Transition metal silyl complexes. 55 intramolecular Si–E (E = Si, Sn) oxidative addition of $Ph_2P(CH_2)_nSiR'_2ER_3$ ligands ($n = 1, 2$) to Pt(0) [1]

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Abstract

The complexes $(Ph_3P)(R_3E)\overline{PtPPh_2(CH_2)_nSiR'_2}$ ($n = 2$: R' = Me: ER_3 = $SiPh_3$, $SiMePh_2$, $SnPh_3$; R' = Ph: ER_3 = $SiPh_3$, $SiMePh_2$; $n = 1$, R' = Me, ER_3 = $SiPh_3$) are obtained by reaction of $Ph_2P(CH_2)_nSiR'_2ER_3$ with $(Ph_3P)_2Pt(\pi\text{-}C_2H_4)$. The bis(silyl) complex $(Ph_3P)(Ph_3Si)\overline{PtPPh_2CH_2SiMe_2}$ was characterized by an X-ray structure analysis, which showed the two silyl groups to be *cis* (Pt–Si 236.8(1) and 237.4(1) pm). © 1997 Elsevier Science S.A.

Keywords: Platinum complexes; Silyl complexes; Oxidative addition; X-ray structure analysis

1. Introduction

Oxidative addition of Si–H bonds to coordinatively unsaturated transition metal complexes is one of most useful methods for the formation of metal–silicon bonds. Stable hydrido silyl complexes are formed with a great variety of metal complex fragments, and complexes of this type are intermediates in the catalytic hydrosilylation of unsaturated compounds. More recently, the palladium-catalyzed bissilylation of alkynes and olefins has emerged as another attractive route to organosilicon compounds [2–5]. These reactions proceed via initial oxidative addition of Si–Si bonds. However, there are relatively few examples for the formation of stable bissilyl complexes from disilanes. The same is true for the oxidative addition of Si–Sn bonds. The more common strategies to stabilize oxidative addition products, such as the use of electron-rich metal complex fragments or the substitution of silicon (tin) by electronegative groups, was only successful for a limited number of metal complex/disilane combinations. The use of strained cyclic compounds is also restricted to a few special cases, such as 1,2-disilacyclobutenes [6,7].

Oxidative addition of a bond can be promoted by its incorporation into a chelate system, as has been shown for the Si–H bonds of $R_2P(CH_2)_nSiR'_2H$ [8–10]. We

have quantified the magnitude of the chelate effect on the oxidative addition of Si–H bonds for (phosphinoethyl)silanes by comparison with that of electronic factors [11]. An A–B bond sometimes can only be added to a metal center by 'chelate-assistance'. For example, while no stable complexes are obtained by addition of the Sn–C bonds of tetra(alkyl)- or tetra(aryl)stannanes to iron carbonyl derivatives, one of the Sn–R groups (R = methyl, phenyl) in $(CO)_4Fe(Ph_2PCH_2CH_2SnR_3)$ readily adds intramolecularly to the iron center [12,13]. The resulting complex $(CO)_3(R)\overline{Fe(Ph_2PCH_2CH_2SnR_2)}$ is stabilized by formation of the five-membered Fe–Sn–C–C–P ring. The Sn–R groups of $Ph_2PCH_2CH_2SnR_3$ ligands also add to the more reactive $L_2Pd(0)$ or $L_2Pt(0)$ fragments [14]. Facilitated oxidative addition of E–E bonds (E = Si, Sn) was also observed for $[Ph_2P(CH_2)_nEMe_2]_2$ [15–17]. A particularly high stabilization can be expected in this case, because *two* chelating (phosphinoalkyl)silyl or -stannyl ligands are simultaneously formed.

2. Results

In an extension of our studies on chelate-assisted oxidative additions of bonds between two main group 4 elements to transition-metal centers, we probed (phosphinoalkyl)disilanes and (phosphinoalkyl)silylstannanes which result in a terminal silyl or stannyl ligand and only *one* chelating ligand upon oxidative addition. The previously unknown compounds

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Ph$_2$PCH$_2$CH$_2$SiMe$_2$SiPh$_2$R   (**1a, b**), Ph$_2$PCH$_2$CH$_2$SiPh$_2$SiPh$_2$R   (**1c, d**)   (R = Me,   Ph), Ph$_2$PCH$_2$CH$_2$SiMe$_2$SnPh$_3$ (**1e**)   and Ph$_2$PCH$_2$SiMe$_2$SiPh$_3$ (**1f**) were prepared by reaction of Ph$_2$P(CH$_2$)$_n$SiR'$_2$Cl (R' = Me, Ph) [18] with LiSiPh$_2$R or LiSnPh$_3$ (Eq. (1)).

Ph$_2$P(CH$_2$)$_n$SiR'$_2$Cl + LiER$_3$

——— ► Ph$_2$P(CH$_2$)$_n$SiR'$_2$ER$_3$ + LiCl
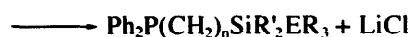
	n	R'	ER$_3$	
1a	2	Me	SiPh$_3$	(1)
1b	2	Me	SiMePh$_2$	
1c	2	Ph	SiMePh$_2$	
1d	2	Ph	SiPh$_3$	
1e	2	Me	SnPh$_3$	
1f	1	Me	SiPh$_3$	

The bis(silyl) complexes **2a, b** were obtained in high yields upon reaction of the (phosphinoethyl)silanes **1a, b** with an equimolar amount of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) in benzene at room temperature (Eq. (2)). Although we did not investigate details of the mechanism, we suppose that in the first step of the reaction the phosphino group of the (phosphinoethyl)disilane substitutes the ethylene ligand. The Si–Si bond then oxidatively adds to the platinum center by replacement of a PPh$_3$ ligand. The reaction is not restricted to the SiMe$_2$ derivatives **1a, b**; the bulkier (diphosphinoethyl)tetraphenylmethylsilane **1c** also gives the corresponding metallacycle (**2c**) by oxidative addition of the Si–Si bond, but only after extended reaction times. However, in the reaction of the pentaphenyl derivative **1d**, the corresponding metallacycle **2d** was only spectroscopically observed, together with another complex, probably (Ph$_5$Si$_2$CH$_2$CH$_2$PPh$_2$) Pt(Ph$_2$PCH$_2$CH$_2$SiPh$_2$)(SiPh$_3$) (**3**), as indicated by its two doublet resonances at 54.4 and

Fig. 1. The structure of **2f** and the labeling scheme used. The hydrogen atoms are omitted for clarity.

