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Synthesis of palladium(II) complexes of bidentate phosphano ligands with carbosilane substituents

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ABSTRACT

The synthesis of carbosilane dendrons with bidentate bis(diphenylphosphanomethyl)amino ligands at the focal point and terminal alkyl or dimethylamino end-groups, together with their palladium(II) complexes and a cationic ammonium-quaternized derivative, is described. All compounds were characterized by elemental analysis and NMR spectroscopy (^{1}H, ^{13}C, ^{31}P and ^{29}Si).

1. Introduction

The development of organic reactions catalyzed by metal complexes in the aqueous phase [1] has encouraged the synthesis of water-soluble versions of the traditional hydrophobic ligands used in organometallic catalysis in the last two decades [2]. Thus, a large variety of aryl- and alkyl-substituted tertiary phosphanes have been rendered water soluble by means of ionic (sulfonate, carboxylate, phosphonate, ammonium…) or nonionic hydrophilic substituents (polyols, carbohydrates, polyethers…) [2,3]. Indeed, amphiphilic phosphanes add phase-transfer abilities to the water-soluble ligand, often resulting in improved catalytic activities and selectivities in biphasic processes [3].

Dendrimers and dendrons are versatile molecules for the construction of catalysts adapted to a particular medium [4]. Thus, functional groups can be methodically introduced into the desired positions of a single dendritic molecule during or after the stepwise construction, and voids and channels in the interior of the branched structure can host molecules in an environment of adjustable polarity, whereas interaction of the end-groups with the solvent modulates the solubility of the macromolecule as a whole [5].

Of the many dendritic structures developed over the last few decades, carbosilane dendrimers [6] have rapidly moved to the forefront as regards the application of these hyperbranched materials in catalysis because of their inertness and the stability imparted by the strong and relatively unpolarized Si–C bonds [7,8]. Krska and Seyferth reported the first examples of amphiphilic carbosilane dendrimers in 1998 and demonstrated their ability to enhance the solubility of lipophilic alkyl-substituted benzene derivatives [9]. We have become interested in the synthesis of metal-functionalized carbosilane-based dendritic catalysts over the last few years [10]. Indeed, and closely related with the topic of this report, we showed the effect of the bonding of triarylphosphane ligands to carbosilane dendrons on the solubilization of palladium catalysts in supercritical CO_2 [11]. Likewise, in a different study, we prepared mono- and bi-dentate phosphanes with ammonium-functionalized (non-dendritic) carbosilane substituents [12], although the metal complexes of these phosphanes were found to be poorly soluble in water. Incorporation of the ligand at the focal point, and the ammonium groups at the periphery, of a carbosilane dendron multiplies the number of solubilizing groups and therefore should increase the water solubility of the whole molecule.

The synthesis of carbosilane structures with reactive functions at both the focal point and periphery is challenging [13] as most such functions are incompatible with the sequence of reactions employed in the divergent growth of a carbosilane and have to be introduced at the focal point after construction of the dendritic structure. The usual strategies employed to solve this problem make use of an inert protector of the focal point during carbosilane synthesis that can be modified or replaced to introduce the desired functionality as the last synthetic step [14]. For instance, we have shown that a phenyl group linked to the core silicon atom of

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a carbosilane can be replaced by nucleophiles upon acid-induced cleavage of the silicon–phenyl bond [15,16]. This route has led to the synthesis of carbosilane dendrons doubly functionalized with Si–Cl bonds at the focal point and group 4 metallocene complexes at the periphery [17].

Herein we extend these studies to the preparation of carbosilane dendrons bearing bidentate bis(diphenylphosphanomethyl)amino ligands at the focal point and alkyl or ammonium groups at the periphery. *para*-Functionalized *N*,*N*-bis(diphenylphosphanomethyl)anilines of formula (4-X–C_6H_4)N(CH_2PPh_2)$_2$ (X = OH, Br) are accessible by simple synthetic procedures and can be grafted onto carbosilane dendrons via the hydroxyl or bromo functionalities (Scheme 1). Their palladium(II) complexes have also been prepared and tested in a model Heck cross-coupling reaction.

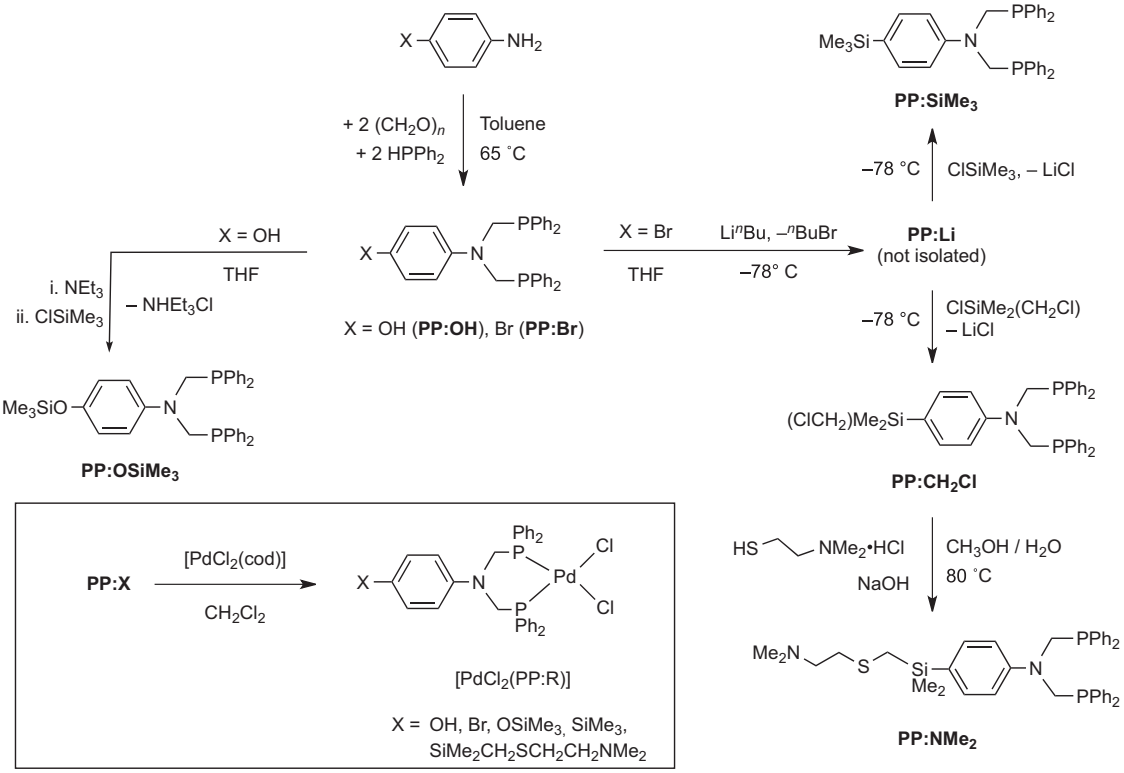
2. Results and discussion

2.1. Synthesis of non-dendritic phosphanes and their palladium complexes

We first explored the synthetic steps involved in the bonding of ligands and hydrophilic groups to a carbosilane structure using simple silanes as model analogs (Scheme 1). In the first step, the modified aryl-bis(diphenylphosphanomethyl)amines **PP**:**OH** and **PP**:**Br** were prepared in almost quantitative yields (>90%) by treating the corresponding *para*-bromo- or *para*-hydroxy-substituted aniline with paraformaldehyde and diphenylphosphane in hot toluene under a rigorously controlled oxygen-free atmosphere, as reported elsewhere [18]. The next step involved silylation of the aniline *para* position by treatment of chlorotrimethylsilane with phenol **PP**:**OH** in the presence of triethylamine or with the lithiated salt of the bromoaryl phosphane **PP**:**Br**. The phenolysis reaction afforded **PP**:**OSiMe**$_3$ in which both moieties are linked through a Si–O–Ar bond, whereas the lithiation afforded **PP**:**SiMe**$_3$, which contains a direct Si–Ar bond. Both **PP**:**OSiMe**$_3$ and **PP**:**SiMe**$_3$ were obtained in good yields (≈75%) as colorless, analytically pure oils. Silicon–aryloxide bonds are, however, moisture-sensitive [19], thus meaning that the palladium dichloride complex of phosphane **PP**:**OSiMe**$_3$ (see below) undergoes partial protolysis when exposed to air. Subsequent studies therefore used direct silicon–carbon bonds only.

The last step of this exploratory work involved functionalization of the ligand with a hydrophilic functionality. Chloro(chloromethyl) dimethylsilane is an interesting synthetic building block for this due to the quite different reactivity of the silicon–chloride and carbon–chloride bonds. As illustrated in Scheme 1, the lithium derivative **PP**:**Li** reacts selectively with the more electrophilic silicon–chloride bond at low temperature to afford the intermediate C_6H_4{1-N(CH_2PPh_2)$_2$}(4-$SiMe_2CH_2Cl$), which was characterized by NMR spectroscopy and subsequently used without prior purification. The carbon–chloride bond of this intermediate reacts with 2-dimethylaminoethanethiol, added as hydrochloride, at 80 °C in methanol/water in the presence of a base to afford the amphiphilic diphosphane **PP**:**NMe**$_2$ as a yellow, analytically pure oil in 69% yield. The methanol/water mixture has to be perfectly deoxygenated before use to avoid oxidation of the phosphane. This reaction was previously reported by Krska and Seyferth for the synthesis of water-soluble carbosilane dendrimers and forms sulfur linkages that are stable in water [9].

Palladium dichloride chelate complexes [$PdCl_2$(**PP**:**X**)] were obtained as yellow-orange solids in high yields (74–87%) by displacement of 1,5-cyclooctadiene (cod) from [$PdCl_2$(cod)] by the **PP**:**X** ligand. Formation of the complexes shifts the ^{31}P resonance downfield from −27 ± 1 ppm in the ligands to ≈10 ppm in the complexes, both of which are typical values for bis(diphenylphosphanomethyl)amines and their Pd complexes, respectively [18,20,21]. Another significant change in the NMR parameters concerns the increase in the ^1J(C–P) coupling constant of the



Scheme 1. Synthesis of non-dendritic phosphanes and their palladium complexes.

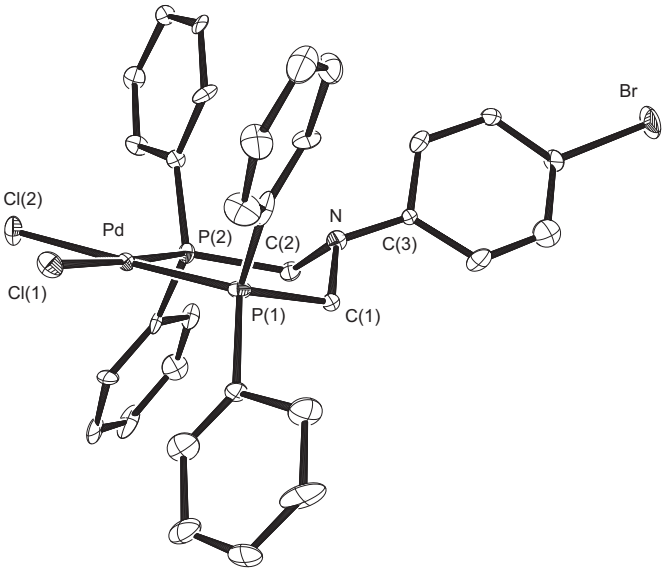


Fig. 1. Molecular structure of complex [$PdCl_2$(**PP**:**Br**)] obtained by X-ray diffraction. Selected bond lengths (Å) and angles (°): Pd–P(1) 2.240(5), Pd–P(2) 2.245(5), Pd–Cl(2) 2.340(5), Pd–Cl(1) 2.366(5), N–C(2) 1.45(2), N–C(1) 1.563(17), P(1)–C(1) 1.804(16), P(2)–C(2) 1.857(19), P(1)–Pd–P(2) 95.06(16), P(1)–Pd–Cl(2) 178.3(2), P(1)–Pd–Cl(1) 87.76(18), P(2)–Pd–Cl(2) 85.73(17), P(2)–Pd–Cl(1) 176.4(2), Cl(2)–Pd–Cl(1) 91.39(17), C(2)–N–C(1) 105.6(11), C(1)–P(1)–Pd 119.2(5), C(2)–P(2)–Pd 116.8(6), N–C(1)–P(1) 112.4(10), N–C(2)–P(2) 115.4(12).

methylene resonance from 13 to 16 Hz in the ligands to 40–47 Hz in the complexes.

