Carbosilane Dendrons as Solubilizers of Metal Complexes in Supercritical Carbon Dioxide[#]

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Palladium complexes of general formula $[PdCl_2(L)_2]$, **3a−c**, were synthesized by reaction of $[PdCl_2(COD)]$ (COD = 1,5-cyclooctadiene) with the appropriate functionalized phosphine L = $[P(C_6H_5)_n((C_6H_4CH_2CH_2Si(CH_2CH_2CH_2SiEtMe_2)_3)_{3-n})]$ (n = 2, **2a**; 1, **2b**; 0, **2c**, respectively), which integrated carbosilane dendritic wedges attached to the *para*-carbon atom of the phenyl group. As a result of the inclusion of the carbosilane dendrons, the solubility of the corresponding palladium complexes **3** in supercritical carbon dioxide ($scCO_2$) was increased in comparison with the palladium complex containing a PPh_3 ligand, which showed negligible solubility. The employment of these complexes as precatalysts in a selected Heck coupling reaction in $scCO_2$ was investigated. Good activities were found for **3a−c** in such a medium due to the acquired solubility, in contrast with the palladium complex containing PPh_3, which showed no activity.

Introduction

There is increasing interest in supercritical carbon dioxide ($scCO_2$) as an alternative reaction medium to environmentally unfriendly organic solvents.[1] Although metal-catalyzed homogeneous reactions in $scCO_2$ would be attractive,[2] the low solubility of many catalysts is a barrier to their use in such processes. For instance, the often used triphenylphosphine metal catalysts show poor solubility, reducing considerably their applications in $scCO_2$.[3] Enhancing the solubility of such catalysts in supercritical media is therefore an important target. In recent years, a number of methodologies have been developed to improve solubility, including the use of "CO_2-philic" ligands, especially fluorinated ligands.[4−6] Drawbacks to their more generalized use include the effect that the strongly electron-withdrawing fluorine can have on the activity of the catalyst[7] and the difficulty and expense involved in synthesizing ligands of this sort. For these reasons, the design of new solubilizers that are easy to prepare but do not alter the chemical properties of the catalyst is highly desirable. Previously we have addressed this issue by preparing a new family of cheaper ligands functionalized with trimethylsilyl groups.[8]

The interaction of a dendritic macromolecule with the solvent medium is adjustable through the choice of peripheral groups, making therefore dendrimers potential solubilizers of hosted catalysts.[9] Remarkably, the first example of nanoparticles catalytically active in $scCO_2$ was based on the encapsulation of Pd(0) in poly(propyleneimine) (PPI) dendrimers with solubilizing perfluorinated chains covalently attached to their periphery.[10] Indeed, the properties of fluorinated dendrimers in supercritical CO_2 have been explored.[11] Metal catalysts can be coordinated to the surface of dendrimers or embedded in the dendritic framework.[9,12] Core-functionalized systems contain a large number of terminal groups per active site and are specially suited for these purposes. Several examples of mono- and diphosphine ligands located in the core of carbosilane dendrimers have been reported up to now.[13−16]

The general aim of our research is (i) to confirm experimentally the increased solubility in $scCO_2$ of metal complexes

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[#] Dedicated to Professor Victor Riera, with best wishes, on the occasion of his 70th birthday.

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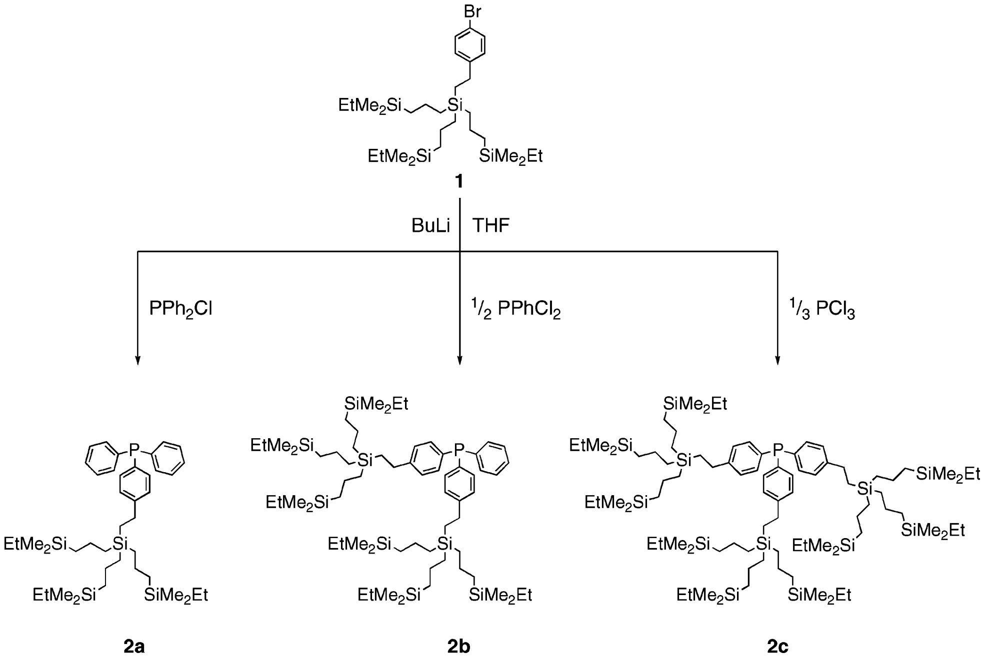
Scheme 1. Synthesis of Carbosilane-Dendronized Phosphines 2a−c