22.1 ppm in the ^{31}P-NMR spectrum. We were able to prove this assumption by reacting (Ph$_3$P)$_3$Pt(C$_2$H$_4$) with two equivalents of **1d** resulting in the formation of **3** and only a small amount of **2d**.

Complex **2e** was analogously obtained in the reaction of **1e**. It contains a terminal stannyl ligand and the same chelated (phosphinoethyl)silyl ligand as in **2a**.

1a–e + (Ph$_3$P)$_2$Pt(C$_2$H$_4$)
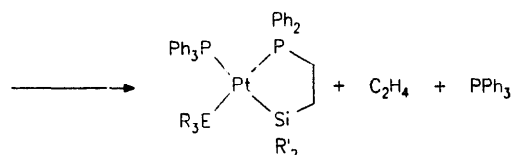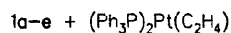
	R'	ER$_3$
2a	Me	SiPh$_3$
2b	Me	SiMePh$_2$
2c	Ph	SiMePh$_2$
2d	Ph	SiPh$_3$
2e	Me	SnPh$_3$

Unstrained five-membered metallacycles are formed from **1a–e**. In the reaction of the phosphinomethyl-substituted disilane **1f**, Si–Si oxidative addition would result in a more strained four-membered metallacycle. Alternatively, a five-membered metallacycle could be formed by oxidative addition of a Si–Ph bond, resulting in a terminal phenyl ligand and a chelated P–C–Si–Si ligand. Reaction of Ph$_2$PCH$_2$SiMe$_2$SiPh$_3$ (**1f**) with (Ph$_3$P)$_2$Pt(C$_2$H$_4$) gives the pale yellow crystalline complex **2f** in high yields. Since it is difficult to distinguish unequivocally between the two possibilities by NMR spectroscopy because of the large number of phenyl groups in the molecule, we performed an X-ray structure analysis of **2f** (Fig. 1). It clearly showed that the Si–Si bond and not the Si–C bond was added (Eq. (3)).

1f + (Ph$_3$P)$_2$Pt(C$_2$H$_4$)

2f
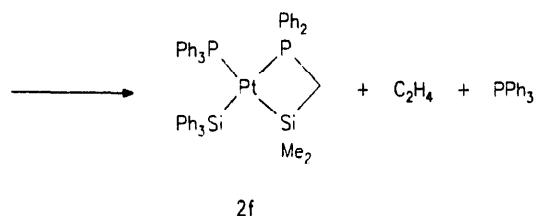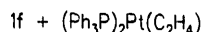
The spectroscopic data of the new complexes are exemplarily discussed for **2a**. In the ^{31}P NMR spectrum, two doublets are observed at 57.8 and 29.9 ppm for the non-equivalent phosphorus nuclei, accompanied by Pt satellites. The value of $^2J_{\text{PP,P}} = 17.1$ Hz is typical for a cis arrangement of the phosphane ligands. Due to the significant low field shift of around 28 ppm, the doublet at 57.8 can be assigned to the phosphorus atom incorpo-
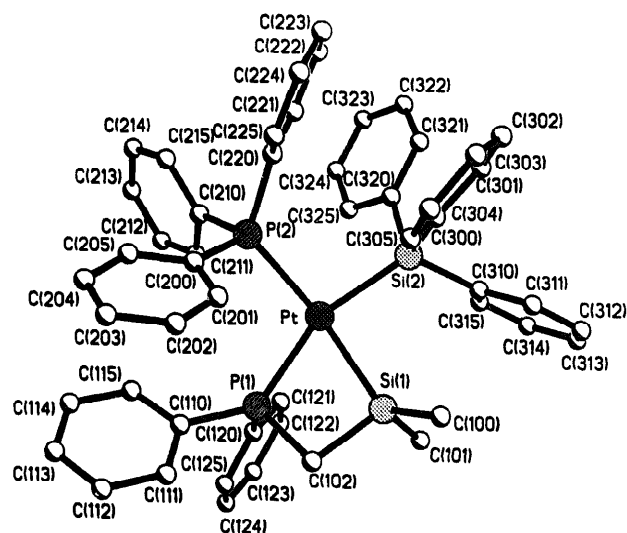
rated into the five-membered ring. The *cis* arrangement is confirmed by the ^{29}Si NMR spectrum showing two doublets of doublets. The resonance at lower field (32.5 ppm) is again assigned to the chelated silicon atom. It shows a J_{PSi} of 7.7 Hz and a *trans*-$^2J_{PPtP}$ of 130.9 Hz. The coupling SiPtP constants of the SiPh$_3$ signal at 9.4 ppm are in the same range (12.9 and 140.5 Hz). The ^{13}C NMR spectrum shows a broad singlet at 4.4 ppm for the SiCH$_3$ group ($^2J_{PtSiC}$ = 72.5 Hz), while the SiCH$_2$ resonance appears as a doublet at 18.1 ppm with a higher $^2J_{PCC}$ coupling constant (17.7 Hz) than in the uncoordinated ligand (10.7 Hz). The doublet at 27.6 ppm assigned to PCH$_2$ also has an increased $^1J_{PC}$ coupling constant (29.4 Hz) compared with the uncoordinated free ligand (14.6 Hz). All signals show the expected downfield shift caused by coordination. The ^{1}H NMR data are in agreement with the proposed structure, which was eventually confirmed by the X-ray structure analysis of **2f** (Fig. 1, Tables 1 and 2).

