oxidative addition of the silylborane to Pt(PnBu$_3$)$_2$ was found to be considerably much faster than that to Pt(PPh$_3$)$_2$. In the chemical reduction of Pt(acac)$_2$ by DIBALH in the presence of PPh_3, no oxidative addition of **1** was observed, although in the presence of 1,3-diene, the reaction proceeded to yield unidentified intermediate complexes and finally the desired 1,4-silaborated product. A more rapid oxidative addition of **1** occurred with PMe_2Ph as ligand, and the resulting Si–Pt^{II}–B complex was shown to react with the diene, giving a η^3-allyl complex. No silaborated product was observed from reactions using PMe_2Ph, due to unfavored reductive elimination.

Experimental Section

General Remarks: All reactions were prepared inside a nitrogen filled glove box by using oven-dried glassware or under a nitrogen atmosphere by using standard Schlenk techniques. Hexane, CH_2Cl_2, and Et_2O were dried by using a Glass-contour solvent dispensing system. Benzene was distilled from CaH_2 prior to use. 2-(Dimethylphenylsilyl)-4,4,5,5-tetrametyl-1,3,2-dioxaborolane (**1**)[15] was synthesized according to a literature procedure. All other chemicals were of at least 97% purity and used as received. ^1H NMR spectra were recorded at 500 or 400 MHz, ^{13}C spectra at 125 MHz, and ^{31}P spectra at 202 MHz. ^1H chemical shifts are reported relative to residual solvent peak, and ^{31}P chemical shifts are reported relative to external 85% H_3PO_4. Cyclic voltammetry was performed under an atmosphere of argon at a steady gold disk electrode (d = 1 mm) with a homemade potentiostat and a wave form generator EG&G Parc Model 175. The voltammograms were recorded with a Nicolet 301 oscilloscope.

Procedure for the Oxidative Addition of PhBr to Electrogenerated Pt^0 Ligated by two PR_3 as Monitored by Cyclic Voltammetry: Experiments were carried out in a three-electrode thermostatted cell connected to a Schlenk line. The counter electrode was a platinum wire of ca. 1-cm^2 apparent surface area; the reference saturated calomel electrode (Radiometer) was separated from the solution by a bridge filled with DMF (2 mL) containing nBu$_4$NBF$_4$ (0.3 M). The working electrode was a steady gold disk electrode (d = 1 mm). To DMF (10 mL) containing nBu$_4$NBF$_4$ (0.3 M) was added Pt(acac)$_2$ (7.9 mg, 0.02 mmol, 2 mM) followed by PPh_3 (10.5 mg, 0.04 mmol). The cyclic voltammetry was performed at different scan rates (from 0.2 to 1 V s^{-1}) in the absence of PhBr and then in the presence of increasing amounts of PhBr [10 (14.5 µL), 20, 50, 100 equiv.] at the same scan rates.

Similar experiments were performed from Pt(acac)$_2$ (7.9 mg, 0.02 mmol, 2 mM) and PnBu$_3$ (10 µL, 0.04 mmol). Cyclic voltammetry was performed at different scan rates (from 0.1 to 2 V s^{-1}) in the absence of PhBr and then in the presence of PhBr (1.45 µL, 0.02 mmol) at the same scan rates.

Procedure for the Oxidative Addition of 1 to Electrogenerated Pt^0 as Monitored by Cyclic Voltammetry: Experiments were performed from Pt(acac)$_2$ (7.9 mg, 0.02 mmol) and PnBu$_3$ (10 µL, 0.04 mmol). The cyclic voltammetry was performed at different scan rates (from 0.2 to 2 V s^{-1}) in the absence of **1** and then in the presence of **1** (5.24 mg, 0.02 mmol) at the same scan rates.

General Procedure for the Oxidative Addition of 1 to Pt^0 as Monitored by ^1H NMR Spectroscopy: Pt(acac)$_2$ (19.65 mg, 0.05 mmol) was dissolved in C_6D_6/CD_2Cl_2 (1:1, 300 µL). $PPhMe_2$ (14.2 µL, 0.10 mmol) was then added by syringe, and the resulting mixture was cooled to –35 °C over 15 min. DIBALH (1 M in cyclohexane, 100 µL, 0.10 mmol) was added by syringe, and the solution was allowed to stand at room temperature for 2 h. Compound **1**

(13.1 mg, 0.05 mmol) dissolved in C_6D_6/CD_2Cl_2 (1:1, 200 µL) was then added to the catalyst solution. The resulting mixture was transferred to an NMR tube equipped with a screw cap, and the reaction was monitored by ^1H NMR spectroscopy. In order to isolate complex **2**, the crude product was dissolved in Et_2O/DCM (1:1) and hexane was added. Precipitated solids and sticky brown residues were removed by filtration (in the glove box) and the solvents removed in vacuo. The solids were washed with Et_2O and then with hexane (3×) to yield complex **2** as a light-yellow solid. ^1H NMR (C_6D_6/CH_2Cl_2, 1:1): δ = 0.47 (s, $J_{Pt,H}$ = 32 Hz, 6 H), 0.92 (d, $J_{P,H}$ = 7 Hz, $J_{Pt,H}$ = 16 Hz, 6 H), 0.96 (s, 12 H), 1.28 (d, $J_{P,H}$ = 7 Hz, $J_{Pt,P}$ = 21 Hz, 6 H), 6.92–7.09 (m, 9 H), 7.15–7.28 (m, 4 H), 7.58–7.63 (m, 2 H) ppm. ^{31}P NMR (C_6D_6/CD_2Cl_2, 1:1): δ = 5.0 (d, $J_{P,P}$ = 29 Hz, $J_{Pt,P}$ = 1400 Hz), 5.7 (br., $J_{Pt,P}$ = 1404) ppm.[6]