The structure of the palladium complex [$PdCl_2$(**PP**:**Br**)] has been confirmed by X-ray diffraction methods (Fig. 1). The asymmetric unit of the unit cell contains three molecules of the complex together with three molecules of chloroform. These molecules are very similar, with the exception of a small difference in the orientation of the 4-bromophenyl groups. The palladium complex displays a *cis*-planar PdP_2Cl_2 coordination environment and a flattened boat conformation for the six-membered PdP_2C_2N ring. The structural parameters of the Pd environment and metallocycle are similar to those found in the parent complex [$PdCl_2\{(PPh_2CH_2)_2NC_6H_5\}$] [22] and in other related aryl-substituted complexes [23].

2.2. Synthesis of dendritic phosphanes and their complexes

In the second part of this work, the chloro(chloromethyl) dimethylsilane synthon was replaced by carbosilane dendrons in order to prepare dendritic hydrophobic alkyl- and amphiphilic ammonium-terminated diphosphanes (Scheme 2). The synthetic strategy was based on our previous reports of the post-functionalization of the focal point of carbosilane dendrons based on the protolytic cleavage of aryl–silicon bonds [15,17].

The process starts with an arylchlorosilane core from which the carbosilane dendron can be grown up to the desired generation by successive alkenylation and hydrosilylation reactions and terminated with the required end-groups in the last preparative step [17]. The three first-generation carbosilane dendrons **Ar**:**G**1:$\mathbf{X}_n$ in Scheme 2 were prepared initially. Two of these are alkyl-terminated dendrons with two (**Ar**:**G**1:$\mathbf{Et}_2$) or three (**Ar**:**G**1:$\mathbf{Et}_3$) branches in which the hydrosilylation step was followed by alkylation of the peripheral Si–Cl bonds with EtMgCl. The third (**Ar**:**G**1:(**CH_2Cl**)$_3$) has three peripheral chloromethyl functionalities that allow the subsequent incorporation of hydrophilic ammonium groups. Three different aryl groups (phenyl, 4-methoxyphenyl or 2,4,6-trimethoxyphenyl) have been incorporated to the focal point of the dendrons as explained below.

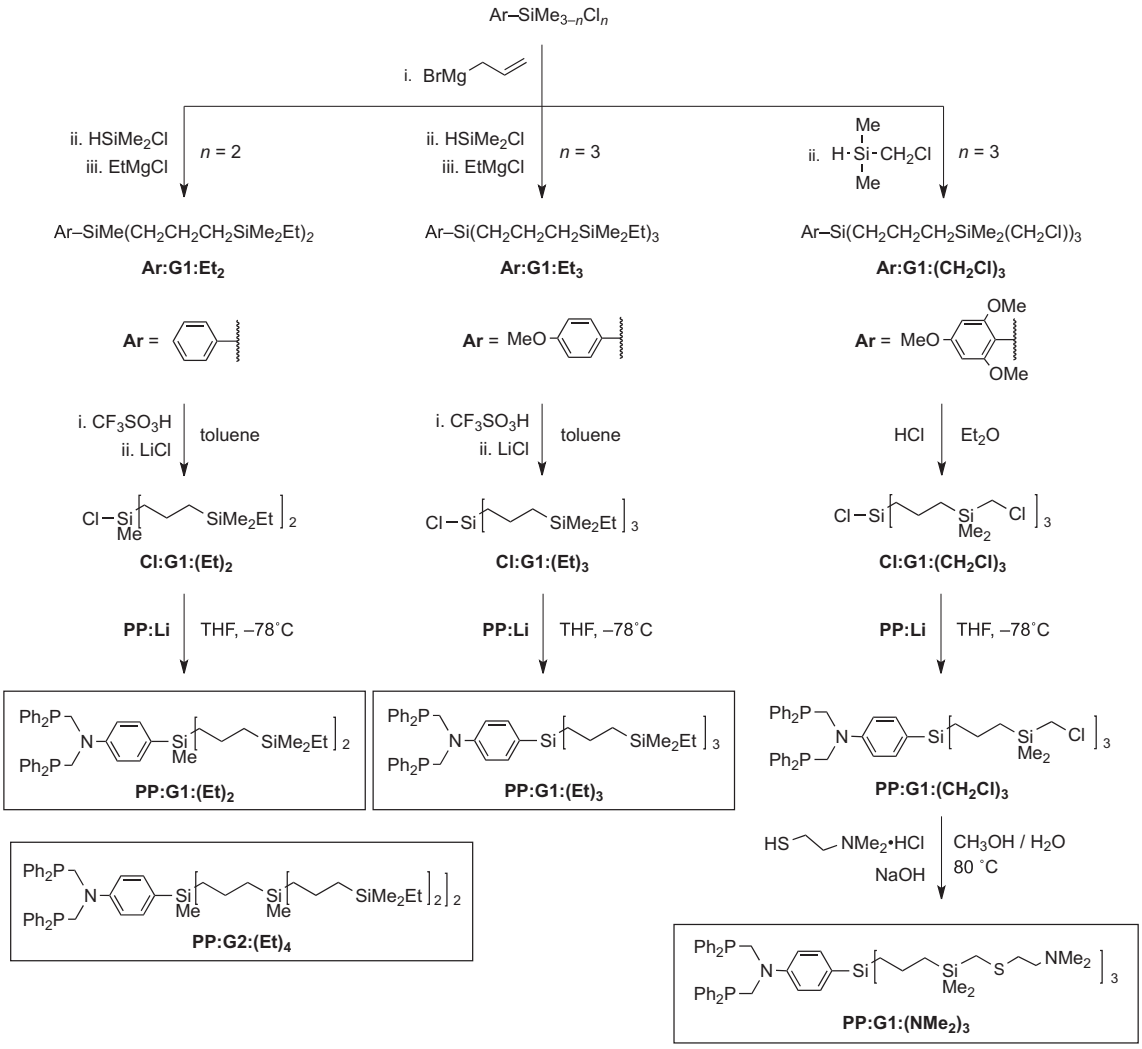
The second part of the preparation is the deprotection step in which the aryl group at the focal point is removed under acidic conditions and replaced by a nucleophile (chloride in the case of dendrons **Cl**:**G**1:$\mathbf{X}_n$ on Scheme 2). Electron-donating substituents on the aryl leaving-group activate the Si–C bond and soften the conditions required for bond cleavage. The order of lability of the aryl groups used in this work is 2,4,6-trimethoxyphenyl > 4-methoxyphenyl > phenyl. Fewer methoxy substituents means harsher deprotection conditions but also means that the silicon–aryl bond is less prone to undesired leaching during dendrimer growth due to the small amounts of HCl generated by hydrolysis of chlorosilane reagents [17].

The more resistant phenyl or 4-methoxyphenyl groups were used during preparation of the alkyl-terminated dendrons **Ar**:**G**1:$\mathbf{Et}_n$, where a chlorosilane reagent ($HSiMe_2Cl$) is used. When analogous preparations were tested with the trisubstituted aryl, the systematic formation of 2,4,6-trimethoxybenzene was observed in the hydrosilylation step (up to 15% by ^{1}H NMR spectroscopy), whereas the 4-methoxyphenyl–silicon bonds remained unaffected under the same experimental conditions. Cleavage of the silicon–aryl bonds was performed with triflic acid to afford dendrons **Cl**:**G**1:$\mathbf{Et}_n$ after addition of lithium chloride. In this case, the use of ethereal solutions of the more convenient HCl reagent resulted in only partial conversions under the conditions tested. The better leaving group (2,4,6-trimethoxyphenyl) was preferred for the preparation of **Cl**:**G**1:(**CH_2Cl**)$_3$. The absence of direct silicon–chloro bonds in the (chloromethyl)dimethylsilane avoids problems of contamination with HCl and therefore of undesired cleavage of the silicon–aryl bonds. Cleavage is in this case conveniently performed with hydrogen chloride, which directly converts the Si-aryl of **Ar**:**G**1:(**CH_2Cl**)$_3$ into a Si–Cl bond in **Cl**:**G**1:(**CH_2Cl**)$_3$ under milder conditions [24].

In the next step of the preparative route, the phosphane functionalities were introduced at the focal point of dendrons **Cl**:**G**1:$\mathbf{X}_3$ by treatment of their silicon–chloride bonds with the lithium derivative of **PP**:**Br** to afford compounds **PP**:**G**1:$\mathbf{X}_3$ under similar conditions to those described in Scheme 1 for simple silanes. The chloromethyl-terminated phosphane **PP**:**G**1:(**CH_2Cl**)$_3$ was then transformed into the ammonium-terminated dendron **PP**:**G**1:(**NMe_2**)$_3$ by treatment with 2-(dimethylamino)ethanethiol in the presence of a base in methanol/water. These phosphanes were obtained in good yields as colorless oils that readily oxidize in the presence of traces of air.

The extension of this preparative approach to the synthesis of larger dendrons is theoretically feasible, as we have demonstrated previously [15,17]. Thus, the initial alkenylation shown in Scheme 2 has to be followed by successive hydrosilylations with trichloro- or di-chloromethylsilane and alkenylations with allylmagnesium bromide to reach the desired generation before introducing the $SiMe_2Cl$ or $SiMe_2(CH_2Cl)$ end-groups. Preparation of the second-generation analogs of the alkyl-terminated dendrons was first attempted with a triply-branched structure. However, the synthesis of **PP**:**G**2:(**Et**)$_6$ failed in the last step when the aryl protector had to be replaced by the diphosphine ligand at the focal-point of the molecule. In contrast, the doubly-branched analog **PP**:**G**2:(**Et**)$_4$ (Scheme 2) was successfully obtained by the same procedure, thus highlighting the importance of steric effects during the focal-point functionalization of dendrons.

