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Palladium(II) complexes of phosphane ligands with ammonium-functionalized carbosilane substituents

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ABSTRACT

The synthesis of diphenylarylphosphane and 1,2-bis(diarylphosphanyl)ethane ligands, where the aryl group is $-C_6H_4CH_2CH_2SiMe_2CH_2OC_6H_4$-3-$NMe_2$, their palladium(II) complexes, and their corresponding ammonium-quaternized derivatives is described. These new phosphanes were devised as models of potentially water-soluble dendritic carbosilane ligands, although the solubility brought about by the quaternized *N*-trimethylanilinium groups is scarce. The palladium(II) complexes have been fully characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and mass spectrometry, and have been tested in the Hiyama cross-coupling reaction between tri(methoxy)phenylsilane and 3-bromopyridine in aqueous sodium hydroxide solution.

1. Introduction

The synthesis and study of ligands and metal complexes for aqueous-phase homogeneous catalysis is currently an active area in organometallic chemistry [1]. Aryl and alkyl tertiary phosphanes are amongst the most common ligands present in transition-metal catalysis, but they are hydrophobic and lack water solubility. Hydrophilicity can be introduced into a phosphane by attaching nonionic groups, for instance hydroxyalkyl or polyether substituents, although water solubility is usually achieved by making use of anionic or cationic functions, such as sulfonate or ammonium groups [2]. We have been involved in the modification of early and late transition-metal catalysts with carbosilane dendrimers and dendrons [3,4]. These macromolecules can serve as solubilizers of hosted catalysts [5] as their interaction with the solvent depends mainly on the type of end-groups they contain. In this direction, we recently reported, in collaboration with Galindo and co-workers, the first example of a metal complex that is soluble in supercritical CO_2 as it contains trialkylsilyl-terminated dendrons that are linked through their focal point to the phenyl groups of a triphenylphosphane ligand [6].

Spherical carbosilane dendrimers have already been rendered water-soluble by the incorporation of sulfonate or ammonium terminal groups [7–9]. One possible approach to render a phosphane ligand water-soluble is to functionalize the focal point and periphery of a carbosilane dendron with the chosen phosphane and hydrophilic groups, respectively. Unlike conventional water-soluble complexes, the metal centre in these dendritic complexes would be surrounded by a relatively hydrophobic block constituted by the carbosilane branches. One possible advantage of such systems could be their double role of water-soluble organometallic catalysts and phase-transfer catalysts. At the water-organic phase interface, the dendrons might change their conformation exposing their hydrophobic interior to the organic solvent and allowing the organic substrates to diffuse into the dendrimer interior where the catalyst is located [10].

Several methods have been reported for the focal-point functionalization of carbosilane dendrons with phosphorus-donor ligands [11–13]. 4-Bromostyrene is a suitable starting point because the carbosilane dendrimer can be grown divergently from the vinyl group by the usual iterative hydrosilylation/allylation reaction sequence. The resulting bromoarene can then be lithiated and finally treated with the appropriate chlorophosphane [11]. For our goal, however, these two processes must be compatible with the incorporation of hydrophilic groups. Herein, we describe an appropriate pathway for the preparation of mono- and bidentate phosphanes functionalized with ammonium groups that are models for carbosilane dendrimers (zeroth-generation dendrimers). Their palladium(II) complexes are also prepared and tested in a Hiyama cross-coupling reaction.

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2. Results and discussion

2.1. Synthesis of phosphane ligands and complexes

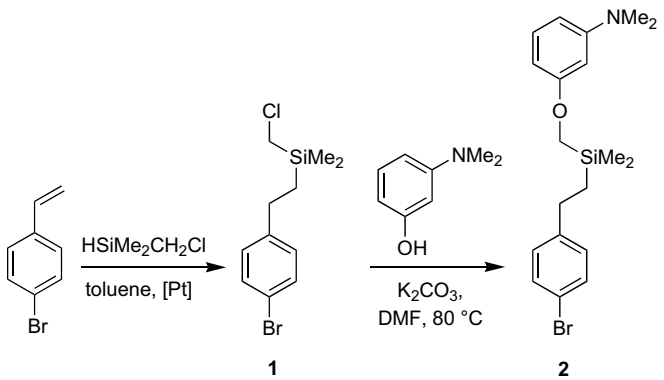
The amino-functionalized aryl bromide ArBr (**2**; Ar = C_6H_4-$CH_2CH_2SiMe_2CH_2OC_6H_4$-3-$NMe_2$) was obtained by the sequence of reactions depicted in Scheme 1. The first step consists of the vinylhydrosilylation of 4-bromostyrene with (chloromethyl)dimethylsilane in toluene at room temperature in the presence of Speier's platinum catalyst (hydrogen hexachloroplatinate). This hydrosilylation reaction affords exclusively the anti-Markovnikov product **1** under these conditions and was monitored by ^{1}H NMR spectroscopy up to completion. Subsequent nucleophilic substitution of the terminal chloride in **1** by the phenolate group of 3-dimethylaminophenol was carried out in dmf at 80 °C with an excess of K_2CO_3 as base. These conditions are based on those reported by Astruc and co-workers [14] with the only difference that addition of NaI as a catalyst was omitted in our case. The reaction was followed by monitoring the shift of the ^{1}H NMR resonance of the $SiCH_2X$ methylene from δ = 2.76 ppm in **1** to δ = 3.56 ppm in **2**.