The four bulky groups bonded to the metal atom are accommodated in the square plane by distortion of the bond angles at Pt. The small P(1)–Pt–Si(1) angle of the four membered metallacycle (70.76(5)°) is compensated by the large angle Si(2)–Pt–P(2). This enlargement is also due to the repulsion of the two bulky ligands PPh$_3$ and SiPh$_3$. The Pt–P and Pt–Si distances of the terminal ligands and the chelated phosphinomethylsilyl ligand do not differ significantly, and the Pt–Si distances are comparable to those in other Pt(II) silyl complexes [19–24].

3. Discussion

Most of the known bis(silyl) complexes of Pt(II) were prepared by dehydrogenative addition of HSiR$_3$ to (R$_3$P)$_2$Pt fragments [25–32]. This includes the bis-chelated complex $\overline{Pt(PPh_2CH_2CH_2SiR_2)_2}$ from Pt(COD)$_2$ and PPh$_2$CH$_2$CH$_2$SiR$_2$H [10]. The formation of bis(silyl) complexes (R$_3$P)$_2$Pt(SiR$'_3$)$_2$ by oxidative addition of Si–Si bonds is favored by electronegative substituents at silicon. The earliest example is the preparation of (Ph$_3$P)$_2$Pt(SiCl$_3$)$_2$ from (Ph$_3$P)$_4$Pt and Si$_2$Cl$_6$ [33,34]. Increasing the basicity of the metal fragment by PEt$_3$ ligands allows to add Si$_2$Me$_5$X and 1,2-Si$_2$Me$_4$X$_2$ (X = F, Cl, Br), but not Si$_2$Me$_4$R$_2$ (R = Me, Ph) [35]. Recently, double oxidative addition of the two Si–Si bonds of 2,2-bis(disilanyl)dithiane to Pt(0) was achieved. It was postulated that this reaction was facilitated by the appropriate orientation of the two Si–Si bonds [36].

Contrary to the latter reaction, the electronically equivalent, but chelating analogues of Si$_2$Me$_4$R$_2$, i.e. the (phosphinoalkyl)disilyl and silyl stannyl derivatives **1a–f**, readily add to the Pt center. The extended reaction times that were observed for **1c**, as well as the fact that the use of pentaphenyl substituted derivative **1d** did

not result in a straightforward reaction, shows that an increased steric bulk renders the reaction more difficult. The by-product (**3**) in the stoichiometric reaction of **1d**

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm$^2 \times 10^6$) for **2f**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U(eq)
Pt	8750(1)	9440(1)	7467(1)	34(1)
P(1)	10222(1)	11174(1)	7151(1)	45(1)
Si(1)	10676(1)	9049(1)	7353(1)	44(1)
P(2)	6778(1)	9702(1)	7173(1)	37(1)
Si(2)	7993(1)	7635(1)	7955(1)	35(1)
C(100)	10535(5)	7518(5)	6710(3)	68(2)
C(101)	11924(4)	9371(5)	8165(3)	61(1)
C(102)	11216(4)	10312(5)	6790(3)	57(1)
C(110)	10029(5)	12172(5)	6531(3)	59(1)
C(111)	10568(8)	12196(8)	5897(4)	128(3)
C(112)	10424(10)	13000(10)	5450(5)	151(4)
C(113)	9710(9)	13719(8)	5616(5)	123(3)
C(114)	9177(6)	13715(6)	6238(4)	87(2)
C(115)	9342(5)	12961(5)	6699(3)	63(2)
C(120)	11250(4)	12342(4)	7964(3)	45(1)
C(121)	11111(5)	12195(5)	8677(3)	62(1)
C(122)	11955(5)	13041(6)	9281(3)	79(2)
C(123)	12931(6)	14045(6)	9181(4)	80(2)
C(124)	13082(5)	14220(6)	8482(4)	71(2)
C(125)	12250(5)	13379(5)	7877(3)	58(1)
C(200)	6762(4)	10070(5)	6256(2)	43(1)
C(201)	7230(6)	9421(7)	5714(3)	88(2)
C(202)	7262(7)	9676(8)	5014(3)	107(3)
C(203)	6860(6)	10614(7)	4856(3)	82(2)
C(204)	6417(5)	11263(6)	5378(3)	74(2)
C(205)	6352(5)	10993(5)	6072(3)	59(1)
C(210)	6479(4)	11009(4)	7773(2)	40(1)
C(211)	7501(5)	11968(5)	8253(2)	49(1)
C(212)	7303(6)	12980(5)	8705(3)	64(2)
C(213)	6123(6)	13044(6)	8690(3)	71(2)
C(214)	5101(6)	12109(6)	8233(3)	69(2)
C(215)	5265(5)	11093(5)	7763(3)	55(1)
C(220)	5250(4)	8375(4)	7053(3)	44(1)
C(221)	4704(4)	8123(5)	7677(3)	49(1)
C(222)	3620(5)	7096(5)	7604(3)	61(2)
C(223)	3082(5)	6315(6)	6926(4)	75(2)
C(224)	3597(6)	6545(6)	6299(4)	83(2)
C(225)	4692(5)	7591(6)	6364(3)	62(2)
C(300)	6966(4)	6204(4)	7199(3)	44(1)
C(301)	6210(5)	5058(5)	7322(3)	70(2)
C(302)	5483(6)	4072(6)	6749(4)	89(2)
C(303)	5466(6)	4148(6)	6024(4)	84(2)
C(304)	6230(6)	5238(6)	5879(3)	79(2)
C(305)	6967(5)	6255(5)	6461(3)	59(1)
C(310)	9146(4)	7050(4)	8461(2)	39(1)
C(311)	9420(4)	5973(5)	8149(3)	58(1)
C(312)	10276(5)	5587(6)	8535(3)	73(2)
C(313)	10867(5)	6235(6)	9242(3)	73(2)
C(314)	10617(5)	7284(6)	9563(3)	66(2)
C(315)	9766(4)	7687(5)	9178(3)	50(1)
C(320)	7087(4)	8020(4)	8742(2)	39(1)
C(321)	6156(4)	7145(5)	8990(3)	55(1)
C(322)	5531(5)	7492(6)	9561(3)	68(2)
C(323)	5821(5)	8708(6)	9917(3)	64(2)
C(324)	6756(5)	9595(6)	9705(3)	66(2)
C(325)	7379(4)	9263(5)	9122(2)	48(1)