All carbosilane derivatives were isolated and characterized by C, H, N, S elemental analysis and ^{1}H, ^{13}C, ^{29}Si, and, if applicable, ^{31}P NMR spectroscopy, as detailed in the Experimental section. ^{1}H NMR spectroscopy was particularly useful for monitoring the growth and deprotection of the carbosilane dendrons. Monitoring of the reactions during the hydrosilylation step is highly recommended [14j,17]. ^{29}Si NMR chemical shifts were especially useful for identifying the different silicon environments that appear in the



Scheme 2. Synthesis of dendritic phosphanes.

expected positions [25]: the $ArSiR_3$-type of silicon atoms (R = alkyl) at the focal point of both **Ar**:**G**1:**X**$_3$ and **PP**:**G**1:**X**$_3$ dendrons appear at −4.5 ± 1 ppm, the SiR_4-type ($SiMe_2Et$ and $SiMe_2(CH_2Cl)$ end groups) are found at around 3 ppm, whereas the SiR_3Cl silicon atoms (focal-point or terminal) are located at 31 ± 1 ppm. The ^{31}P nuclei of phosphanes **PP**:**G**1:**X**$_3$ are found in the same range of chemical shifts as those described above for the parent **PP**:**X** phosphanes (−27 ± 1 ppm).

The corresponding [$PdCl_2$(**PP**:**G**1:**X**$_3$)] complexes were prepared by treatment of [$PdCl_2$(cod)] with the appropriate phosphane in THF (see Scheme 3). They were isolated as orange solids after elimination of volatiles and characterized by elemental analysis and NMR spectroscopy, as detailed in the Experimental section.

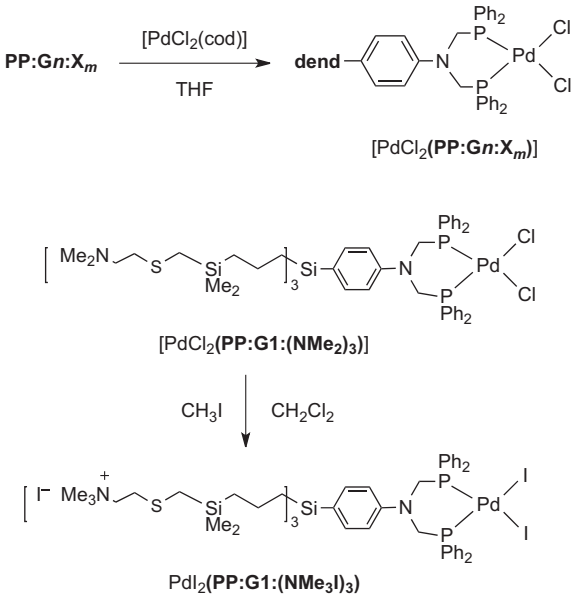
The palladium dichloride complex of the dimethylamino-terminated dendron **PP**:**G**1:(**NMe**)$_2$ was found to be completely insoluble in water but soluble in organic solvents such as toluene, THF and CH_2Cl_2. The terminal dimethylamino groups were quaternized by treatment with an excess of iodomethane, although this quaternization was accompanied by chlorido/iodido ligand exchange at the metal centers [12]. This exchange was reflected in the ^{31}P NMR resonance, which shifted from a typical value of 10 ppm found in the dichloride complexes to −10.4 ppm, a similar value to that reported for [PdI_2\{$(Ph_2PCH_2)_2NPh$\}] [22]. This cationic palladium complex was obtained as a dark-orange solid and fully characterized by elemental analysis and NMR spectroscopy. It was found to be fairly insoluble in most common organic solvents, except dimethyl sulfoxide, and was also found to be insoluble in water at room temperature.

2.3. Catalytic tests on the Heck reaction

The palladium complexes reported here, together with the reference derivative [$PdCl_2$\{$(Ph_2PCH_2)_2NPh$\}], were tested in the palladium-catalyzed Mizoroki–Heck reaction between 4-iodotoluene and methyl acrylate (Table 1). The reaction was carried out in acetonitrile at 80 °C, with palladium loadings of 1 mol % and triethylamine as the base. Methyl 4-methylcinnamate was the only product detected by GC analysis with all the catalysts tested. These palladium precursors are not very active under these reaction conditions, affording conversions ranging from 15% to 62% after 24 h of reaction. They also showed extensive decomposition by precipitation of black palladium with the exception of dimethylamino-substituted complex **PP**:**G**1:(**NMe**$_2$)$_3$ which is also the less active catalyst.

3. Conclusions

We have described the synthesis of carbosilane dendrons with bidentate phosphanes at the focal point and alkyl or dimethylamino groups at the periphery following a synthetic procedure



Scheme 3. Synthesis of palladium complexes.

involving bifunctionalization of dendrons using activated phenyl groups bonded to the core silicon atom as protecting groups. The versatility of this synthetic strategy allows the deprotection step to be performed at the right time during the synthesis depending on the nature of the functionalities selected for the focal point and the periphery. Palladium complexes of phosphine-functionalized carbosilane dendrons were also prepared and terminal dimethylamino groups quaternized. These complexes were tested as catalysts in the Heck reaction but they showed poor activities and stabilities, giving extensive precipitation of palladium black.

4. Experimental

4.1. Reagents and general techniques

All operations were performed under argon using Schlenk or dry-box techniques. Unless otherwise stated, reagents were obtained from commercial sources and used as received. Diallyl(methyl) phenylsilane [26], trichloro(2,4,6-trimethoxyphenyl)silane [24], trichloro(4-methoxyphenyl)silane, triallyl(4-methoxyphenyl)silane [27], 4-bromo-*N*,*N*-bis(diphenylphosphanomethyl)aniline (**PP**:**Br**), 4-(bis(diphenylphosphanomethyl)amino)phenol (**PP**:**OH**) [18], $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene) [28], and $[PdCl_2\{(P(Ph)_2CH_2)_2NPh\}]$ [22] were prepared according to reported procedures. Solvents were dried prior to use and distilled under argon, as described elsewhere [29]. ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded with Varian Gemini-200, Mercury VX-300, or UnityPlus-500 spectrometers. Chemical shifts (δ, ppm) are quoted relative to $SiMe_4$ (^1H, ^{13}C, and ^{29}Si) or 85% H_3PO_4 (^{31}P), and were measured by internal referencing to the deuterated solvent (^{13}C and residual ^1H resonances), or by the substitution method (^{31}P and ^{29}Si). Coupling constants (J) are given in Hz. Elemental analyses were performed in duplicate by the Analytical Laboratories of the University of Alcalá with a LECO CHNS-932 microanalyzer. Chromatographic analysis were performed using an HP-5890 Series II gas chromatograph fitted with an Agilent DB-1-capillary column (15 m length, 0.25 mm internal diameter, 0.10 μm film thickness) under the following conditions: injector temperature, 250 °C; detector temperature, 260 °C; oven temperature program, isothermal 120 °C/5 min.

4.2. Synthesis of non-dendritic phosphanes and their complexes

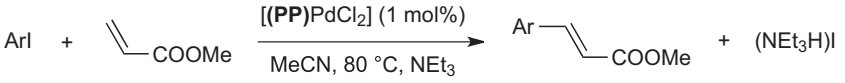
4.2.1. $(Ph_2PCH_2)_2N(C_6H_4O\text{-}4\text{-}SiMe_3)$ (**PP**:**OSiMe**$_3$)

Triethylamine (0.073 mL, 0.53 mmol) and chlorotrimethylsilane (0.067 mL, 0.53 mmol) were added to a solution of **PP**:**OH** (0.240 g, 0.48 mmol) in THF (15 mL). The mixture was stirred for 3 h and the volatiles then evaporated under vacuum. Diethyl ether was added to the residue and the ammonium salt filtered off. The solution was evaporated under vacuum to afford an oily off-white solid identified as diphosphine **PP**:**OSiMe**$_3$ (0.22 g, 78%). Anal. Calc. for $C_{35}H_{37}NOP_2Si$: C, 72.77; H, 6.46; N, 2.42. Found: C, 72.14; H, 6.12; N, 2.31%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.29 (m, 20H, PC_6H_5), 6.69 (d, $^3J_{H,H}$ = 8.9, 2H, C_6H_4), 6.62 (d, $^3J_{H,H}$ = 8.9, 2H, C_6H_4), 4.01 (d, $^2J_{P,H}$ = 4.03, 4H, CH_2P), 0.22 ppm (s, 9H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 147.8 (C_6H_4O, C_{ipso}), 143.6 (C_6H_4N, C_{ipso}), 137.6 (d, $J_{C,P}$ = 14.9, PC_6H_5, C_{ipso}), 133.1 (d, $J_{C,P}$ = 20.4, PC6H5, C_{ortho}) 128.5 (d, $J_{C,P}$ = 17.3, PC6H5, C_{meta}), 128.3 (d, $J_{C,P}$ = 6.1, PC6H5, C_{para}) 120.2 (C_6H_4O, C_{ortho}), 117.8 (C_6H_4N, C_{ortho}), 55.5 (dd, $^1J_{C,P}$ = 13.6 and $^3J_{C,P}$ = 8.1, CH_2P), 0.2 ppm (s, $SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = −25.9 ppm.

4.2.2. $(Ph_2PCH_2)_2N(C_6H_4\text{-}4\text{-}SiMe_3)$ (**PP**:**SiMe**$_3$)

A 1.6 M solution of *n*-butyllithium in hexane (0.60 mL, 0.92 mmol) was slowly added to a solution of **PP**:**Br** (0.350 g, 0.62 mmol) at −78 °C in THF (20 mL). Stirring was continued at the

Table 1
Heck coupling of 4-iodotoluene and methyl acrylate in acetonitrile.[a]



ArI = 4-iodotoluene

PP ligand	Conv. after 24 h [%][b]
$PhN(CH_2PPh_2)_2$	44
PP:**SiMe**$_3$	60
PP:**G1**:(**Et**)$_2$	50
PP:**G1**:(**Et**)$_3$	54
PP:**G2**:(**Et**)$_4$	62
PP:**NMe**$_2$	41
PP:**G1**:(**NMe**$_2$)$_3$	15
PP:**G1**:(**NMe**$_3$**I**)$_3$	56

[a] Conditions: 0.5 mmol of 4-iodotoluene, 0.5 mmol of methyl acrylate, 0.5 mmol of triethylamine, 5 μmol (1 mol%) of Pd catalyst were reacted in 5 mL of acetonitrile at 80 °C for 24 h. See Experimental section for details.
[b] Conversions determined by Gas Chromatography using naphthalene as an internal standard.

same temperature for 15 min, then chlorotrimethylsilane (0.08 mL, 0.62 mmol) was added and the reaction mixture allowed to warm to room temperature. The solvent was then removed under vacuum and the residue extracted with hexane (3 × 10 mL). Evaporation of the combined hexane solutions to dryness yielded **PP**:**SiMe**$_3$ as an oily off-white solid (0.26 g, 75%). Anal. Calc. for $C_{35}H_{37}NP_2Si$: C, 74.84; H, 6.64; N, 2.49. Found: C, 75.08; H, 6.77; N, 2.34%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.33 (m, 22H, PC_6H_5 overlapped with 2H signal of C_6H_4), 6.84 (d, $^3J_{H,H}$ = 8.8, 2H, C_6H_4), 3.93 (d, $^2J_{H,P}$ = 4.4, 4H, NCH_2P), 0.25 ppm (s, 9H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 148.1 (C_6H_4N, C_{ipso}), 137.3 (d, $J_{C,P}$ = 15.3, PC_6H_5, C_{ipso}), 134.2 (C_6H_4Si, C_{ortho}), 133.2, (d, $J_{C,P}$ = 18.4, PC_6H_5, C_{ortho}), 128.6 (d, $J_{C,P}$ = 17.2, PC_6H_5, C_{meta}), 128.4 (d, $J_{C,P}$ = 6.5, PC_6H_5, C_{para}), 126.6 (C_6H_4Si, C_{ipso}), 113.5 (C_6H_4N, C_{ortho}), 53.7 (dd, $^1J_{C,P}$ = 14.9 and $^3J_{C,P}$ = 6.5, NCH_2P), −0.8 ppm (s, $SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = −27.8 ppm.