The monophosphane PPh_2Ar (**3**) and the diphosphane $Ar_2PCH_2CH_2PAr_2$ (**4**) were synthesized by treatment of LiAr, which was obtained in situ, with the corresponding chlorophosphane at −78 °C (Scheme 2). The use of *tert*- instead of *n*-butyllithium for the lithiation of bromoarene **2** was found to be essential as the less nucleophilic *n*BuLi produces important quantities of the homocoupled biaryl (Ar–Ar) product, which was identified by mass spectrometry. The new phosphane ligands were isolated as described in Section 4 and characterized spectroscopically. The chemical shifts of their ^{31}P resonances (δ = −5.0 ppm for **3** and δ = −13.0 ppm for **4**) are very similar to those found in PPh_3 (δ = −4.2 ppm) and $PPh_2CH_2CH_2PPh_2$ (δ = −12.1) [15]. In addition, the ethylene bridge protons of **4** give a broad resonance at δ = 2.05 ppm in the ^{1}H NMR spectrum due to coupling with the two magnetically nonequivalent phosphorus nuclei, as in the parent 1,2-bis(diphenylphosphanyl)ethane. Both dimethylamine-functionalized phosphanes were obtained as colorless oils that readily oxidize in the presence of traces of air. They were therefore prepared and used in situ in subsequent reactions.

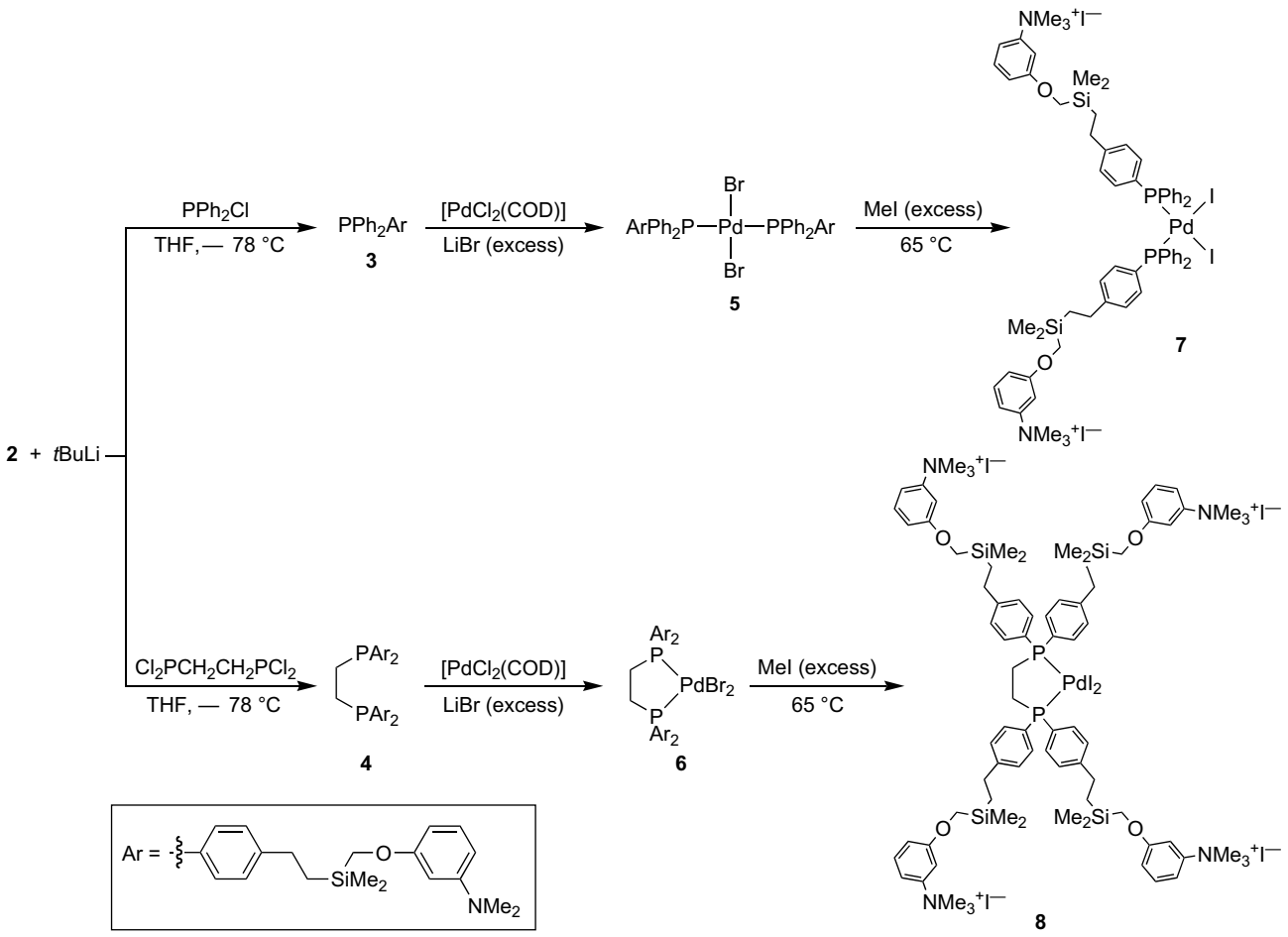
Palladium complexes of monodentate **3** and bidentate phosphane **4** were obtained by displacement of the labile 1,5-cyclooctadiene (COD) ligand from [$PdCl_2$(COD)] with the corresponding phosphane in thf. However, the residues obtained after elimination of volatiles were found to contain a mixture of three different complexes. For instance, the ^{31}P{^{1}H} NMR spectrum of the residue obtained from the reaction with diphosphane **4** contains a singlet at δ = 64.1 ppm, a set of two doublets at δ = 64.2 and 64.8 ppm ($J_{P,P}$ = 13.1 Hz), and a singlet at δ = 65.3 ppm in approximately a 4:4:1 ratio. These resonances were respectively assigned to the expected dichlorido [$PdCl_2$(**4**)], chloridobromido [PdClBr(**4**)], and dibromido [$PdBr_2$(**4**)] complexes after an analysis of the position and isotopic distribution of peaks appearing in the ESI + MS spectrum of the crude reaction mixture. Several experiments were performed to corroborate the existence of halide exchange between palladium dichloride and a bromide salt contaminating the phosphane ligand. Thus, the ^{31}P{^{1}H} NMR spectrum of the product contains almost exclusively the ^{31}P resonance assigned to the dichlorido complex when the sample of **4** used for the reaction was previously isolated and purified (see Section 4), the dibromidopalladium complex was the only product detected when an excess of lithium bromide was added to the reaction mixture, and, finally, a solution of the dibromido derivative in [D_6]acetone turned from yellow to intense red after addition of sodium iodide due to the formation of the diiodido complex (δ_P = 63.6 ppm). The most likely source of bromide is lithium bromide, which could be already present in the commercial solution of *tert*-butyllithium or could be originated as a by-product in the lithiation of bromoarene **2** [16]. Treatment of the non-isolated monophosphane **3** with [$PdCl_2$(COD)] also afforded a mixture of dichlorido (δ_P = 23.8 ppm), bromidochlorido (δ_P = 23.5 ppm), and dibromido (δ_P = 21.4 ppm) complexes, all as *trans* diastereoisomers.