Procedure for the Reaction of 2 with 1,3-Cyclohexadiene: The reaction was performed according to the general procedure, with the addition of 1,3-cyclohexadiene (50 µL, 0.5 mmol) before the solution was transferred into the NMR tube. Characterization of complex **4**: ^1H NMR (400 MHz, C_6D_6/CD_2Cl_2, 1:1): δ = 0.23 (s, $J_{H,Pt}$ = 30 Hz, 3 H), 0.28 (s, $J_{H,Pt}$ = 30 Hz, 3 H), 3.6 (br., 1 H), 4.54 (app t, J = 7 Hz, 1 H), 4.92 (d, J = 7 Hz, 1 H) ppm. The other ^1H NMR signals were obscured due to overlap with the signals from **1**, **2**, and **3**. H,H-COSY correlations were observed between protons appearing at δ = 3.6 ppm and δ = 4.54 ppm and also between those at δ = 4.54 ppm and δ = 4.92 ppm (Supporting Information). ^{31}P NMR (C_6D_6/CD_2Cl_2, 1:1): δ = 3.20 (s, $J_{P,Pt}$ = 3524 Hz) ppm.

Preparation of 3: $Pt(acac)_2$ (98.3 mg, 0.25 mmol) was dissolved in benzene/CH_2Cl_2 (1:1, 1.5 mL). $PPhMe_2$ (71 µL, 0.50 mmol) was then added by syringe, and the resulting mixture was cooled to –35 °C over 15 min. DIBALH (1 M in cyclohexane, 500 µL, 0.50 mol) was added by syringe, and the solution was allowed to stand at room temperature for 2 h. Compound **1** (13.1 mg, 0.05 mmol) dissolved in benzene/CH_2Cl_2 (1:1, 1 mL) was then added to the catalyst solution. The resulting solution was heated in a sealed vial at 50 °C for 48 h, giving a ca. 1:1 mixture of complexes **2** and **3**. The solvents were removed over the manifold. The residue was suspended in CH_2Cl_2 (0.4 mL) and Et_2O (6 mL) was then gently layered on top, and the mixture was left at room temperature overnight. The solvents were removed by syringe, and the remaining solid was washed repeatedly with Et_2O (6 × 3 mL) until the washings were colorless. The resulting solid was dried in vacuo, yielding **3** (12 mg, 6%) as a light-yellow solid. ^1H, ^{31}P, and ^{13}C NMR spectra (CD_2Cl_2) were in accordance with previously reported data[10] and showed the compound to be of more than 95% purity.

Procedure for Catalytic Reactions Involving PPh_3: The reaction was performed according to the general procedure, except for PPh_3 (26.5 mg, 0.10 mmol) replacing $PPhMe_2$ as the ligand and the addition of 1-methoxynaphthalene (7.25 µL, 0.05 mmol) and 1,3-cyclohexadiene (50 µL, 0.5 mmol) before the solution was transferred into the NMR tube.

Supporting Information (see footnote on the first page of this article): Graphs for the determination of rate constants; ^{31}P, ^{13}C, and ^1H NMR spectra.

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[11] When 1,3-cyclohexadiene was added to complex **3** in C_6D_6/DCM (1:1) and heated at 50 °C overnight a 0.84:1:0.48 ratio of **2/3/4** was obtained, along with considerable amounts (>10% of total amount of -Si*Me*$_2$Ph) of unidentified products.

[12] The reaction was performed in C_6D_6/CD_2Cl_2 (1:1) at 0.1 M concentration [$Pt(acac)_2$] on a 0.70:1.16:0.33 mixture of complexes **1/2/3**; values calibrated to internal standard (1-methoxynaphthalene). 1,3-Cyclohexadiene (10 equiv.) was added and the formation of **4** was monitored by ^1H NMR spectroscopy at 24 h intervals. After 6 d, a 0.54:0.62:0.35:0.62 mixture of **1/2/3/4** was obtained.

[13] After 24 h at 80 °C, no trace of complexes **2**–**4** was present. No product of silaboration (**5**) was found.

[14] Crystallization from Et_2O, benzene, DCM, or $CDCl_3$ with hexane or pentane was attempted by direct precipitation, diffusion chamber, or diffusion in the NMR tube. Typically, a brown oil was obtained, or complex **3** was isolated in pure form. Further attempts to isolate complex **4** were also made, but met with little success: reaction conditions were optimized in terms of stoichiometries, order and time of addition, and temperature, but no increase in the yield of **4** relative to that obtained under the standard conditions was observed. Exchange of $Pt(acac)_2$ for $Pt(cod)_2$ or addition of 1,3-cyclohexadiene to complex **2** isolated in pure form did not lead to any increase in amount or purity of complex **4**. Finally, attempts to react **4** with sodium dimethyl malonate (A. J. Blacker, M. L. Clarke, M. S. Loft, M. F. Mahon, M. E. Humphries, J. M. J. Williams, *Chem. Eur. J.* **2000**, *6*, 353–360) met with no success – heating at 60 °C overnight only led to decomposition.

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