Table 2
Selected bond lengths (pm) and angles (°) for **2f**

Pt–P(1)	236.6(1)
Pt–Si(2)	236.8(1)
Pt–P(2)	237.3(1)
Pt–Si(1)	237.4(1)
P(1)–C(102)	180.7(4)
P(1)–C(110)	182.3(5)
P(1)–C(120)	182.9(5)
Si(1)–C(100)	187.5(5)
Si(1)–C(101)	186.6(5)
Si(1)–C(102)	182.7(5)
P(2)–C(200)	182.9(4)
P(2)–C(210)	182.8(4)
P(2)–C(220)	186.6(5)
Si(2)–C(300)	190.4(5)
Si(2)–C(310)	190.5(4)
Si(2)–C(320)	190.8(4)
P(1)–Pt–Si(2)	158.65(4)
P(1)–Pt–P(2)	103.34(4)
Si(2)–Pt–P(2)	97.84(4)
P(1)–Pt–Si(1)	70.76(5)
Si(2)–Pt–Si(1)	89.74(4)
P(2)–Pt–Si(1)	162.14(4)
C(102)–P(1)–C(110)	109.1(2)
C(102)–P(1)–C(120)	103.3(2)
C(110)–P(1)–C(120)	101.5(2)
C(102)–P(1)–Pt	95.0(2)
C(110)–P(1)–Pt	131.7(2)
C(120)–P(1)–Pt	113.1(2)
Pt–P(1)–Si(1)	54.75(4)
C(101)–Si(1)–C(100)	108.2(2)
C(101)–Si(1)–C(102)	109.6(2)
C(100)–Si(1)–C(102)	105.8(2)
C(101)–Si(1)–Pt	123.2(2)
C(100)–Si(1)–Pt	115.7(2)
C(102)–Si(1)–Pt	91.6(1)
C(210)–P(2)–Pt	117.2(2)
C(200)–P(2)–Pt	106.5(1)
C(220)–P(2)–Pt	121.4(1)
C(300)–Si(2)–Pt	111.4(2)
C(310)–Si(2)–Pt	120.5(1)
C(320)–Si(2)–Pt	108.1(2)

probably results from an interchange of phosphane ligands in the stage of the intermediate $Pt(PR_3)_3$ complexes, favored by the significantly prolonged reaction times (5 days for **1d** vs. 30 h for **1c**). The complex $Pt(PPh_3)(PPh_2CH_2CH_2Si_2Ph_5)_2$ obviously is only formed to a significant extent if oxidative addition of the Si–Si bond is slowed down by steric effects. The validity of this assumption is also supported by the observation that raising the reaction temperature to 60°C in the stoichiometric reaction of **1d** results in an increased amount of **3**.

The complexes **2a–e** are stable towards reductive elimination, i.e. no decomposition with reformation of the Si–Si or Si–Sn bond was observed. There was no indication for a competing Si–C or Sn–C oxidative addition.

4. Experimental

4.1. Preparation of $Ph_2PCH_2CH_2SiMe_2SiR_3$ (**1a, b**)

Finely cut lithium (0.40 g, 57.6 mmol) was added to a solution of 6.13 g (14.0 mmol) of Ph_3SiCl [4.19 g (18.0 mmol) of $Ph_2MeSiCl$] in 50 ml of THF. The deep brown reaction mixture was stirred for 12 (18 h), filtered through glass wool and then added to a solution of 4.30 g (14.0 mmol) [5.52 g (18.0 mmol)] of $Ph_2PCH_2CH_2SiMe_2Cl$ in 60 ml of THF within 20 min. The solution was stirred for 1 h. Then the solvent was evaporated in vacuo and the obtained oil dissolved in 60 ml of toluene.

1a: The toluene solution was treated with 50 ml of degassed water. The toluene layer was separated and the water phase extracted two times with 30 ml of toluene each. The united toluene phases were dried over Na_2SO_4. After filtration, all volatiles were removed in vacuo, and the residue was washed two times with 10 ml of petrolether each. Yield 5.6 g (75%), white solid, m.p. 113°C. Anal. Calcd. for $C_{34}H_{35}PSi_2$: C, 76.90; H, 6.65. Found C, 76.41; H, 6.70. ^{31}P NMR (D_6-acetone): δ −8.8 ($^3J_{SiCP}$ = 21.3 Hz). ^{29}Si NMR (D_6-acetone): δ −15.1 (d, SiMe$_2$, $^3J_{PCCSi}$ = 21.8 Hz), −21.3 (s, SiPh$_3$). ^{13}C NMR (D_6-acetone): δ −2.6 (s, SiMe), 12.2 (d, SiCH$_2$, $^2J_{PCC}$ = 10.7 Hz), 22.8 (d, PCH$_2$, $^1J_{PC}$ = 14.6 Hz), 128.0–140.1 ppm (Ph). ^{1}H NMR (D_6-acetone): δ 0.24 (s, 6 H, SiMe), 0.77–0.88 (m, 2 H, SiCH$_2$), 1.87–1.94 (m, 2 H, PCH$_2$), 7.20–7.64 (m, 25 H, Ph).