The dibromido complexes **5** and **6** were obtained on a preparative scale by addition of an excess of LiBr to the reaction media (Scheme 2) and were isolated after workup as spectroscopically and analytically pure yellow solids. The dimethylamine groups of these complexes were quaternized by treatment with an excess of iodomethane at 65 °C in thf to give complexes **7** and **8**, respectively. A bromido/iodido ligand exchange was also observed at the metal centers in **7** and **8** (MS and ^{31}P NMR evidence) whereby the iodide ions originating from quaternization of the amine apparently exchange their positions with the bromido ligands bound to palladium. However, elemental analysis of the isolated solids indicated that the halido ligands and halide counterions were both iodine. The most likely explanation for this is that the bromido/iodido ligand exchange is followed by a Finkelstein substitution [17] in which the bromide anions react with the excess of iodomethane to give bromomethane [18,19]. Compounds **7** and **8** were obtained as red solids that are fairly insoluble in most common organic solvents, therefore their NMR characterization was performed in [D_6]DMSO. Although they are soluble in the aqueous catalytic medium at the temperature and under the conditions described below, they were found to be insoluble in water at room temperature.

The palladium complexes **5**–**8** were fully characterized by elemental analysis, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and mass spectrometry. The ESI+ mass spectra show the molecular peaks with the expected isotopic distributions for the neutral complexes **5** and **6**, and the molecular peaks after the loss of one or more iodide anions for **7** and **8**. Mass spectra and elemental analyses served to confirm the replacement of bromide by iodide in the quaternized complexes. The ^{31}P NMR chemical shifts of the bidentate ligands in the dibromido (**6**) and diiodido (**8**) complexes (δ_P = 65.3 and 66.3 ppm, respectively) are similar to those reported for their 1,2-bis(diphenylphosphanyl)ethane analogues [PdX_2(dppe)] (δ_P = 64.4 and 66.7 ppm for X = Br [20] and I [21], respectively). According to the NMR spectroscopic data, the two monophosphane complexes are obtained as a unique isomer but with opposite stereochemistry (*trans* for neutral **5** and *cis* for dicationic **7**). For instance, the ^{31}P chemical shift of **5** (δ_P = 21.4 ppm) is very similar to that observed for the *trans* PPh_3 analogue (δ_P = 22.1 ppm) [22] and to that expected from the empirical correlation reported between the chemical shifts of free and coordinated phosphines ($\delta_P \approx 23$ and 35 ppm for *trans* and *cis*, respectively) [23]. Moreover, the ^{13}C resonance of the *ipso* phenyl carbon (δ_C = 131.4 ppm) appears as a pseudo triplet



Scheme 1.



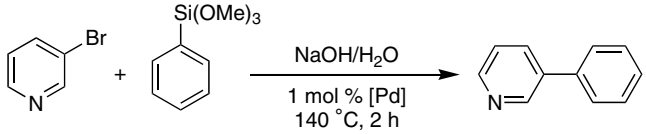
Scheme 2.

[$^1J(^{13}C–^{31}P) + {}^3J(^{13}C–^{31}P) = 50$ Hz], as expected for *trans* palladium phosphane complexes where the $^2J(^{31}P–^{31}P)$ coupling constant is of the order of a few hundred hertz [24]. The *cis* stereochemistry of complex **7** is in agreement with the splitting of the aromatic ^{13}C resonances coupled to ^{31}P into doublets, as expected for the normal value of around 0 Hz for the $^2J(^{31}P–^{31}P)$ coupling constant in *cis* palladium complexes [24,25]. This *cis* arrangement of complex **7** ($\delta_P = 31.6$ ppm), in spite of the cationic nature of the ligands, contrasts with the *trans* stereochemistry found in the neutral analogue $[PdI_2(PPh_2Ar)_2]$ ($\delta_P = 12.3$ ppm) [26] and in $[PdI_2(PPh_3)_2]$ ($\delta_P = 13.3$ ppm) [27].