4.2.3. *(Ph$_2$PCH$_2$)$_2$N(C$_6$H$_4$-4-SiMe$_2$CH$_2$SCH$_2$CH$_2$NMe$_2$) (**PP**:**NMe$_2$**)*

A 1.6 M solution of *n*-butyllithium in hexane (1.10 mL, 1.76 mmol) was slowly added to a solution of **PP**:**Br** (1.00 g, 1.76 mmol) at −78 °C in THF (20 mL). The reaction mixture was stirred for 15 min and then an excess of chloromethyl(dimethyl) chlorosilane (0.30 mL, 2.21 mmol) in THF (5 mL) was added at −78 °C. The reaction mixture was allowed to warm slowly to room temperature and then the solvent was removed under vacuum. The residue was extracted with hexane (2 × 10 mL) and the combined hexane solutions evaporated to dryness under vacuum to give the intermediate $C_6H_4\{1\text{-}N(CH_2PPh_2)_2\}(4\text{-}SiMe_2CH_2Cl)$ as a spectroscopically pure colorless oil which was used without further purification. Spectroscopic data for $C_6H_4\{1\text{-}N(CH_2PPh_2)_2\}(4\text{-}SiMe_2CH_2Cl)$: ^{1}H NMR ($C_6D_6$, 300 MHz): δ = 7.30 (m, 12H, PC_6H_5), 7.03 (m, 8H, PC_6H_5), 7.27 (d, $^3J_{H,H}$ = 8.8, 2H, C_6H_4), 6.90 (d, $^3J_{H,H}$ = 8.8, 2H, C_6H_4), 4.05 (d, $^2J_{H,P}$ = 4.5, 4H, NCH_2P), 2.72 (s, 2H, $SiCH_2Cl$), 0.30 ppm (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ = 149.5 (C_6H_4N, C_{ipso}), 138.0 (d, $J_{C,P}$ = 16.2, PC_6H_5, C_{ipso}),135.1 (C_6H_4Si, C_{ortho}), 133.6 (d, $J_{C,P}$ = 19.9, PC_6H_5, C_{ortho}), 128.9 (d, $J_{C,P}$ = 14.0, PC_6H_5, C_{meta}), 128.7 (d, $J_{C,P}$ = 5.9, PC_6H_5, C_{para}), 114.4 (C_6H_4N, C_{ortho}), 54.0 (d, $J_{C,P}$ = 8.8, NCH_2P), 30.9 ($SiCH_2Cl$), −4.4 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz): δ = −27.1 ppm. $^1H-^{29}Si$ gHMBC (C_6D_6): δ = −4.4 ppm.

Subsequently, a deoxygenated aqueous solution (5 mL) of NaOH (0.260 g, 98% purity, 6.37 mmol) and 2-(dimethylamino)ethanethiol hydrochloride (0.270 g, 1.92 mmol) was added to a solution of the above intermediate (1.09 g, 1.84 mmol) in deoxygenated ethanol (20 mL). This mixture was stirred at 80 °C overnight. The reaction mixture was then cooled to room temperature and extracted with diethyl ether (3 × 10 mL). The combined diethyl ether solutions were dried over $MgSO_4$ and evaporated to dryness to give **PP**:**NMe$_2$** as a slightly yellow oil (0.84 g, 69%). Anal. Calc. for $C_{39}H_{46}N_2P_2SSi$: C, 70.45; H, 6.97; N, 4.21; S, 4.82. Found: C, 70.15; H, 7.02; N, 3.96, S, 4.78%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30 (m, 22H, PC_6H_5 overlapped with 2H signal of C_6H_4), 6.79 (d, $^3J_{H,H}$ = 8.5, 2H, C_6H_4), 3.87 (d, $^2J_{H,P}$ = 4.6, 4H, NCH_2P), 2.56 (m, 4H, $SCH_2CH_2NMe_2$), 2.23 (s, 6H, $N(CH_3)_2$), 1.97 (s, 2H, $SiCH_2S$), 0.32 ppm (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 148.5 (C_6H_4N, C_{ipso}), 137.3 (d, $J_{C,P}$ = 15.0, PC_6H_5, C_{ipso}), 134.6 (C_6H_4Si, C_{ortho}), 133.2 (d, $J_{C,P}$ = 18.6, PC_6H_5, C_{ortho}), 128.7 (d, $J_{C,P}$ = 19.4, PC_6H_5, C_{meta}), 128.5 (d, $J_{C,P}$ = 6.2, PC_6H_5, C_{para}), 113.4 (C_6H_4N, C_{ortho}), 58.3 (SCH_2CH_2N), 53.6 (d, $J_{C,P}$ = 8.5, NCH_2P), 44.6 ($N(CH_3)_2$), 33.7 (SCH_2CH_2N), 18.5 ($SiCH_2S$), −3.1 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = −27.8 ppm.

4.2.4. *[PdCl$_2${(Ph$_2$PCH$_2$)$_2$N(C$_6$H$_4$-4-OH)}] ([PdCl$_2$(**PP**:**OH**)])*

A solution of $[PdCl_2(cod)]$ (0.090 g, 0.31 mmol) in CH_2Cl_2 and **PP**:**OH** (0.160 g, 0.31 mmol) in CH_2Cl_2 (10 mL) was stirred for 3 h at room temperature. The orange solution was then evaporated under vacuum and the residue washed with hexane (2 × 10 mL) to give [PdCl$_2$(**PP**:**OH**)] as an orange solid (0.17 g, 82%). Anal. Calc. for $C_{32}H_{29}Cl_2NOP_2Pd$ (682.8): C, 56.28; H, 4.28; N, 2.05. Found: C, 56.24; H, 4.61; N, 1.74%. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 7.85 (m, 8H, PC_6H_5), 7.51 (m, 12H, PC_6H_5), 6.49 (br., 4H, C_6H_4), 4.23 ppm (br., 4H, CH_2P). $^{13}C\{^1H\}$ NMR ([D_6]DMSO, 75 MHz): δ = 153.0 (C_6H_4O, C_{ipso}), 143.9 (C_6H_4N, C_{ipso}), 133.5 (d, $J_{C,P}$ = 10.0, PC_6H_5, C_{ortho}), 130.8 (s, PC_6H_5, C_{para}), 127.8 (d, $J_{C,P}$ = 10.5, PC_6H_5, C_{meta}), 121.5 (C_6H_4N, C_{ortho}), 115.1 (C_6H_4O, C_{ortho}), 54.3 ppm (d, $J_{C,P}$ = 40.9, NCH_2P). $^{31}P\{^1H\}$ NMR ([D_6]DMSO, 202 MHz): δ = 10.0 ppm.

4.2.5. *[PdCl$_2${(Ph$_2$PCH$_2$)$_2$N(C$_6$H$_4$-4-Br)}] ([PdCl$_2$(**PP**:**Br**)])*

This complex was obtained as a slightly yellow solid (0.32 g, 75%) as described above in Section 4.2.4, starting from **PP**:**Br** (0.330 g, 0.58 mmol) and $[PdCl_2(cod)]$ (0.16 g, 0.58 mmol). Anal. Calc. for $C_{32}H_{28}BrCl_2NP_2Pd$: C, 51.54; H, 3.78; N, 1.88. Found: C, 50.99; H, 3.73; N, 1.92%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32 (m, 8H, PC_6H_5), 7.44 (m, 12H, PC_6H_5), 7.26 (d, $^3J_{H,H}$ = 8.9, 2H, C_6H_4), 6.45 (d, $^3J_{H,H}$ = 8.9, 2H, C_6H_4), 3.92 (br., 4H, NCH_2P). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 150.2 (C_6H_4O, C_{ipso}), 133.9 (d, $J_{C,P}$ = 10.5, PC_6H_5, C_{ortho}), 132.7 (C_6H_4Br, C_{ortho}), 131.9 (s, PC_6H_5, C_{para}), 128.9 (d, $J_{C,P}$ = 11.8, PC_6H_5, C_{meta}), 128.6 (C_6H_4Br, C_{ipso}), 127.8 (d, $J_{C,P}$ = 57.6, PC_6H_5, C_{ipso}) 120.2 (C_6H_4N, C_{ortho}), 53.4 (dd, $^1J_{C,P}$ = 47.1, $^3J_{C,P}$ = 3.6, NCH_2P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 10.0 ppm.

4.2.6. *[PdCl$_2${(Ph$_2$PCH$_2$)$_2$N(C$_6$H$_4$-4-OSiMe$_3$)}] ([PdCl$_2$(**PP**:**OSiMe$_3$**)])*

This complex was obtained as an orange solid (0.09 g, 87%) (0.32 g, 75%) as described in Section 4.2.4, starting from **PP**:**OSiMe**$_3$ (0.080 g, 0.14 mmol) and $[PdCl_2(cod)]$ (0.040 g, 0.14 mmol). Anal. Calc. for $C_{35}H_{37}Cl_2NOP_2PdSi$: C, 55.68; H, 4.94; N, 1.86. Found: C, 55.95; H, 4.71; N, 1.99%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.85 (m, 8H, $P(C_6H_5)_2$), 7.41 (m, 12H, $P(C_6H_5)_2$), 6.68 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 6.60 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 3.82 (br., 4H, NCH_2P), 0.20 ppm (s, 9H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 152.4 (C_6H_4O, C_{ipso}), 146.7 (C_6H_4N, C_{ipso}), 134.0 (d, $J_{C,P}$ = 10.5, PC_6H_5, C_{ortho}), 131.6 (s, PC_6H_5, C_{para}), 128.7(d, $J_{C,P}$ = 11.4, PC_6H_5, C_{meta}), 128.3 (d, $J_{C,P}$ = 57.0, PC_6H_5, C_{ipso}), 122.5 and 121.1 (C_6H_4N, C_{ortho} and C_{meta}), 56.5 (d, $J_{C,P}$ = 46.4, NCH_2P), 0.1 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 10.7 ppm.

4.2.7. *[PdCl$_2${(Ph$_2$PCH$_2$)$_2$N(C$_6$H$_4$-4-SiMe$_3$)}] ([PdCl$_2$(**PP**:**SiMe$_3$**)])*

This complex was obtained as a yellow solid (0.13 g, 74%) as described in Section 4.2.4, starting from **PP**:**SiMe**$_3$ (0.130 g, 0.24 mmol) and $[PdCl_2(cod)]$ (0.070 g, 0.24 mmol). Anal. Calc. for $C_{35}H_{37}Cl_2NP_2PdSi$: C, 56.88; H, 5.05; N, 1.90. Found: C, 56.40; H, 4.96, N, 1.85%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.85 (m, 8H, PC_6H_5), 7.46 (m, 12H, PC_6H_5), 7.32 (d, $^3J_{H,H}$ = 8.5, 2H, C_6H_4), 6.63 (d, $^3J_{H,H}$ = 8.5, 2H, C_6H_4), 3.94 (br., 4H, NCH_2P), 0.19 ppm (s, 9H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.9 (C_6H_4N, C_{ipso}), 134.9 (C_6H_4Si, C_{ortho}), 133.9 (d, $J_{C,P}$ = 9.9, PC_6H_5, C_{ortho}), 131.8 (s, PC_6H_5, C_{para}), 129.8 (C_6H_4Si C_{ipso}), 128.8 (d, $J_{C,P}$ = 11.2, PC_6H_5, C_{meta}), 128.1 (d, $J_{C,P}$ = 57.7, PC_6H_5, C_{ipso}), 118.2 (s, C_6H_4N, C_{ortho}), 53.8 (d, $J_{C,P}$ = 43.4, NCH_2P), −1.2 ppm (s, $SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 9.9 ppm.