1b: The solution was filtered, and then all volatiles were removed in vacuo. The colorless oil remained was chromatographed on 10 cm of silica with petroleum ether. The product was eluated with toluene. Yield 5.2 g (62%), opaque oil. ^{31}P NMR (D_6-acetone): δ −8.9. ^{29}Si NMR (D_6-acetone): δ −15.3 (d, SiMe$_2$, $^2J_{PCCSi}$ = 21.3 Hz), −22.4 (s, SiPh$_2$Me). ^{13}C NMR (CDCl$_3$): δ −4.2 (s, SiPh$_2$Me), −3.2 (s, SiMe$_2$), 11.2 (d, SiCH$_2$, $^2J_{PCC}$ = 16.8 Hz), 22.6 (d, PCH$_2$, $^1J_{PC}$ = 22.7 Hz), 128.1–139.0 (Ph). ^{1}H NMR (CDCl$_3$): δ 0.25 (s, 6 H, SiMe$_2$), 0.69 (s, 3 H, SiMe), 0.75–0.90 (m, 2 H, SiCH$_2$), 1.91–2.14 (m, 2 H, PCH$_2$), 7.25–7.78 (m, 20 H, Ph).

1c: The reaction was carried out as described for **1a, b** using 1.25 g (5.4 mmol) $SiPh_2MeCl$ and 2.33 g (5.4 mmol) of $Ph_2PCH_2CH_2SiPh_2Cl$. After removal of all

volatiles from the toluene phase, the remaining yellow oil was dissolved in 30 ml of petroleum ether and filtered over glass wool/celite. All volatiles were removed from the filtered solution. Yield 2.20 g (69%), opaque oil. ^{31}P NMR (CDCl$_3$): δ -8.3 (s). ^{29}Si NMR (CDCl$_3$): δ -19.7 (d, SiPh$_2$, $^3J_{PCCSi}$ = 28.3 Hz), -23.8 ppm (s, SiPh$_2$Me). ^{1}H NMR (CDCl$_3$): δ 0.71 (s, 3 H SiCH$_3$), 1.27–1.37 (m, 2 H, SiCH$_2$), 1.90–2.20 (m, 2 H, PCH$_2$), 7.20–7.77 (m, 30 H, pH).

1d: The reaction and purification was carried out as described for **1a** using 2.56 g (8.7 mmol) SiPh$_3$Cl and 3.75 g (8.5 mmol) Ph$_2$PCH$_2$CH$_2$SiPh$_2$Cl. Yield 3.95 g (70%), colorless solid, m.p. 175°C. Anal. Calcd. for C$_{44}$H$_{39}$PSi$_2$: C, 80.69; H, 6.00. Found: C, 79.24; H, 6.15. ^{31}P-NMR (C$_6$D$_6$): δ -8.8 ppm (s). ^{29}Si-NMR (C$_6$D$_6$): δ -19.8 ppm (d, $^3J_{PCCSi}$ = 24.0 Hz, SiPh$_2$), -23.4 ppm (s, SiPh$_3$). ^{13}C-NMR (C$_6$D$_6$): δ 9.9 ppm (d, $^2J_{PCC}$ = 12.5 Hz, SiCH$_2$), 23.9 ppm (d, $^1J_{PC}$ = 15.3 Hz, PCH$_2$), 128.3–139.8 ppm (Ph). ^{1}H-NMR (C$_6$D$_6$): δ 1.72–1.83 ppm (m, 2 H, SiCH$_2$), 2.19–2.36 ppm (m, 2 H, PCH$_2$), 7.10–7.75 ppm (m, 35 H, PH).

4.2. Preparation of Ph$_2$PCH$_2$CH$_2$SiMe$_2$SnPh$_3$ (1e)

A solution of freshly prepared LiSnPh$_3$ in 25 ml of THF (from 5.38 g (13.9 mmol) of SnPh$_3$Cl) was added to a solution of 3.79 g (13.9 mmol) Ph$_2$PCH$_2$CH$_2$SiMe$_2$Cl in 20 ml of THF at 0°C during 20 min. After warming to room temperature and additional stirring for 2 h, the solvent was removed in vacuo from the green–brown solution leaving. The resulting brown oil was treated with 60 ml of toluene, and the solution filtered over glasswool/celite. After removal of the toluene, the yellow oil (containing some Sn$_2$Ph$_6$) was extracted three times with 25 ml of petroleum ether each. From the combined solutions the solvent was removed in vacuo. The resulting white solid was recrystallized from 10 ml of petroleum ether at -30°C. Yield 1.28 g (15%), m.p. 56°C (dec.). Anal. Clc. for C$_{34}$H$_{35}$SiPSn: C, 65.70; H, 5. 68. Found: C, 65.12; H, 5.81. ^{31}P NMR (CDCl$_3$): δ -9.2 (s). ^{29}Si NMR (C$_6$D$_6$): δ 0.2 (d, $^3J_{PCCSi}$ = 22.5 Hz). ^{119}Sn NMR (C$_6$D$_6$): δ -137.2 (s). ^{13}C-NMR (CDCl$_3$): δ -0.3 (s, SiMe), 13.7 (d, SiCH$_2$, $^2J_{PCC}$ = 14.3 Hz), 23.1 (d, PCH$_2$, $^1J_{PC}$ = 14.33 Hz), 128.0–140.2 (Ph). ^{1}H NMR (CDCl$_3$): δ 0.50 (s, 6 H, SiMe, $^3J_{SnSiCH}$ = 32.8 Hz), 0.97–1.08 (m, 2 H, SiCH$_2$), 2.00–2.07 (m, 2 H, PCH$_2$), 7.22–7.66 (m, 25 H, Ph).