We tried to increase the water solubility of the ionic compounds by replacing the iodide with nitrate. In a test carried out in an NMR tube, a suspension of **7** in D_2O became solubilized into the aqueous phase after treatment with two equivalents of $AgNO_3$ for 1 h. The ^1H NMR spectrum of the yellow solution obtained after filtration showed the signals of a single species with a similar pattern of resonances to that of compound **7** [28]. However, all attempts to scale the preparation up failed to give a pure product.

2.2. Hiyama coupling in aqueous solution

The palladium-catalyzed aryl–aryl cross-coupling reaction is a simple, efficient, and versatile route to the formation of carbon–carbon bonds that is commonly used in modern organic synthesis [29,30] to give complex products in a one-step reaction between an aryl halide and an organoborane (Suzuki reaction) [31], organostannane (Stille reaction) [32], or organosilane (Hiyama reaction) [33], amongst other organometallic reagents. Hiyama reactions in water have recently been described by our group and others using a variety of Pd precatalysts and, usually, organosiloxanes activated with sodium or potassium hydroxide [34–38]. We chose the coupling of tri(methoxy)phenylsilane and 3-bromopyridine, under our previously reported conditions [36] (Scheme 3), to test the efficiency of the palladium complexes **7** and **8** as aqueous-phase catalysts. We also tested the neutral complexes **5** and **6** for comparison. Table 1 summarizes our results. Conversions obtained with the cationic precursors **7** and **8** were high (80–95%) but lower than those obtained with the neutral precursors **5** and **6**. We have previously observed that $[PdCl_2(PPh_3)_2]$ and other precursors without water-solubilizing groups afford nearly quantitative yields for the same reaction under the same conditions but are more prone to deactivate by precipitation of Pd black [36]. This role of the water-solubilizing ligands might also lay behind the activities shown by the aqueous solutions that were reused after extraction of the organic compounds (Table 1), where the complete inactivity



Scheme 3.

Table 1
Hiyama coupling of 3-bromopyridine and tri(methoxy)phenylsilane in aqueous alkaline medium catalyzed by Pd complexes **5**–**8**

Pd catalyst[a]	Conv. (%)[b]	Conv. (2nd run) (%)[c]
5	100	0
6	100	0
7	95	5
8	80	1

[a] 1 mol% of Pd catalyst with respect to 3-bromopyridine, see Section 4 for details.
[b] Conversions determined by ^{1}H NMR spectroscopy.
[c] Conversions obtained using the aqueous solution from the first run after extraction of the organic products and addition of further reagents.

of the neutral complexes contrasts with the very poor but positive activities shown by the cationic catalysts.

3. Conclusions

The phosphanes described in this work are models for the synthesis of potentially water-soluble dendritic ligands, although the solubility brought about by the hydrophilic *N*-trimethylanilinium groups is poor at present. Nevertheless, enhancements are possible by tuning the nature and multiplying the number of the hydrophilic end-groups of the carbosilane dendrons during the construction of the phosphane ligands.

4. Experimental

4.1. Reagents and general techniques

All operations were performed under argon by using Schlenk or dry box techniques. Solvents were dried and distilled under argon (thf and diethyl ether from sodium benzophenone ketyl; hexane and pentane from sodium/potassium alloy; CH_2Cl_2 from P_2O_5; acetonitrile and $CDCl_3$ from finely ground calcium hydride) [39]. Unless otherwise stated, reagents were obtained from commercial sources and used as received. [$PdCl_2$(COD)] (COD = 1,5-cyclooctadiene) was prepared according to reported procedures [40]. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Varian Gemini-200, Mercury VX-300, or UnityPlus-500 spectrometers. Chemical shifts (δ, ppm) are quoted relative to $SiMe_4$ (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P), and were measured by internal referencing to the deuterated solvent (^{13}C and residual ^{1}H resonances), or by the substitution method (^{31}P). Coupling constants (J) are given in Hz. The coupling constants of pseudo triplets in the ^{13}C NMR spectra (see results and discussion) correspond to $J(^{13}C–^{31}P_A) + J(^{13}C–^{31}P_{A'})$. Samples for MALDI-TOF mass spectrometry were prepared in a 1,8,9-trihydroxyanthracene (dithranol) matrix and spectra were recorded with a Bruker Reflex II spectrometer equipped with a nitrogen laser emitting at 337 nm and operated in the reflection mode at an accelerating voltage in the range 23–25 kV. The Analytical Services of the Universidad de Alcalá recorded the ESI mass spectra in methanol with a Thermoquest–Finnigan Automass Multi spectrometer. The C, H, and N analyses were performed in duplicate by the above services with a LECO CHNS-932 microanalyzer.