4.2.8. *[PdCl$_2${(Ph$_2$PCH$_2$)$_2$N(C$_6$H$_4$-4-SiMe$_2$CH$_2$SCH$_2$CH$_2$NMe$_2$)}] ([PdCl$_2$(**PP**:**NMe$_2$**)])*

This complex was obtained as a yellow solid (1.27 g, 86%). as described in Section 4.2.4, starting from **PP**:**NMe**$_2$ (1.16 g, 1.75 mmol) and $[PdCl_2(cod)]$ (0.500 g, 1.75 mmol). However, in this case the reagents were mixed at −78 °C instead of room temperature and the residue was washed with pentane instead of hexane. Anal. Calc. for $C_{39}H_{46}Cl_2N_2P_2PdSSi$: C, 55.62; H, 5.51; N, 3.33; S, 3.81.

Found: C, 55.84; H, 5.28; N, 2.99; S, 3.96%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.84 (m, 8H, PC_6H_5), 7.43 (m, 14H, PC_6H_5 overlapped with 2H signal of C_6H_4), 6.60 (d, $^3J_{H,H}$ = 8.5, 2H, C_6H_4), 3.95 (br., 4H, NCH_2P), 2.50 (m, 4H, $SCH_2CH_2NMe_2$), 2.20 (s, 6H, $N(CH_3)_2$), 1.93 (s, 2H, $SiCH_2S$), 0.29 ppm (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 152.1 (s, C_6H_4N, C_{ipso}), 135.2 (s, C_6H_4Si, C_{ortho}), 133.9 (d, $J_{C,P}$ = 10.7, PC_6H_5, C_{ortho}), 131.8 (s, PC_6H_5, C_{para}), 128.8 (d, $J_{C,P}$ = 11.5, PC_6H_5, C_{meta}), 127.9 (d, $J_{C,P}$ = 57.6, PC_6H_5, C_{ipso}) 117.9 (C_6H_4N, C_{ortho}), 58.8 (s, SCH_2CH_2N), 53.3 (d, $J_{C,P}$ = 47.6, NCH_2P), 45.3 (s, $N(CH_3)_2$), 34.2 (s, SCH_2CH_2N), 18.0 (s, $SiCH_2S$), −3.1 ppm (s, $(SiCH_3)$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 10.0 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = −4.2 ppm.

4.3. Synthesis of dendritic phosphanes and their complexes

4.3.1. Triallyl(2,4,6-trimethoxyphenyl)silane

A solution of trichloro(2,4,6-trimethoxyphenyl)silane (17.85 g, 59.2 mmol) in THF (100 mL) was slowly added via a dropping funnel to a 1 M diethyl ether solution of allylmagnesium bromide (180 mL, 180 mmol) in 50 mL of diethyl ether at 0 °C. The mixture was subsequently heated at reflux for 4 h, then cooled to room temperature and hydrolyzed with a saturated aqueous solution of ammonium chloride. The ethereal phase was decanted and the aqueous phase washed with diethyl ether (3 × 20 mL). The combined ethereal solutions were dried over $MgSO_4$ and filtered. The solvent was then removed under vacuum to yield the title compound as a slightly brown oil (16.21 g, 86%). Anal. Calc. for $C_{18}H_{26}O_3Si$: C, 67.88; H, 8.23. Found: C, 67.36; H, 7.88%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.04 (s, 2H, C_6H_2), 5.78 (m, 3H, $Si(CH_2-CH=CH_2)_3$), 4.79 (m, 6H, $Si(CH_2-CH=CH_2)_3$), 3.79 (s, 3H, OCH_3), 3.71 (s, 6H, OCH_3), 1.86 (m, 6H, $Si(CH_2-CH=CH_2)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 166.5 and 163.4 ($C_6H_2O_3$, C_{ipso}), 135.8 ($CH_2CH=CH_2$), 112.9 ($CH_2CH=CH_2$), 101.1 (C_6H_2Si, C_{ipso}), 90.1 (C_6H_2), 55.0 and 54.9 (CH_3O), 21.4 ($CH_2CH=CH_2$). $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = −7.8 ppm.

4.3.2. $(C_6H_5)SiMe(CH_2CH_2CH_2SiMe_2Et)_2$ (**Ar**:**G**1:(**Et**)$_2$)

A 5.6 × 10^{-3} M solution of tetrabutylammonium hexachloroplatinate(IV) in dichloromethane (1.0 mL, 5.6 mmol) and an excess of chloro(dimethyl)silane (1.8 mL, 16.9 mmol) were added via a syringe to diallyl(methyl)phenylsilane (1.140 g, 5.65 mmol) in a 25 mL ampoule fitted with a PTFE stopcock. The solution was stirred at room temperature until the reaction was complete (ca. 6 h, ^{1}H NMR monitoring), then the excess of silane and other volatiles were removed under vacuum. The crude product was dissolved in THF (20 mL) and added dropwise (15 min) to an ice-cooled 2.0 M THF solution of ethylmagnesium chloride (8.5 mL, 17.0 mmol) diluted in THF (20 mL). After the addition had finished, the reaction mixture was allowed to reach room temperature and stirring was continued overnight. The excess ethylmagnesium chloride was hydrolyzed with a concentrated aqueous solution of ammonium chloride (50 mL). The organic phase was separated by decantation, and the aqueous solution washed with diethyl ether (3 × 15 mL). The combined organic extracts were dried with anhydrous $MgSO_4$, filtered off, and evaporated in vacuo to yield **Ar**:**G**1:(**Et**)$_2$ as a colorless oil (1.65 g, 77%). Anal. Calc. for $C_{21}H_{42}Si_3$: C, 66.58; H, 11.18. Found: C, 66.11; H, 10.96%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.45 (m, 2H, C_6H_5), 7.33 (m, 3H, C_6H_5), 1.35 (m, 4H, $SiCH_2CH_2CH_2Si$), 0.85 (t, $^3J_{H,H}$ = 7.9, 6H, CH_2CH_3), 0.81 (m, 4H, $PhSiCH_2CH_2CH_2Si$), 0.55 (m, 4H, $SiCH_2CH_2CH_2SiEt$), 0.44 (q, $^3J_{H,H}$ = 7.9, 4H, CH_2CH_3), 0.23 (s, 3H, $PhSiCH_3$), −0.09 ppm (s, 12 H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 139.0 (C_6H_5Si, C_{ipso}), 133.8 (C_6H_5Si, C_{ortho}), 128.6 (C_6H_5Si, C_{para}), 127.6 (C_6H_5Si, C_{meta}), 19.6, 18.9 and 18.4 ($SiCH_2CH_2CH_2Si$), 7.4 and 7.0 (CH_2CH_3), −3.8 ($Si(CH_3)_2$), −4.9 ppm ($C_6H_5SiCH_3$). $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 3.2 ($Si(CH_3)_2$), −3.6 ppm (SiC_6H_5).

4.3.3. $(C_6H_4\text{-}4\text{-}OMe)(CH_2CH_2CH_2SiMe_2Et)_3$ (**Ar**:**G**1:(**Et**)$_3$)

This compound was synthesized as described above for **Ar**:**G**1:(**Et**)$_2$, starting from triallyl(4-methoxyphenyl)silane (1.50 g, 5.8 mmol) and chloro(dimethyl)silane (2.50 mL, 22.7 mmol) for the hydrosilylation step, and subsequent treatment with ethylmagnesium chloride (11.40 mL, 22.8 mmol). **Ar**:**G**1:(**Et**)$_3$ was isolated as a colorless oil (2.61 g, 86%). Anal. Calc. for $C_{28}H_{58}OSi_4$: C, 64.29; H, 11.18. Found: C, 64.12; H, 11.18. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.37 (d, $^3J_{H,H}$ = 7.7, 2H, C_6H_4), 6.88 (d, $^3J_{H,H}$ = 7.7, 2H, C_6H_4), 3.80 (s, 3H, CH_3O), 1.35 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.89 (t, $^3J_{H,H}$ = 8.0, 9H, $SiCH_2CH_3$), 0.81 (m, 6H, $SiCH_2CH_2CH_2SiEt$), 0.56 (m, 6H, $SiCH_2CH_2CH_2SiEt$), 0.43 (q, $^3J_{H,H}$ = 8.0, 6H, $SiCH_2CH_3$), −0.09 ppm (s, 18H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 160.0 (C_6H_4O, C_{ipso}), 128.9 (C_6H_4Si, C_{ipso}), 135.4 (C_6H_4Si, C_{ortho}), 113.4 (C_6H_4O, C_{ortho}), 54.9 (CH_3O), 19.8, 18.4 and 17.6 ($SiCH_2CH_2CH_2Si$), 7.3 and 7.0 ($SiCH_2CH_3$), −3.8 ppm ($Si(CH_3)_2$). $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 2.8 ($SiCH_2CH_3$), −4.5 ppm (SiC_6H_4).

4.3.4. $(C_6H_4\text{-}2,4,6\text{-}(OMe)_3)Si(CH_2CH_2CH_2SiMe_2(CH_2Cl))_3$ (**Ar**:**G**1:(**CH$_2$Cl**)$_3$)

Triallyl(2,4,6-trimethoxyphenyl)silane (0.440 g, 1.40 mmol) was combined with chloromethyl(dimethyl)silane (0.52 mL, 4.26 mmol) in a 25 mL ampoule fitted with a PTFE stopcock. Three drops of the Karstedt catalyst (3–3.5% based on Pt of a platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution) were added. After stirring overnight, all volatiles were removed under reduced pressure to leave a slightly yellow oil that was identified as **Ar**:**G**1:(**CH$_2$Cl**)$_3$ (0.90 g, 98%). Anal. Calc. for $C_{28}H_{55}Cl_3O_3Si_4$: C, 51.08; H, 8.42. Found: C, 51.10; H, 8.21%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.04 (s, 2H, C_6H_2), 3.80 (s, 3H, OCH_3), 3.70 (s, 6H, OCH_3), 2.72 (s, 6H, $SiCH_2Cl$), 1.33 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.85 (m, 6H, $C_6H_2SiCH_2CH_2CH_2Si$), 0.67 (m, 6H, C_6H_2-$SiCH_2CH_2CH_2Si$), 0.05 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 166.5 and 163.1 ($C_6H_2(OCH_3)_3$, C_{ipso}), 92.9 (C_6H_2Si, C_{ipso}), 90.1 (C_6H_2Si, C_{meta}), 55.1 and 55.0 (OCH_3), 30.6 ($SiCH_2Cl$), 19.2, 18.6 and 18.5 ($SiCH_2CH_2CH_2Si$), −4.5 ppm ($Si(CH_3)_2$). $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 3.2 ($SiCH_2Cl$), −4.2 ppm (SiC_6H_2).