4.3. Preparation of Ph$_2$PCH$_2$SiMe$_2$SiPh$_3$ (1f)

The compound **1f** was prepared from Ph$_2$PCH$_2$SiMe$_2$Cl (1.21 g, 4.1 mmol) and LiSiPh$_3$ (from 1.20 g (4.1 mmol) Ph$_3$SiCl in THF) as described for **1a**, except for the use of benzene instead of THF as the solvent for Ph$_2$PCH$_2$SiMe$_2$Cl. The reaction solution

was treated with 50 ml of degassed water. The organic layer was separated and the water phase was extracted two times with 30 ml of toluene each. The combined organic phases were dried over Na$_2$SO$_4$. After filtration, all volatiles were removed in vacuo, and the residue was washed two times with 10 ml of petroleum ether each. Yield 1.22 g (58%), white solid, m.p. 132°C. Anal. Calcd. for C$_{33}$H$_{33}$PSi$_2$: C, 76.70; H, 6.44. Found C, 76.25; H, 6.59. ^{31}P NMR (C$_6$D$_6$): δ -22.3. ^{29}Si NMR (C$_6$D$_6$): δ -16.9 (d, SiMe$_2$, $^2J_{PCSi}$ = 14.8 Hz), -19.7 (d, SiPh$_3$, $^3J_{PCCSi}$ = 8.3 Hz). ^{13}C NMR (C$_6$D$_6$): δ -1.4 (d, SiMe, $^3J_{PCSiC}$ = 6.0 Hz), 13.1 (d, CH$_2$, $^1J_{PC}$ = 34.2 Hz), 128.6–142.0 ppm (Ph). ^{1}H NMR (C$_6$D$_6$): δ 0.34 (s, 6 H, SiMe), 1.74 (s, br, 2 H, CH$_2$), 7.08–7.76 (m, 25 H, Ph).

4.4. Preparation of (Ph$_3$P)(R$_3$E)Pt$\overline{PPh_2(CH_2)_n}$SiR$_3'$ (2a–c,d,f)

The solution of **1a–f** in 5 ml of benzene was added to a solution of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) in 15 ml of benzene. The color of the solution immediately changed to deep yellow, and gas was evolved. After about 30 min the gas evolution ceased. The reaction mixture was stirred for additional 16 h during which the color slowly changed to bright yellow. Then the benzene was removed in vacuo. On washing the remaining yellow oil three times with 3–5 ml of petroleum ether each resulted in pale yellow solids.

2a: 100 mg (0.134 mmol) of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) and 75 mg (0.134 mmol) of **1a**. Yield: 112 mg (85%), m.p. 78°C (dec.). Anal. Calc. for C$_{52}$H$_{50}$Si$_2$P$_2$Pt: C, 63.2; H. 5.10. Found C, 63.7; H, 5.41. ^{31}P NMR (C$_6$D$_6$): δ 57.8 (d, Ph$_2$PCH$_2$, $^2J_{PP}$ = 17.1 Hz, $^1J_{PtP}$ = 1647.9 Hz), 29.9 (d, Ph$_3$P, $^2J_{PP}$ = 17.1 Hz, $^1J_{PtP}$ = 1762.7 Hz). ^{29}Si NMR (C$_6$D$_6$): δ 32.5 (dd, SiMe$_2$, $^2J_{PtSi}$ = 7.7 Hz, $^2J_{PPSi}$ = 130.9 Hz), 9.38 (dd, SiPh$_3$, $^2J_{PPSi}$ = 12.9 Hz, $^2J_{PPSi}$ = 140.5 Hz). ^{13}C-NMR (C$_6$D$_6$): δ 4.74 (s, br, SiMe, $^2J_{PtSiC}$ = 72.5 Hz), 18.1 (d, SiCH$_2$, $^2J_{PCC}$ = 17.7 Hz), 27.6 (d, PCH$_2$, $^1J_{PC}$ = 29.4 Hz), 127.0–138.2 (m, Ph). ^{1}H NMR (C$_6$D$_6$): δ 0.52 (s, 6 H, SiCH$_3$, $^3J_{PtSiCH}$ = 23.2 Hz), 0.58–1.03 (m, 2 H, SiCH$_2$), 2.23–2.32 (m, 2 H, PCH$_2$), 6.80–7.79 (m, Ph).