4.2. Synthesis of 4-Br$C_6H_4CH_2CH_2SiMe_2CH_2Cl$ (**1**)

An excess of (chloromethyl)dimethylsilane (1.5 mL, 12.3 mmol) was added dropwise to a solution of 4-bromostyrene (1.40 g, 7.65 mmol) at 0 °C in toluene (25 mL) containing hydrogen hexachloroplatinate (5 drops of a 2×10^{-3} M solution in 2-propanol) as hydrosilylation catalyst and this mixture was stirred overnight at room temperature. The solvent was then removed under vacuum and the residue extracted with pentane (2×15 mL). The combined pentane solutions were evaporated to dryness to give **1** as a white oily solid (2.1 g, 94%). Anal. Calc. for $C_{11}H_{16}BrClSi$ (291.69): C, 45.29; H, 5.53. Found: C, 45.72; H, 5.48%. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.37 (d, $^3J_{H,H}$ = 8.5, 2H, C_6H_4), 7.06 (d, $^3J_{H,H}$ = 8.5, 2H, C_6H_4), 2.76 (s, 2H, CH_2Cl), 2.61 (m, 2H, PhCH_2), 0.98 (m, 2H, CH_2Si), 0.12 (s, 6H, SiMe_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 143.3 (s, C_6H_4, C bonded to CH_2), 131.3 (s, C_6H_4), 129.5 (s, C_6H_4), 119.3 (s, C_6H_4, C_{ipso} bonded to Br), 30.1 (s, CH_2Cl), 29.2 (s, PhCH_2), 15.6 (s, CH_2Si), −4.52 ppm (s, SiMe_2).

4.3. Synthesis of BrAr (**2**; Ar = C_6H_4-4-$CH_2CH_2SiMe_2CH_2OC_6H_4$-3-$NMe_2$)

A mixture of **1** (2.10 g, 7.20 mmol), 3-(dimethylamino)phenol (1.02 g, 7.20 mmol), and K_2CO_3 (4.50 g, 32.6 mmol) in dmf (25 mL) was stirred overnight at 80 °C. The solvent was then removed under vacuum at 60 °C and the residue extracted with pentane (2×25 mL). The combined pentane solutions were evaporated to dryness to give **2** as a pale-brown solid (2.5 g, 88%). Anal. Calc. for $C_{19}H_{26}BrNOSi$ (392.41): C, 58.16; H, 6.68; N, 3.57. Found: C, 58.15; H, 6.43; N, 4.13%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35 (d, $^3J_{H,H}$ = 8.2, 2H, BrC_6H_4), 7.06 (d, $^3J_{H,H}$ = 8.2, 2H, BrC_6H_4), 7.12 (t, $^3J_{H,H} \approx$ 8.2, 1H, C_6H_4N), 6.31 (overlapped m, 3H, C_6H_4N), 3.56 (s, 2H, CH_2O), 2.92 (s, 6H, NMe_2), 2.65 (m, 2H, PhCH_2), 1.00 (m, 2H, CH_2Si), 0.12 (s, 6H, SiMe_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 162.5 (s, C_6H_4N, C bonded to O), 151.9 (s, C_6H_4N, C bonded to N), 143.8 (s, BrC_6H_4, C bonded to CH_2), 131.2 (s, BrC_6H_4), 129.6 (s, BrC_6H_4), 129.5 (s, C_6H_4N), 119.1 (s, BrC_6H_4, C bonded to Br), 105.5 (s, C_6H_4N), 101.9 (s, C_6H_4N), 99.2 (s, C_6H_4N), 59.6 (s, CH_2O), 40.6 (s, NMe_2), 29.2 (s, $C_6H_4CH_2$), 15.7 (s, CH_2Si), −4.76 ppm (s, SiMe_2). MALDI-TOF MS: m/z 392.1 $[M+H]^+$ (calcd. 392.1).

4.4. Synthesis of $P(C_6H_5)_2Ar$ (**3**)

A 1.7 M solution of *tert*-butyllithium in pentane (1.00 mL, 1.68 mmol) was added with a syringe to a solution of bromoarene **2** (0.659 g, 1.68 mmol) at −78 °C in thf (25 mL). Stirring was continued at the same temperature for 60 min, then PPh_2Cl (0.31 mL, 1.7 mmol) was added and the reaction mixture was allowed to slowly warm to room temperature overnight. The solvent was then removed under vacuum and the residue extracted with toluene (2×10 mL). Evaporation of the toluene solution to dryness yielded **3** as a spectroscopically pure colorless oil (0.79 g, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.34–7.10 (overlapped m, 15H, PC_6H_5, PC_6H_4, and C_6H_4N), 6.35 (overlapped m, 3H, C_6H_4N), 3.60 (s, 2H, CH_2O), 2.94 (s, 6H, NMe_2), 2.73 (m, 2H, $C_6H_4CH_2$), 1.06 (m, 2H, CH_2Si), 0.15 (s, 6H, SiMe_2) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ = 163.2 (C_6H_4N, C bonded to O), 152.4 (s, C_6H_4N, C bonded to N), 145.9 (s, PC_6H_4, C bonded to CH_2), 138.4 (d, $J_{C,P}$ = 12, PC_6H_5, C_{ipso}), 134.5 (d, $J_{C,P}$ = 20, PC_6H_4, C_{ortho}), 134.1 (d, $J_{C,P}$ = 20, PC_6H_5, C_{ortho}), 129.9 (s, C_6H_4N), 128.7 (d, $J_{C,P}$ = 20, PC_6H_5, C_{para}), 128.6 (d, $J_{C,P}$ = 7, PC_6H_5, C_{meta}), 128.5 (d, $J_{C,P}$ = 7, PC_6H_4, C_{meta}), 102.2 (s, C_6H_4N), 106.2 (s, C_6H_4N), 100.0 (s, C_6H_4N), 59.7 (s, CH_2O), 40.3 (s, NMe_2), 29.9 (s, $C_6H_4CH_2$), 15.8 (s, CH_2Si), −4.73 ppm (s, SiMe_2); C bonded to P in PC_6H_4 not observed. ^{31}P{^{1}H} NMR (C_6D_6, 202 MHz): δ = −5.0 ppm.