4.3.5. $ClSiMe(CH_2CH_2CH_2SiEtMe_2)_2$ (**Cl**:**G**1:(**Et**)$_2$)

Compound **Ar**:**G**1:(**Et**)$_2$ (1.64 g, 4.33 mmol) was dissolved in toluene (5 mL). Trifluoromethanesulfonic acid (0.38 mL, 4.33 mmol) was then added dropwise from a syringe to the above solution previously cooled to 0 °C. Stirring was continued for 15 min at room temperature, and an excess of lithium chloride (0.730 g, 17.3 mmol) was then added. After stirring the reaction mixture for 1 h, the volatiles were removed in vacuo and the residue extracted with hexane (10 mL). The mixture was then filtered and the solvent evaporated to yield **Cl**:**G**1:(**Et**)$_2$ as a colorless oil (1.43 g, 98%). Anal. Calc. for $C_{15}H_{37}ClSi_3$: C, 53.43; H, 11.06. Found: C, 53.64; H, 11.23%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.41 (m, 4H, $SiCH_2CH_2CH_2Si$), 0.87 (t, $^3J_{H,H}$ = 8.0, 6H, CH_2CH_3), 0.82 (m, 4H, $ClSiCH_2CH_2CH_2Si$), 0.56 (m, 4H, $ClSiCH_2CH_2CH_2Si$), 0.46 (q, $^3J_{H,H}$ = 8.0, 4H, CH_2CH_3), 0.34 (s, 3H, $SiCH_3$), −0.07 ppm (s, 12 H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 22.3, 19.1 and 17.6 ($SiCH_2CH_2CH_2Si$), 7.4 and 6.9 (CH_2CH_3), 0.2 ($SiCH_3$), −3.9 ppm ($Si(CH_3)_2$). $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 31.4 ($SiCl$), 3.2 ppm ($Si(CH_3)_2$).

4.3.6. $ClSi(CH_2CH_2CH_2SiEtMe_2)_3$ (**Cl**:**G**1:(**Et**)$_3$)

This compound was synthesized as a pale-brown oil (0.44 g, 99%) following the procedure described above for **Cl**:**G**1:(**Et**)$_2$, starting from **Ar**:**G**1:(**Et**)$_3$ (0.500 g, 0.98 mmol), trifluoromethanesulfonic acid (0.10 mL, 1.17 mmol), and lithium chloride (0.130 g, 3 mmol). Anal. Calc. for $C_{21}H_{51}ClSi_4$: C, 55.87; H,

11.39. Found: C, 55.87; H, 11.86%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.41 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.90 (t, $^3J_{H,H}$ = 8.1, 9H, CH_2CH_3), 0.84 (m, 6H, $SiCH_2CH_2CH_2SiEt$), 0.57 (m, 6H, $SiCH_2CH_2CH_2SiEt$), 0.45 (q, $^3J_{H,H}$ = 8.1, 6H, CH_2CH_3), −0.07 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 21.0, 19.2 and 17.7 ($SiCH_2CH_2CH_2Si$), 7.3 and 6.9 (CH_2CH_3), −3.9 ppm ($SiCH_3$). $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 29.8 ($SiCl$), 2.8 ppm ($SiCH_3$).

4.3.7. $ClSi(CH_2CH_2CH_2SiMe_2(CH_2Cl))_3$ (**Cl**:**G**1:(**CH$_2$Cl**)$_3$)

Compound **Ar**:**G**1:(**CH$_2$Cl**)$_3$ (0.680 g, 1.04 mmol) was dissolved in 20 mL of diethyl ether and an excess of hydrogen chloride in the form of a 1 M diethyl ether solution (1.20 mL, 1.2 mmol) was added via a syringe. The solution was stirred at room temperature for 30 min and then evaporated under vacuum. 1,3,5-Trimethoxybenzene was removed by sublimation at 120 °C and 1 mbar of pressure to leave a brown oil that was subsequently identified as **Cl**:**G**1:(**CH$_2$Cl**)$_3$ (0.52 g, 96%). Anal. Calc. for $C_{19}H_{44}Cl_4Si_4$: C, 43.33; H, 8.42. Found: C, 43.03; H, 8.20%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.76 (s, 6H, $SiCH_2Cl$), 1.46 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.86 (m, 6H, $ClSiCH_2CH_2CH_2Si$), 0.72 (m, 6H, $ClSiCH_2CH_2CH_2Si$), 0.10 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 30.3 ($SiCH_2Cl$), 20.7, 17.9 and 17.5 ($SiCH_2CH_2CH_2Si$), −4.5 ppm ($SiCH_3$). $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 30.3 ($SiCl$), 3.3 ppm ($SiCH_2Cl$).

4.3.8. $(Ph_2PCH_2)_2N(C_6H_4$-4-$SiMe(CH_2CH_2CH_2SiEtMe_2)_2)$ (**PP**:**G**1:(**Et**)$_2$)

A 1.6 M solution of *n*-butyllithium in hexane (0.98 mL, 1.56 mmol) was slowly added to a solution of 4-bromo-*N*,*N*-bis(-diphenylphosphanomethyl)aniline (0.890 g, 1.56 mmol) at −78 °C in THF (15 mL). Stirring was continued at the same temperature for 15 min, then a solution of**Cl**:**G**1:(**Et**)$_2$ (0.08 mL, 0.62 mmol) was added and the reaction mixture allowed to warm to room temperature. The solvent was then removed under vacuum and the residue extracted with hexane (3 × 10 mL). Evaporation of the hexane solution to dryness yielded **PP**:**G**1:(**Et**)$_2$ as a slightly yellow oil (0.99 g, 81%). Anal. Calc. for $C_{47}H_{65}NP_2Si_3$: C, 71.44; H, 8.29; N, 1.77. Found: C, 70.98, H, 8.34; N, 1.79%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30 (m, 20H, PC_6H_5), 7.27 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 6.77 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 3.89 (br., 4H, NCH_2P), 1.33 (m, 4H, $SiCH_2CH_2CH_2Si$), 0.89 (t, $^3J_{H,H}$ = 8.0, 6H, CH_2CH_3), 0.75 (m, 4H, $SiCH_2CH_2CH_2SiEt$), 0.55 (m, 4H, $SiCH_2CH_2CH_2SiEt$), 0.45 (q, $^3J_{H,H}$ = 8.0, 4H, CH_2CH_3), 0.16 (s, 3H, $C_6H_4SiCH_3$), −0.08 (s, 12 H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 148.1 (C_6H_4N, C_{ipso}), 137.5 (d, $J_{C,P}$ = 15.3, PC_6H_5, C_{ipso}), 134.7 (C_6H_4Si, C_{ortho}), 133.2 (d, $J_{C,P}$ = 19.1, PC_6H_5, C_{ortho}), 128.8 (d, $J_{C,P}$ = 16.9, PC_6H_5, C_{meta}), 128.4 (d, $J_{C,P}$ = 6.2, PC_6H_5, C_{para}), 125.2 (C_6H_4Si, C_{ipso}), 113.4 (C_6H_4N, C_{ortho}), 53.6 (dd, $^1J_{C,P}$ = 18.4 and $^3J_{C,P}$ = 8.4, NCH_2P), 19.7, 19.3 and 18.5 ($SiCH_2CH_2CH_2Si$), 7.5 and 7.1 (CH_2CH_3), −3.7 ($Si(CH_3)_2$), −4.6 ppm ($C_6H_4SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = −26.6 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 2.9 ($SiCH_2CH_3$), −4.8 ppm (SiC_6H_4).

4.3.9. $(Ph_2PCH_2)_2N(C_6H_4$-4-$Si(CH_2CH_2CH_2SiMe_2Et)_3)$ (**PP**:**G**1:(**Et**)$_3$)

This compound was obtained as a slightly yellow oil (1.16 g, 92%) following the procedure described above for **PP**:**G**1:(**Et**)$_2$, starting from 4-bromo-*N*,*N*-bis(diphenylphosphanomethyl)aniline (0.790 g, 1.39 mmol), *n*-butyllithium (0.90 mL, 1.39 mmol) and **Cl**:**G**1:(**Et**)$_3$ (0.630 g, 1.39 mmol). Anal. Calc. for $C_{53}H_{79}NP_2Si_4$: C, 70.38; H, 8.80; N, 1.55. Found: C, 70.29; H, 8.83; N, 1.52%. ^{1}H NMR (C_6D_6, 300 MHz): δ = 7.30 (m, 20H, PC_6H_5), 7.23 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 6.75 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 3.90 (d, $^2J_{H,P}$ = 4.4, 4H, NCH_2P), 1.35 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.89 (t, $^3J_{H,H}$ = 7.9, 9H, CH_2CH_3), 0.77 (m, 6H, $SiCH_2CH_2CH_2SiEt$), 0.56 (m, 6H, $SiCH_2CH_2CH_2SiEt$), 0.44 (q, $^3J_{H,H}$ = 7.9, 6H, CH_2CH_3), −0.08 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ = 148.1 (C_6H_4N, C_{ipso}), 137.4 (d, $J_{C,P}$ = 14.2, PC_6H_5, C_{ipso}), 134.9 (C_6H_4Si, C_{ortho}), 133.3 (d, $J_{C,P}$ = 18.6, PC_6H_5, C_{ortho}), 128.6 (d, $J_{C,P}$ = 21.7, PC_6H_5, C_{meta}), 128.4 (s, PC_6H_5, C_{para}), 124.4 (C_6H_4Si, C_{ipso}), 113.4 (C_6H_4N, C_{ortho}), 53.6 (d, $J_{C,P}$ = 8.0, NCH_2P), 19.9, 18.5 and 17.8 ($SiCH_2CH_2CH_2Si$), 7.4 and 7.1 (CH_2CH_3), −3.7 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 202 MHz): δ = −26.2 ppm. $^1H-^{29}Si$ gHMBC (C_6D_6): δ = 2.8 ($SiCH_3$), −4.8 ppm (SiC_6H_4).

4.3.10. $(Ph_2PCH_2)_2N(C_6H_4$-4-$SiMe((CH_2)_3SiMe(CH_2)_3SiEtMe_2)_2)$ **PP**:**G**2:(**Et**)$_4$

This compound was obtained as a slightly yellow oil (0.76 g, 92%) following the procedure described above for **PP**:**G**1:(**Et**)$_2$, starting from 4-bromo-*N*,*N*-bis(diphenylphosphanomethyl)aniline (0.39 g, 0.68 mmol), *n*-butyllithium (0.43 mL, 0.68 mmol) and the second generation dendron **Cl**:**G**2:(**Et**)$_4$ (0.52 g, 0.68 mmol), which was prepared following similar procedure to those reported previously [14,16]. This compound was obtained with small amounts of **Cl**:**G**2:(**Et**)$_6$ and $PhN(CH_2PPh_2)_2$ but was used without prior purification. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.29 (m, 22H, PC_6H_5 overlapped with 2H signal of C6*H*4), 6.77 (d, $^3J_{H,H}$ = 8.3, 2H, C_6H_4), 3.88 (br., 4H, NCH_2P), 1.30 (m, 12H, SiCH2CH_2CH2Si), 0.89 (t, $^3J_{H,H}$ = 7.9, 12H, $SiCH_2CH_3$), 0.75 (m, 4H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.53 (m, 20H, $SiCH_2CH_2CH_2Si$), 0.44 (q, $^3J_{H,H}$ = 7.9, 8H, $SiCH_2CH_3$), 0.16 (s, 3H, $C_6H_4SiCH_3$), 0.08 (s, 24H, $Si(CH_3)_2$), −0.10 ppm (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 148.2 (C_6H_4N, C_{ipso}), 137.3 (d, $J_{C,P}$ = 15.3, PC_6H_5, C_{ipso}), 134.7 (C_6H_4Si, C_{ortho}), 133.2 (d, $J_{C,P}$ = 21.2, PC_6H_5, C_{ortho}), 128.5 (d, $J_{C,P}$ = 23.6, PC_6H_5, C_{meta}), 128.4 (s, PC_6H_5, C_{para}), 113.5 (s, C_6H_4N, C_{ortho}), 53.8 (dd, $^1J_{C,P}$ = 24.8, $^3J_{C,P}$ = 7.4, NCH_2P), 19.7, 18.5 and 17.9 ($SiCH_2CH_2CH_2SiEt$), 19.5, 18.7 and 17.7 ($C_6H_4SiCH_2CH_2CH_2Si$), 7.4 and 7.0 ($SiCH_2CH_3$), −3.8 ($Si(CH_3)_2$), −4.9 ppm ($C_6H_4SiCH_3$ and $SiCH_3$ overlapped). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = −27.5 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 3.2 ($SiEt$), 1.3 ($SiMe$), −4.5 ppm (SiC_6H_4).