2b: 145 mg (0.194 mmol) of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) and 91 mg (0.194 mmol) of **1b**. Yield 145 mg (81%), m.p. 85°C (dec.). Anal. Calc. for C$_{47}$H$_{48}$Si$_2$P$_2$Pt: C, 60.95; H, 5.22. Found C, 60.87; H, 4.94. ^{31}P NMR (C$_6$D$_6$): δ 60.5 (d, Ph$_2$PCH$_2$, $^2J_{PPtP}$ = 19.5 Hz, $^1J_{PtP}$ = 1641.3 Hz), 29.5 (d, Ph$_3$P, $^2J_{PPtP}$ = 20.7 Hz, $^1J_{PtP}$ = 1598.0 Hz). ^{29}Si NMR (C$_6$D$_6$): δ 31.7 (d, br, SiMe$_2$, $^2J_{PPtS}$ = 135.0 Hz), 1.1 (dd, SiPh$_2$Me, $^2J_{PPtSi}$ = 143.3 Hz, $^2J_{PPtSi}$ = 14.8 Hz). ^{13}C NMR (C$_6$D$_6$): δ 4.9 (s, br, SiMe, $^2J_{PtSiC}$ = 59.1 Hz), 7.4 (s, br, SiPh$_2$Me, $^2J_{PtSiC}$ = 52.2 Hz), 19.9 (d, br, SiCH$_2$, $^2J_{PCC}$ = 31.1 Hz), 32.6 (d, br, PCH$_2$, $^1J_{PC}$ = 35.2 Hz), 127.0–139.2 (Ph). ^{1}H NMR (C$_6$D$_6$): δ 0.54 (d, 6 H, SiMe$_2$, $^4J_{PPtSiCH}$ = 2.4 Hz,

$^3J_{PtSiCH}$ = 23.2 Hz), 0.62 (d, 3 H, SiMe, $^4J_{PPtSiCH}$ = 2.45 Hz, $^3J_{PtSiCH}$ = 24.4 Hz), 0.64–0.95 (m, 2 H, SiCH$_2$), 2.14–2.24 (m, 2 H, PCH$_2$), 6.85–7.95 (m, Ph).

2c: 135 mg (0.181 mmol) of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) and 107 mg (0.181 mmol) of **1c**. Yield 112 mg (59%) m.p. 69°C (dec). Anal. Calc. for C$_{57}$H$_{52}$P$_2$Si$_2$Pt: C, 65.2; H, 4.99. Found C, 63.1; H, 4.99. ^{31}P NMR (C6D6): δ 56.4 (d, Ph$_2$PCH$_2$, $^2J_{PPtP}$ = 20.8 Hz, $^1J_{PtP}$ = 1500.2 Hz), 28.7 (d, Ph$_3$P, $^2J_{PPtP}$ = 20.8 Hz, $^1J_{PtP}$ = 1783.4 Hz). ^{29}Si (C$_6$D$_6$): δ 28.2 (dd, SiPh$_2$, J_{PSi} = 9.2 Hz, $^2J_{PPtSi}$ = 143.8 Hz), −1.7 (dd, SiPh$_2$Me, $^2J_{PPtSi}$ = 12.9 Hz, $^2J_{PPtSi}$ = 137.8 Hz). ^{13}C NMR (C$_6$D$_6$): δ 6.9 (s, br, SiMe) 19.7 (d, br, SiCH$_2$, $^2J_{PCC}$ = 30.3 Hz), 30.4 (d, br, PCH$_2$, $^1J_{PC}$ = 38.2 Hz), 127.6–141.3 (Ph). ^{1}H NMR (C$_6$D$_6$): δ 1.01 (d, 3 H, SiCH$_3$, J_{PH} = 2.45 Hz, $^3J_{PtSiCH}$ = 27.3 Hz), 1.29–1.44 (m, 2 H, SiCH$_2$), 2.19–2.28 (m, 2 H, PCH$_2$), 6.81–8.08 (m, Ph).

2e: 102 mg (0.135 mmol) of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) and 84 mg (0.135 mmol) of **1e**. Yield: 97 mg (67%), m.p. 69°C. Anal. Calc. for C$_{52}$H$_{50}$P$_2$SiSnPt: C, 57.9; H, 4.67. Found: C, 58.0; H, 4.80. ^{31}P NMR (C$_6$D$_6$): δ 28.8 (d, $^2J_{PPtP}$ = 17.1 Hz, $^1J_{PtP}$ = 1659.5 Hz, $^2J_{SnPtP}$ = 186.1 Hz), 62.1 (d, $^2J_{PPtP}$ = 17.1 Hz, $^1J_{PtP}$ = 2692.7 Hz, $^2J_{117SnPtP}$ = 1491.6 Hz, $^2J_{119SnPtP}$ = 1560.6 Hz). ^{119}Sn NMR (C$_6$D$_6$): δ −32.6 (dd, *trans*-$^2J_{PPtSn}$ = 1561.5, *cis*-$^2J_{PPtSn}$ = 188.2 Hz). ^{29}Si NMR (C$_6$D$_6$): δ 31.9 (dd, J_{PSi} = 8.3 Hz, $^2J_{PPtSi}$ = 131.3 Hz). ^{13}C NMR (C$_6$D$_6$): δ 5.5 (d, SiMe, J_{PC} = 6.5 Hz, $^3J_{SnPtSiC}$ = 74.5 Hz), 19.6 (dd, SiCH$_2$, $^2J_{PCC}$ = 28.9 Hz, J_{PC} = 6.5 Hz), 33.1 (dd, PCH$_2$, $^1J_{PC}$ = 37.5 Hz, J_{PC} = 9.7 Hz), 126.5–150.7 (m, Ph). ^{1}H NMR (C$_6$D$_6$): δ 0.75 (d, 6 H, SiMe, $^4J_{PPtSiCH}$ = 2.4 Hz, $^3J_{PtSiCH}$ = 22.0 Hz), 0.70–0.99 (m, 2 H, SiCH$_2$), 2.15–2.25 (m, 2 H, PCH$_2$), 6.71–7.90 (m, Ph).