4.5. Synthesis of $Ar_2PCH_2CH_2PAr_2$ (**4**)

A 1.7 M solution of *tert*-butyllithium in pentane (0.77 mL, 1.3 mmol) was added with a syringe to a solution of bromoarene **2** (0.51 g, 1.30 mmol) at −78 °C in thf (25 mL). This mixture was stirred at the same temperature for 60 min and then $Cl_2PCH_2CH_2PCl_2$ (48 μL, 0.32 mmol) was added with a syringe. The reaction mixture was allowed to warm slowly to room temper-

ature overnight, then the solvent was removed under vacuum and the residue extracted with toluene (2 × 10 mL). Evaporation of the toluene solution to dryness gave **4** as a spectroscopically pure colorless oil (0.36 g, 84%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.23 (m, 8H, PC_6H_4, H_{ortho}), 7.10 (overlapped m, 12H, PC_6H_4 and C_6H_4N), 6.34 (overlapped m, 12H, C_6H_4N), 3.59 (s, 8H, CH_2O), 2.93 (s, 24H, NMe_2), 2.69 (m, 8H, $C_6H_4CH_2$), 2.05 (br. pseudo t, 4 H, PCH_2), 1.03 (m, 8H, CH_2Si), 0.13 (s, 24H, $SiMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 162.6 (s, C_6H_4N, C bonded to O), 152.0 (s, C_6H_4N, C bonded to N), 145.4 (s, PC_6H_4, C bonded to CH_2), 135.1 (d, $J_{C,P}$ = 12, PC_6H_4, C bonded to P), 132.8 (pseudo t, $J_{C,P}$ = 20, PC_6H_4, C_{ortho}), 129.6 (s, C_6H_4N), 127.9 (pseudo t, $J_{C,P}$ = 7, PC_6H_4, C_{meta}), 105.5 (s, C_6H_4N), 101.9 (s, C_6H_4N), 99.2 (s, C_6H_4N), 59.8 (s, CH_2O), 40.7 (s, NMe_2), 29.6 (s, $C_6H_4CH_2$), 24.1 (br. s, CH_2CH_2), 15.6 (s, CH_2Si), −4.72 (s, $SiMe_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = −13.0 ppm.

4.6. Synthesis of $[PdBr_2\{P(C_6H_5)_2Ar\}_2]$ (**5**)

A thf solution (25 mL) of phosphane **3** was prepared according to the procedure described above from *tert*-butyllithium (0.88 mL, 1.5 mmol, 1.7 M in pentane), bromoarene **2** (0.585 g, 1.49 mmol), and PPh_2Cl (0.27 mL, 1.41 mmol). Once the reaction mixture had reached room temperature (16 h) a solution of $[PdCl_2(COD)]$ (0.200 g, 0.70 mmol) in thf (20 mL) and a large excess of LiBr (0.2 g) were added and stirring was maintained overnight at room temperature. The solvent was then removed under vacuum and the residue extracted with CH_2Cl_2 (2 × 10 mL). After evaporation of the solvent, the residue was washed with pentane (2 × 15 mL) and dried in vacuo to yield **5** as a yellow solid (0.73 g, 83%). Anal. Calc. for $C_{62}H_{72}Br_2N_2O_2P_2PdSi_2$ (1261.6): C, 59.03; H, 5.75; N, 2.22. Found: C, 59.08; H, 5.75; N, 2.06%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (overlapped m, 12H, PC_6H_5), 7.35 (overlapped m, 12H, PC_6H_5 and PC_6H_4), 7.20 (d, $^3J_{H,H}$ = 7.9, 4 H, PC_6H_4), 7.11 (t, $^3J_{H,H}$ = 8.0, 2H, C_6H_4N), 6.33 (overlapped m, 6H, C_6H_4N), 3.58 (s, 4H, CH_2O), 2.91 (s, 12H, NMe_2), 2.71 (m, 4H, $C_6H_4CH_2$), 1.03 (m, 4H, CH_2Si), 0.12 (s, 12H, $SiMe_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 162.6 (s, C_6H_4N, C bonded to O), 152.0 (s, C_6H_4N, C bonded to N), 147.7 (s, PC_6H_4, C bonded to CH_2), 135.4 (pseudo t, $J_{C,P}$ = 13, PC_6H_4, C_{ortho}), 134.9 (pseudo t, $J_{C,P}$ = 12, PC_6H_5, C_{ortho}), 131.4 (pseudo t, $J_{C,P}$ = 50, PC_6H_5, C_{ipso}), 130.3 (br. s, PC_6H_5, C_{para}), 129.6 (s, C_6H_4N), 127.7 (pseudo t, $J_{C,P}$ = 10, PC_6H_5, C_{meta}), 127.5 (pseudo t, $J_{C,P}$ = 10, PC_6H_4, C_{meta}), 105.5 (s, C_6H_4N), 101.8 (s, C_6H_4N), 99.3 (s, C_6H_4N), 59.7 (s, CH_2O), 40.7 (s, NMe_2), 29.7 (s, $C_6H_4CH_2$), 133.3 (br, s, PC_6H_4, C_{ortho}), 133.0 (s, C_6H_4N), 15.4 (s, CH_2Si), −4.74 ppm (s, $SiMe_2$); C_{ipso} of PC_6H_4 was not found. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 21.4 ppm. ESI+MS: *m*/*z* 1260.0 $[M+H]^+$ (calcd. 1259.2).