4.3.11. $(Ph_2PCH_2)_2N(C_6H_4$-4-$Si(CH_2CH_2CH_2SiMe_2(CH_2Cl))_3)$ (**PP**:**G**1:(**CH$_2$Cl**)$_3$)

This compound was isolated as a pale-yellow oil (1.89 g, 94%) following the procedure described above for **PP**:**G**1:(**Et**)$_2$, starting from 4-bromo-*N*,*N*-bis(diphenylphosphanomethyl)aniline (1.16 g, 2.05 mmol), *n*-butyllithium (0.82 mL, 2.05 mmol) and **Cl**:**G**1:(**CH$_2$Cl**)$_3$ (1.19 g, 2.27 mmol). Anal. Calc. for $C_{51}H_{72}Cl_3NP_2Si_4$: C, 62.52; H, 7.41; N, 1.43. Found: C, 62.49; C, 7.38; N, 1.45%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.30 (m, 20H, PC_6H_5), 7.21 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 6.76 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 3.89 (d, $^2J_{H,P}$ = 3.6, 4H, NCH_2P), 2.75 (s, 6H, $SiCH_2Cl$), 1.34 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.79 (m, 6H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.70 (m, 6H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.08 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 148.1 (C_6H_4N, C_{ipso}), 137.3 (d, $J_{C,P}$ = 15.3, PC_6H_5, C_{ipso}), 134.9 (C_6H_4Si, C_{ortho}), 133.2 (d, $J_{C,P}$ = 18.4, PC_6H_5, C_{ortho}), 128.6 (d, $J_{C,P}$ = 17.7, PC_6H_5, C_{meta}), 128.4 (d, $J_{C,P}$ = 6.1, PC_6H_5, C_{para}), 123.2 (C_6H_4Si, C_{ipso}), 113.4 (s, C_6H_4N, C_{ortho}), 53.5 (d, $J_{C,P}$ = 8.4, NCH_2P), 30.6 (CH_2Cl), 18.6, 18.3 and 17.5 ($SiCH_2CH_2CH_2Si$), −4.4 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = −27.5 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 3.4 ($SiCH_2Cl$), −4.8 ppm (SiC_6H_4).

4.3.12. $(Ph_2PCH_2)_2N(C_6H_4$-4-$Si(CH_2CH_2CH_2SiMe_2(CH_2S(CH_2)_2NMe_2))_3)$ (**PP**:**G**1:(**NMe$_2$**)$_3$)

This compound was isolated as a slightly yellow oil (1.48 g, 86%) following the procedure described above for **PP**:**NMe$_2$**, starting from **PP**:**G**1:(**CH$_2$Cl**)$_3$ (1.40 g, 1.45 mmol), 2-(dimethylamino)ethanethiol hydrochloride (0.640 g, 4.49 mmol) and NaOH (0.890 g, 21.8 mmol). Anal. Calc. for $C_{63}H_{102}N_4P_2S_3Si_4$: C, 63.80; H, 8.67; N, 4.62; S, 8.11. Found: C, 63.85; H, 8.75, N, 4.71; S, 8.09%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.29 (m, 20H, PC_6H_5), 7.22 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 6.75 (d, $^3J_{H,H}$ = 8.6, 2H, C_6H_4), 3.89 (d, $^2J_{H,P}$ = 4.0, 4H, NCH_2P),

2.61 (m, 6H, SCH_2CH_2N), 2.53 (m, 6H, SCH_2CH_2N), 2.26 (s, 18H, $N(CH_3)_2$), 1.78 (s, 6H, $SiCH_2S$), 1.36 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.78 (m, 6H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.66 (m, 6H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.05 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 148.1 (C_6H_4N, C_{ipso}), 137.1 (d, $J_{C,P}$ = 14.7, PC_6H_5, C_{ipso}), 134.7 (C_6H_4Si, C_{ortho}), 133.0 (d, $J_{C,P}$ = 19.1, PC_6H_5, C_{ortho}), 123.5 (C_6H_4Si, C_{ipso}), 128.4 (d, $J_{C,P}$ = 29.5, PC_6H_5, C_{meta}), 128.3 (d, $J_{C,P}$ = 5.9, PC_6H_5, C_{para}), 113.3 (C_6H_4N, C_{ortho}), 58.7 (SCH_2CH_2N), 53.3 (br., NCH_2P), 45.2 (NCH_3), 33.9 (SCH_2CH_2N), 18.2 ($SiCH_2S$), 19.7, 17.6 and 17.4 ($SiCH_2CH_2CH_2Si$), −3.4 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = −26.4 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 1.6 ($SiCH_3$), −5.0 ppm (SiC_6H_4).

4.3.13. [$PdCl_2${$(Ph_2PCH_2)_2N(C_6H_4$-4-$SiMe(CH_2CH_2CH_2SiEtMe_2)_2)$}] ([$PdCl_2$(**PP**:**G1**:(**Et**)$_2$)])

A solution of [$PdCl_2$(cod)] (0.220 g, 0.76 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **PP**:**G1**:(**Et**)$_2$ (0.600 g, 0.76 mmol) in CH_2Cl_2 (15 mL). After stirring for 3 h at room temperature, the orange solution was evaporated under vacuum and the residue extracted with hexane (2 × 10 mL). Volatiles were removed under vacuum to leave **[**$PdCl_2$(**PP**:**G1**:(**Et**)$_2$)] as a yellow solid (0.17 g, 82%). Anal. Calc. for $C_{47}H_{65}Cl_2NP_2PdSi_3$: C, 58.34; H, 6.77; N, 1.45. Found: C, 58.34; H, 6.28; N, 1.63%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.85 (m, 8H, PC_6H_5), 7.44 (m, 12H, PC_6H_5), 7.28 (d, $^3J_{H,H}$ = 8.2, 2H, C_6H_4), 6.62 (d, $^3J_{H,H}$ = 8.2, 2H, C_6H_4), 3.95 (br., 4H, NCH_2P), 1.27 (m, 4H, $SiCH_2CH_2CH_2Si$), 0.85 (t, $^3J_{H,H}$ = 7.9, 6H, CH_2CH_3), 0.73 (m, 4H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.50 (m, 4H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.39 (q, $^3J_{H,H}$ = 7.9, 4H, CH_2CH_3), 0.16 (s, 3H, $C_6H_4SiCH_3$), −0.12 ppm (s, 12 H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.7 (C_6H_4N, C_{ipso}), 135.3 (C_6H_4Si, C_{ortho}), 133.8 (d, $J_{C,P}$ = 9.9, PC_6H_5, C_{ortho}), 131.8 (s, PC_6H_5, C_{para}), 128.8 (d, $J_{C,P}$ = 12.8, PC_6H_5, C_{meta}), 127.9 (d, $J_{C,P}$ = 57.1, PC_6H_5, C_{ipso}), 129.8 (C_6H_4Si, C_{ipso}), 118.9 (s, C_6H_4N, C_{ortho}), 53.7 (d, $J_{C,P}$ = 47.7, NCH_2P), 19.5, 18.9 and 18.3 ($SiCH_2CH_2CH_2Si$), 7.3 and 7.0 (CH_2CH_3), −3.8 ($Si(CH_3)_2$), −4.9 ppm ($C_6H_4SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 10.9 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 3.6 ($SiCH_2CH_3$), −3.5 ppm (SiC_6H_4).

4.3.14. [$PdCl_2${$(Ph_2PCH_2)_2N(C_6H_4$-4-$Si(CH_2CH_2CH_2SiEtMe_2)_3)$}] ([$PdCl_2$(**PP**:**G1**:(**Et**)$_3$)])

This compound was isolated as an orange solid (0.54 g, 72%) following the procedure described above for (**PP**:**G1**:(**Et**)$_2$)$PdCl_2$, starting from **PP**:**G1**:(**Et**)$_3$ (0.630 g, 0.70 mmol) and [$PdCl_2$(cod)] (0.200 g, 0.70 mmol). Anal. Calc. for $C_{53}H_{79}Cl_2NP_2PdSi_4$: C, 58.84; H, 7.36; N, 1.29. Found: C, 58.77; H, 6.83; N, 1.45%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.83 (m, 8H, PC_6H_5), 7.40 (m, 12H, PC_6H_5), 7.26 (d, $^3J_{H,H}$ = 8.2, 2H, C_6H_4), 6.60 (d, $^3J_{H,H}$ = 8.2, 2H, C_6H_4), 3.96 (br., 4H, NCH_2P), 1.28 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.86 (t, $^3J_{H,H}$ = 8.0, 9H, CH_2CH_3), 0.75 (m, 6H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.52 (m, 6H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.41 (q, $^3J_{H,H}$ = 8.0, 6H, CH_2CH_3), −0.12 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.6 (C_6H_4N, C_{ipso}), 135.5 (C_6H_4Si, C_{ortho}), 133.9 (d, $J_{C,P}$ = 10.3, PC_6H_5, C_{ortho}), 131.8 (s, PC_6H_5, C_{para}), 129.8 (C_6H_4Si, C_{ipso}), 128.8 (d, $J_{C,P}$ = 11.1, PC_6H_5, C_{meta}), 127.9 (d, $J_{C,P}$ = 57.6, PC_6H_5, C_{ipso}), 118.0 (C_6H_4N, C_{ortho}), 53.6 (d, $J_{C,P}$ = 47.0, NCH_2P), 19.7, 18.4 and 17.3 ($SiCH_2CH_2CH_2Si$), 7.4 and 7.0 (CH_2CH_3), −3.8 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 10.9 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 2.9 ($SiCH_3$), −4.1 ppm (SiC_6H_4).