2f: 102 mg (0.136 mmol) of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) and 70 mg of **1f**. Yield: 115 mg (87%), m.p. 69°C (dec). Anal. Calc. for C$_{51}$H$_{48}$P$_2$Si$_2$Pt: C, 62.88; H, 4.97. Found: C, 62.86; H, 4.90. ^{31}P NMR (C$_6$D$_6$): δ 32.4 (d, $^2J_{PPtP}$ = 29.3 Hz, $^1J_{PtP}$ = 1533.2 Hz), −12.6 (d, $^2J_{PPtP}$ = 29.3 Hz, $^1J_{PtP}$ = 1150.5 Hz). ^{29}Si NMR (C$_6$D$_6$): δ −26.4 (dd, SiMe$_2$, *trans*-$^2J_{PPtSi}$ = 134.3 Hz, J_{PSi} = 47.6 Hz, $^1J_{PtSi}$ = 927.7 Hz), 2.7 ppm (dd, SiPh$_3$, $^2J_{PPtSi}$ = 159.5 Hz, $^2J_{PPtSi}$ = 11.0 Hz, $^1J_{PtSi}$ = 1411.1 Hz). ^{13}C NMR (C$_6$D$_6$): δ 4.3 (s, br, SiMe), 30.3 (d, br, CH$_2$, $^1J_{PC}$ = 18.7 Hz), 127.6–146.5 (m, Ph). ^{1}H NMR (C$_6$D$_6$): δ 0.31 (d, 6 H, SiMe, $^4J_{PPtSiCH}$ = 3.6 Hz, $^3J_{PtSiCH}$ = 24.4 Hz), 2.66 (dd, 2 H, CH$_2$, $^2J_{PCH}$ = 11.9 Hz, J_{PH} = 3.6 Hz, $^3J_{PtPCH}$ = 57.9 Hz), 6.79–8.17 (m, Ph).

4.5. Reaction of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) with one equivalent of 1d

83 mg (0.111 mmol) of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) and 73 mg (0.111 mmol) of **1d** were allowed to react as described for **2a**. After stirring for 5 d at room temperature and removal of the solvent, the ^{31}P-NMR spectrum indi-

cated the formation of a mixture of **2d** and **3** in an approximate 2:1 ratio, and some Pt(PR$_3$)$_3$ species.

2d: ^{31}P NMR (C$_6$D$_6$): δ 53.9 (d, $^2J_{PPtP}$ = 20.8 Hz, $^1J_{PtP}$ = 1532.2 Hz), 29.1 (d, $^2J_{PPtP}$ = 20.8 Hz, $^1J_{PtP}$ = 1750.5 Hz).

4.6. Reaction of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) with two equivalents of 1d

50 mg (0.067 mmol) of (Ph$_3$P)$_2$Pt(C$_2$H$_4$) were reacted with 88 mg (0.134 mmol) of **1d** in 10 ml of benzene for 4 d. The solvent was then removed from the light yellow solution. A ^{31}P- and ^{29}Si-NMR spectrum of the resulting pale yellow, slightly oily solid proved the formation of **3** and a small amount (about 5% as indicated by ^{31}P-NMR) of **2d**.

3: ^{31}P NMR (C$_6$D$_6$): δ 54.4 (d, 2J_{PPtP} = 22.0 Hz, $^1J_{PtP}$ = 1533.2 Hz) 22.1 (d) $^2J_{PPtP}$ = 22,0 $^1J_{PtP}$ = 1622.5 Hz. ^{29}Si NMR (C$_6$D$_6$): 27.8 (dd, $^2J_{PPtSi}$ = 140.1 Hz, J_{PSi} = 10.2 Hz), 3.7 (dd, $^2J_{PPtSi}$ = 146.6 Hz, $^2J_{PPtSi}$ = 14.8 Hz), −23.0 (d, $^3J_{PCCSi}$ = 30.5 Hz), −23.6 (s). ^{1}H NMR (C$_6$D$_6$): 1.00–1.53 (overlapping m, SiCH$_2$, 4H), 2.11–2.47 (overlapping m, PCH$_2$, 4H), 6.89–7.98 (m, Ph).

X-ray structure analysis of **2f**: Pale yellow crystals (0.22 × 0.11 × 0.07 mm^3). Cell parameters: triclinic, a = 1128.1 (2), b = 1152.4(2), c = 1851.9(3) pm, α = 101.36(1), β = 94.69 (1), γ = 108.60(1)°, V = 2209.6 (6) × 10^6 pm^3, space group $P-1$ (Z = 2), d_{calc} = 1.466 g/cm^3. Data collection: The crystals were mounted on a Siemens SMART diffractometer (area detector) in a sealed capillary. Mo-K$_\alpha$ radiation (λ = 71.069 pm, graphite monochromator) was used for all measurements. The data collection at 293 K covered over a hemisphere of the reciprocal space, by a combination of three sets of exposures. Each set had a different Φ angle for the crystal, and each exposure took 20s and covered 0.3° in ω. The crystal-to-detector distance was 3.85 cm. The data was collected in the range $1.14 \leq \Phi \leq 30.51°$, $-14 \leq h \leq 16$, $-16 \leq k \leq 11$, $-22 \leq l \leq 26$. 19131 reflections were collected. 13238 unique reflections (R_{int} = 0.0381) were obtained after correction for polarization and Lorentz effects (μ = 33.36 cm^{-1}) and used for calculations. The structure was solved by direct methods (SHELX86). The positions of the hydrogen atoms were calculated according to an idealized geometry. Refinement was performed by the full-matrix least-squares method based on F^2 (SHELX93) with anisotropic thermal parameters for all non-hydrogen atoms. The parameters of the hydrogen atoms were not refined. R = 0.046, R_w = 0.061 for 8198 reflections with $I > 2\sigma(I)$; $w = 1/[\sigma^2(F_0^2) + (0.0097P)^2]$. The largest residual electron density was 0.836 e/Å3. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldsha-

fen (Germany), on quoting the depository number CSD-405992.

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