4.7. Synthesis of $[PdBr_2(Ar_2PCH_2CH_2PAr_2)]$ (**6**)

Chelate ligand **4** was prepared in thf (25 mL), as described above, from *tert*-butyllithium (0.90 mL, 1.53 mmol, 1.7 M solution in pentane), bromoarene **2** (0.600 g, 1.53 mmol), and Cl_2PCH_2-CH_2PCl_2 (58 μL, 0.382 mmol). The reaction mixture was allowed to warm slowly to room temperature for 16 h before the addition of a solution of $[PdCl_2(COD)]$ (0.110 g, 0.385 mmol) in thf (20 mL) and a large excess of LiBr (0.2 g). This mixture was stirred overnight at room temperature, then the solvent was removed under vacuum and the residue extracted with CH_2Cl_2 (2 × 10 mL). After evaporation of the solvent, the residue was washed with pentane (2 × 15 mL) and dried in vacuo to yield **6** as a yellow solid (0.50 g, 81%). Anal. Calc. for $C_{78}H_{108}Br_2N_4O_4P_2PdSi_4$ (1606.3): C, 58.33; H, 6.78; N, 3.49. Found: C, 57.61; H, 6.87; N, 3.03%. ^{1}H NMR ([D$_6$]acetone, 300 MHz): δ = 7.77 (dd, $^3J_{H,P}$ = 11.6, $^3J_{H,H}$ = 8.2, 8H, PC_6H_4, H_{ortho}), 7.38 (d, $^3J_{H,H}$ = 8.2, 8H, PC_6H_4, H_{meta}), 7.08 (t, $^3J_{H,H}$ = 8.4, 4H, C_6H_4N), 6.40 (m, 12H, C_6H_4N), 3.63 (s, 8H, CH_2O), 2.90 (s, 24H, NMe_2), 2.80 (m, 8H, $C_6H_4CH_2$), 2.44 (m, 4H, PCH_2CH_2P), 1.09 (m, 8H, CH_2Si), 0.15 (s, 24H, $SiMe_2$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.69 (dd, $^3J_{H,P}$ = 11.6, $^3J_{H,H}$ = 8.2, 8H, PC_6H_4, H_{ortho}), 7.28 (d, $^3J_{H,H}$ = 8.2, 8H, PC_6H_4, H_{meta}), 7.08 (t, $^3J_{H,H}$ = 8.4, 4H, C_6H_4N), 6.37 (br., 12H, C_6H_4N), 3.58 (s, 8H, CH_2O), 2.93 (s, 24H, NMe_2), 2.74 (m, 8H, $C_6H_4CH_2$), 2.22 (br., 4H, PCH_2CH_2P), 1.04 (m, 8H, CH_2Si), 0.14 (s, 24H, $SiMe_2$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]acetone, 75 MHz): δ = 163.5 (s, C_6H_4N, C bonded to O), 152.2 (s, C_6H_4N, C bonded to N), 150.1 (s, PC_6H_4, C bonded to CH_2), 134.7 (pseudo t, $J_{C,P}$ = 12, PC_6H_4, C_{ortho}), 130.4 (s, C_6H_4N), 129.1 (pseudo t, $J_{C,P}$ = 12, PC_6H_4, C_{meta}), 127.2 (dd, $J_{C,P}$ = 59 and 4, PC_6H_4, C bonded to P), 106.7 (s, C_6H_4N), 103.8 (s, C_6H_4N), 100.5 (s, C_6H_4N), 60.3 (s, CH_2O), 41.2 (s, NMe_2), 16.1 (s, CH_2Si), −4.61 ppm (s, $SiMe_2$); the $C_6H_4CH_2$ resonance is obscured by the solvent and PCH_2CH_2P was not found. $^{31}P\{^1H\}$ NMR ([D$_6$]acetone, 202 MHz): δ = 65.3 ppm. MALDI-TOF MS: *m*/*z* 1602.5 $[M]^+$ (calcd. 1602.4), 1523.5 $[M-Br]^+$ (calcd. 1523.5), 1444.6 $[M-2Br]^+$ (calcd. 1444.6).