4.3.15. [$PdCl_2${$(Ph_2PCH_2)_2N(C_6H_4$-4-$SiMe((CH_2)_3SiMe(CH_2)_3$ $SiEtMe_2)_2)$}] ([$PdCl_2$(**PP**:**G2**:(Et)$_4$)])

Compound [$PdCl_2$(**PP**:**G2**:(**Et**)$_4$)] was isolated as a yellow solid (0.70 g, 74%) following the procedure described above for [$PdCl_2$(**PP**:**G1**:(**Et**)$_2$)], starting from **PP**:**G2**:(**Et**)$_4$ (0.83 g, 0.68 mmol) and [$PdCl_2$(cod)] (0.19 g, 0.68 mmol). Anal. Calc. for $C_{69}H_{117}Cl_2NP_2PdSi_7$: C, 59.34; H, 8.44; N, 1.00. Found: C, 58.88; H, 8.98; N, 1.21%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.84 (m, 8H, PC_6H_5), 7.45 (m, 12H, PC_6H_5), 7.26 (d, $^3J_{H,H}$ = 8.8, 2H, C_6H_4), 6.63 (d, $^3J_{H,H}$ = 8.8, 2H, C_6H_4), 3.94 (br., 4H, NCH_2P), 1.26 (m, 12H, $SiCH_2CH_2CH_2Si$), 0.87 (t, $^3J_{H,H}$ = 8.0, 12H, CH_2CH_3), 0.72 (m, 4H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.49 (m, 20H, $SiCH_2CH_2CH_2SiCH_2CH_2CH_2Si$), 0.42 (q, $^3J_{H,H}$ = 8.0, 8H, CH_2CH_3), 0.16 (s, 3H, $C_6H_4SiCH_3$), −0.11 (s, 24 H, $Si(CH_3)_2$), −0.15 ppm (s, 6H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.8 (C_6H_4N, C_{ipso}), 135.3 (C_6H_4Si, C_{ortho}), 133.9 (d, $J_{C,P}$ = 9.9, PC_6H_5, C_{ortho}), 131.8 (s, PC_6H_5, C_{para}), 128.8 (d, $J_{C,P}$ = 11.2, PC_6H_5, C_{meta}), 127.9 (d, $J_{C,P}$ = 57.6, PC_6H_5, C_{ipso}), 118.1 (C_6H_4N, C_{ortho}), 53.7 (d, $J_{C,P}$ = 47.1, NCH_2P), 19.7, 18.7 and 18.4 ($SiCH_2CH_2CH_2Si$), 19.1, 18.9 and 18.4 ($C_6H_4SiCH_2CH_2CH_2Si$), 7.4 and 7.0 (CH_2CH_3), −3.8 ($Si(CH_3)_2$), −4.9 ppm ($C_6H_4SiCH_3$ and $SiCH_3$ overlapped). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 10.0 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 2.9 ($SiEt$), 1.0 ($SiMe$), −3.8 ppm (SiC_6H_4).

4.3.16. [$PdCl_2${$(Ph_2PCH_2)_2N(C_6H_4$-4-$Si(CH_2CH_2CH_2SiMe_2(CH_2SCH_2$-$CH_2NMe_2))_3)$}] ([$PdCl_2$(**PP**:**G1**:(**NMe**$_2$)$_3$)])

A solution of [$PdCl_2$(cod)] (0.100 g, 0.36 mmol) in CH_2Cl_2 (5 mL) was added to a solution of phosphane **PP**:**G1**:(**NMe**$_2$)$_3$ (0.420 g, 0.36 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred overnight at room temperature and then the solvent was evaporated under vacuum to afford [$PdCl_2$(**PP**:**G1**:(**NMe**$_2$)$_3$)] as a yellow solid (0.47 g, 96%) after washing with hexane (3 × 10 mL). Anal. Calc. for $C_{63}H_{102}Cl_2N_4P_2PdS_3Si_4$: C, 55.50; H, 7.54; N, 4.11; S, 7.06. Found: C, 55.46; H, 7.62; N, 4.07; S, 6.97%. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.85 (m, 8H, PC_6H_5), 7.45 (m, 12H, PC_6H_5), 7.25 (d, $^3J_{H,H}$ = 8.1, 2H, C_6H_4), 6.61 (d, $^3J_{H,H}$ = 8.1, 2H, C_6H_4), 3.99 (br., 4H, NCH_2P), 2.58 (m, 6H, SCH_2CH_2N), 2.49 (m, 6H, SCH_2CH_2N), 2.30 (s, 18H, $N(CH_3)_2$), 1.76 (s, 6H, $SiCH_2S$), 1.30 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.76 (m, 6H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.63 (m, 6H, C_6H_4-$SiCH_2CH_2CH_2Si$), 0.01 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 152.0 (C_6H_4N, C_{ipso}), 135.5 (C_6H_4Si, C_{ortho}), 133.8 (d, $J_{C,P}$ = 10.3, PC_6H_5, C_{ortho}), 131.7 (s, PC_6H_5, C_{para}), 128.7 (d, $J_{C,P}$ = 11.2, PC_6H_5, C_{meta}), 127.9 (d, $J_{C,P}$ = 55.3, PC_6H_5, C_{ipso}), 117.9 (C_6H_4N, C_{ortho}), 129.7 (C_6H_4Si, C_{ipso}), 58.8 (SCH_2CH_2N), 53.6 (dd, $^1J_{C,P}$ = 42.2, $^3J_{C,P}$ = 3.4, NCH_2P), 45.3 ($N(CH_3)_2$), 34.0 (SCH_2CH_2N), 18.3 ($SiCH_2S$), 19.8, 17.8 and 17.2 ($SiCH_2CH_2CH_2Si$), −3.2 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 10.8 ppm. $^1H-^{29}Si$ gHMBC ($CDCl_3$): δ = 1.7 ($SiCH_2S$), −4.1 ppm (SiC_6H_4).

4.3.17. [PdI_2{$(Ph_2PCH_2)_2N(C_6H_4$-4-$Si(CH_2CH_2CH_2SiMe_2(CH_2SCH_2CH_2$-$NMe_3))_3)$}]$I_3$ (PdI_2(**PP**:**G1**:(**NMe$_3$I**)$_3$))

Methyl iodide (0.34 mL, 0.69 mmol) was added to a solution of [$PdCl_2$(**PP**:**G1**:(**NMe**$_2$)$_3$)] (0.150 g, 0.12 mmol) in CH_2Cl_2 (15 mL) with a syringe. The reaction mixture was stirred overnight at room temperature and the solvent then removed under vacuum. The residue thus obtained was washed with diethyl ether (3 × 10 mL) and dried in vacuo to yield PdI_2(**PP**:**G1**:(**NMe$_3$I**)$_3$) as an orange solid (0.17 g, 80%). Anal. Calc. for $C_{66}H_{111}I_5N_4P_2PdS_3Si_4$: C, 40.20; H, 5.67; N, 2.84; S, 4.88. Found: C, 40.04; H, 5.63; N, 2.84; S, 4.95%. ^1H NMR ([D_6]DMSO, 300 MHz): δ = 7.98 (m, 8H, PC_6H_5), 7.51 (m, 12H, PC_6H_5), 6.83 (d, $^3J_{H,H}$ = 8.2, 2H, C_6H_4), 6.33 (d, $^3J_{H,H}$ = 8.2, 2H, C_6H_4), 4.72 (br., 4H, NCH_2P), 3.50 (m, 6H, SCH_2CH_2N), 3.05 (s, 27H, $N(CH_3)_3$), 2.83 (m, 6H, SCH_2CH_2N), 1.87 (s, 6H, $SiCH_2S$), 1.23 (m, 6H, $SiCH_2CH_2CH_2Si$), 0.65 (m, 6H, $C_6H_4SiCH_2CH_2CH_2Si$), 0.58 (m, 6H, C_6H_4Si-$CH_2CH_2CH_2Si$), −0.08 ppm (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ([D_6]DMSO, 75 MHz): δ = 145.2 (C_6H_4N, C_{ipso}), 134.0 (d, $J_{C,P}$ = 9.3, PC_6H_5, C_{ortho}), 133.6 (C_6H_4Si, C_{ortho}), 130.7 (s, PC_6H_5, C_{para}), 127.6 (d, $J_{C,P}$ = 7.3, PC_6H_5, C_{meta}), 114.0 (C_6H_4N, C_{ortho}), 63.5 (SCH_2CH_2N), 51.7 ($N(CH_3)_3$, overlapped with NCH2P), 26.7 (SCH_2CH_2N), 17.3 ($SiCH_2S$), 18.5, 16.2 and 15.8 ($SiCH_2$-CH_2CH_2Si), −3.9 ppm ($SiCH_3$). $^{31}P\{^1H\}$ NMR ([D_6]DMSO, 202 MHz): δ = −10.4 ppm. $^1H-^{29}Si$ gHMBC ([D_6]DMSO): δ = 1.8 ($SiCH_2S$), −4.7 ppm (SiC_6H_4).

Table 2
Selected crystallographic data and structure refinement details for [$PdCl_2$(**PP**:**Br**)].

Empirical formula	$C_{32}H_{18}BrCl_2NP_2Pd\cdot CHCl_3$
Formula weight	2595.22
Color	Yellow
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21
a (Å)	17.281(4)
b (Å)	17.358(4)
c (Å)	18.260(5)
α (°)	90
β (°)	102.73(2)
γ (°)	90
Volume (Å^3)	5343(2)
Z	6
Calculated density (g/cm^3)	1.613
Absorption coefficient (mm^{-1})	2.132
F(000)	2580
Crystal size (mm)	0.5 × 0.4 × 0.3
θ range (°)	3.05 to 27.57
Limiting indices	$-22 \le h \le 21$, $-22 \le k \le 22$, $0 \le l \le 23$
Reflections collected/unique	24,508/24,147 [R(int) = 0.0419]
Completeness to θ_{max}	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.444 and 0.376
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	24147/1/1117
Goodness of fit on F^2	0.952
Final R[a] indices [$I > 2\sigma(I)$]	$R1 = 0.0540$, $wR2 = 0.0998$
R indices (all data)	$R1 = 0.1838$, $wR2 = 0.1216$
Largest diff. peak and hole (e/Å^3)	0.969 and −0.676

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{[\Sigma\omega(F_o^2 - F_c^2)]/[\Sigma\omega(F_o^2)^2]\}^{1/2}$.

4.4. X-ray crystallographic studies

Suitable monocrystals of [$PdCl_2$(**PP**:**Br**)] were obtained by slow diffusion of hexane into a chloroform solution. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Table 2. Crystals were glued to a glass fiber using an inert polyfluorinated oil and mounted in the low temperature N_2 stream (200 K) of a Bruker-Nonius Kappa-CCD diffractometer equipped with an area detector and an Oxford Cryostream 700 unit. Intensities were collected using graphite-monochromated Mo–K_α radiation (λ = 0.71073 Å). Data were measured with an exposure time of 40 s per frame (eight sets; 479 frames; phi/omega scans 2.0° scan-width). Raw data were corrected for Lorenz and polarization effects.

The structure was solved by direct methods, completed by subsequent difference Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL-97) [30]. Anisotropic thermal parameters were used in the last cycles of refinement for almost all non-hydrogen atoms. Absorption correction procedures were carried out using the multiscan SORTAV program [31]. The hydrogen atoms were included from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system [32].

4.5. Procedure for the Heck reaction

The corresponding catalyst precursor was weighed (5 μmol) into a 10 mL screw-capped glass vial equipped with a magnetic stirrer. The vial was fitted with a magnetic stirring bar, capped and sealed with a septum, and purged by repeated argon/vacuum operations. Methyl acrylate (0.5 mmol), 4-iodotoluene (0.5 mmol), triethylamine (0.5 mmol), and naphthalene as internal GC standard (0.1 mmol) were dissolved in acetonitrile (5 mL) and syringed into the vial. The vial was immediately placed in an oil bath thermostated at 80 °C, with vigorous stirring, taking that instant as the starting time of the reaction. Stirring of the mixture was maintained and 1 μL samples were withdrawn periodically and analyzed by GC using naphthalene as internal standard.

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Appendix A. Supplementary material

CCDC 874139 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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