4.8. Synthesis of $[PdI_2\{P(C_6H_5)_2Ar^+\}_2][I]_2$ (7; $Ar^+ = C_6H_4$-4-$CH_2CH_2SiMe_2CH_2OC_6H_4$-3- NMe_3^+)

Methyl iodide (0.20 mL, 3.21 mmol) was added with a syringe to a solution of **5** (0.600 g, 0.476 mmol) in thf (25 mL). The reaction mixture was stirred at 65 °C for 16 h and the solvent then removed under vacuum. The residue thus obtained was washed with diethyl ether (2 × 15 mL) and dried in vacuo to yield **7** as a red solid (0.74 g, 95%). Anal. Calc. for $C_{64}H_{78}I_4N_2O_2P_2PdSi_2$ (1639.5): C, 46.89; H, 4.80; N, 1.71. Found: C, 45.76; H, 4.41; N, 1.74%. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 7.75–7.19 (overlapped m, 36H, C_6H_5 and C_6H_4), 3.73, (s, 4H, CH_2O), 3.56 (s, 18H, NMe_3I), 2.74 (m, 4H, $C_6H_4CH_2$), 1.03 (m, 4H, CH_2Si), 0.12 (s, 12H, $SiMe_2$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 75 MHz): δ = 161.3 (s, C_6H_4N, C bonded to O), 148.3 (s, C_6H_4N, C bonded to N), 147.7 (s, PC_6H_4, C_{ipso} bonded to CH_2), 134.5 (d, $J_{C,P}$ = 10, PC_6H_4, C_{ortho}), 133.8 (d, $J_{C,P}$ = 10, PC_6H_5, C_{ortho}), 130.9 (s, C_6H_4N), 130.8 (s, PC_6H_5, C_{para}), 128.3 (d, $J_{C,P}$ = 12, PC_6H_5, C_{meta}), 127.6 (d, $J_{C,P}$ = 12, PC_6H_4, C_{meta}), 114.6 (s, C_6H_4N), 111.3 (s, C_6H_4N), 106.9 (s, C_6H_4N), 60.3 (s, CH_2O), 55.8 (s, NMe_3I), 28.5 (s, $C_6H_4CH_2$), 14.3 (s, CH_2Si), −5.29 ppm (s, $SiMe_2$); C_{ipso} of PC_6H_4 and PC_6H_4 were not found. $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO, 202 MHz): δ = 31.4 ppm. ESI+MS: *m*/*z* 1510.5 $[M-I]^+$ (calcd. 1511.1), 691.7 $[M-2I]^{2+}$ (calcd. 692.1).

4.9. Synthesis of $[PdI_2(Ar^+{}_2PCH_2CH_2\ PAr^+{}_2)_2][I]_4$ (**8**)

Methyl iodide (0.10 mL, 1.61 mmol) was added with a syringe to a solution of **6** (0.30 g, 0.187 mmol) in thf (25 mL) and the reaction mixture was stirred at 65 °C for 16 h. The solvent was then removed under vacuum and the residue washed with diethyl ether (2 × 15 mL) and dried in vacuo to yield **8** as a red solid (0.41 g, 96%). Anal. Calc. for $C_{82}H_{120}I_6N_4O_4P_2PdSi_4$ (2268.0): C, 43.43; H, 5.33; N, 2.47. Found: C, 43.61; H, 5.38; N, 2.51%. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 7.67 (br. t, $^3J_{H,P} \approx {}^3J_{H,H} \approx 10$, 8H, PC_6H_4, H_{ortho}), 7.50 (overlapped m, 12H, C_6H_4N), 7.41 (d, $^3J_{H,H}$ = 7.3, 8H, PC_6H_4, H_{meta}), 7.20 (d, $^3J_{H,H}$ = 7.3, 4H, C_6H_4N), 3.79 (s, 8H, CH_2O), 3.59 (s, 36H, NMe_3I), 2.75 (m, 8H, $C_6H_4CH_2$), 2.39 (br., 4H, PCH_2CH_2P), 1.04 (m, 8H, CH_2Si), 0.13 (s, 24H, $SiMe_2$) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 75 MHz): δ = 161.4 (s, C_6H_4N, C bonded to O), 148.3 (s, C_6H_4N, C bonded to N), 147.8 (s, PC_6H_4, C bonded to CH_2), 130.3 (s, C_6H_4N), 133.3 (br. s, PC_6H_4, C_{ortho}), 127.6 (br. s, PC_6H_4, C_{meta}), 126.1 (d, $J_{C,P}$ = 54, PC_6H_4, C bonded to P), 114.7 (s, C_6H_4N), 111.4 (s, C_6H_4N), 106.8 (s, C_6H_4N), 60.4 (s, CH_2O), 55.9 (s, NMe_3I), 28.5 (s, $C_6H_4CH_2$), 14.2 (CH_2Si), −5.2 ppm (s, $SiMe_2$); PCH_2CH_2P was not found. $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO, 202 MHz): δ = 66.3 ppm. ESI+ MS: *m*/*z* 628.45 $[M-3I]^{3+}$ (calcd. 628.47), 581.14 $[M-4I-CH_3]^{3+}$ (calcd. 581.16), 439.62 $[M-4I]^{4+}$ (calcd. 439.63).

4.10. Cross-coupling procedure

In a typical experiment, $PhSi(OMe_3)$ (0.20 mL, 1.07 mmol) was introduced into a PTFE-valved ampoule and dissolved at room temperature in 5 mL of a 0.5 M solution of NaOH in degassed water. This solution was stirred for 10 min. 3-Bromopyridine (0.086 mL, 0.89 mmol) and the appropriate amount of palladium complex (1.0 mol%; 11 mg for **5**, 14 mg for **6**, 15 mg for **7**, and 20 mg for **8**) were then added and the mixture was stirred for 2 h at 140 °C. The reaction mixture was allowed to cool to room temperature, quenched with water, and extracted with diethyl ether (3×20 mL). The combined organic layers were washed with brine (15 mL) and dried over magnesium sulfate. The solution was filtered off and the solvent removed in vacuo. Conversions were determined by ^{1}H NMR spectroscopy. For the recycling tests, the aqueous phase was recovered, recharged with $PhSi(OMe)_3$ (0.20 mL, 1.07 mmol) and 3-bromopyridine (0.086 mL, 0.89 mmol), and the procedure was repeated under the same conditions specified above.

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