incorporating arylphosphine ligands that contain solubilizing fluor-free groups; (ii) to investigate the use of these complexes as catalyst precursors in selected homogeneous catalyzed processes; and (iii) to compare the results obtained in the supercritical medium with other conventional solvents. This general plan was realized experimentally in the work described here by selecting carbosilane dendrons as solubilizers to be appended to the arylphosphine ligands coordinated to palladium and investigating the behavior of these complexes as catalysts in a specific example of a Heck coupling reaction. Recently, a similar approach for increasing the solubility was taken by Kerton, Rayner, and co-workers,[17] who used poly(dimethylsiloxane) chains, macromolecules that differ from dendrimers in the monodisperse and ramified nature of the latter.

Results and Discussion

Synthesis and Characterization of Carbosilane-Dendronized Phosphines, 2, and their Palladium Complexes, 3. The inclusion of dendronized alkylsilyl chains linked to phosphine ligands was performed by means of an adaptation of a published synthetic procedure.[14] The first-generation dendron **1** (Scheme 1) was obtained from 4-bromostyrene by the appropriate sequence of hydrosilylation/allylation reactions. Phosphines **2a−c**, which contain 1 to 3 carbosilane dendritic wedges and 3 to 9 terminal $SiMe_2Et$ groups per ligand, were prepared by reaction in situ of the phenyllithium derivative from **1** and PPh_2Cl, $PPhCl_2$, or PCl_3, respectively. They were obtained in good yields as colorless oils and were characterized straightforwardly by NMR spectroscopy and analytical methods (see Experimental Section). The corresponding $[PdCl_2(L)_2]$ (L = **2a−c**) complexes (**3a−c**, see Scheme 2) were prepared by reaction of $[PdCl_2(COD)]$ (COD = 1,5-cyclooctadiene) with the appropriate phosphine in CH_2Cl_2 (see Experimental Section). They were obtained as orange oils and characterized by NMR as *trans*-only isomers.

The formation of *trans* isomers in dichloromethane is not due to the congestion caused by the carbosilane dendrons, as shown by the fact that the *cis* isomer of **3c**, which contains the bulkiest phosphine **2c**, is obtained when THF is used as the reaction solvent. Moreover, it was observed by NMR that *trans* isomer transforms, although very slowly, into the *cis* isomer after several months in $CDCl_3$. The observed δ_P values range from 22.5 to 23.7 ppm for *trans* complexes **3**, whereas the resonance is shifted 10 ppm downfield ($\delta_P = 32.7$ ppm) in the case of ***cis*-3c**, in agreement with the general tendency observed for $[PdCl_2(L)_2]$ phosphine complexes.[18] Also in agreement with the proposed stereochemistry are the values estimated through the empirical correlation reported between chemical shifts of free and coordinated phosphines (≈23 and ≈34 ppm for *cis* and *trans*, respectively).[19] In the $^{13}C\{^1H\}$ NMR spectra, the *ortho* and *meta* phenyl carbon signals of *trans*-Pd complexes appear as pseudotriplets due to their virtual coupling (≈11−12 Hz) with both ^{31}P nuclei, in contrast with the doublets observed in the complex ***cis*-3c**, as expected for $^2J(^{31}P-^{31}P) \approx 0$ Hz.

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Scheme 2. Synthesis of Palladium Complexes 3a−c

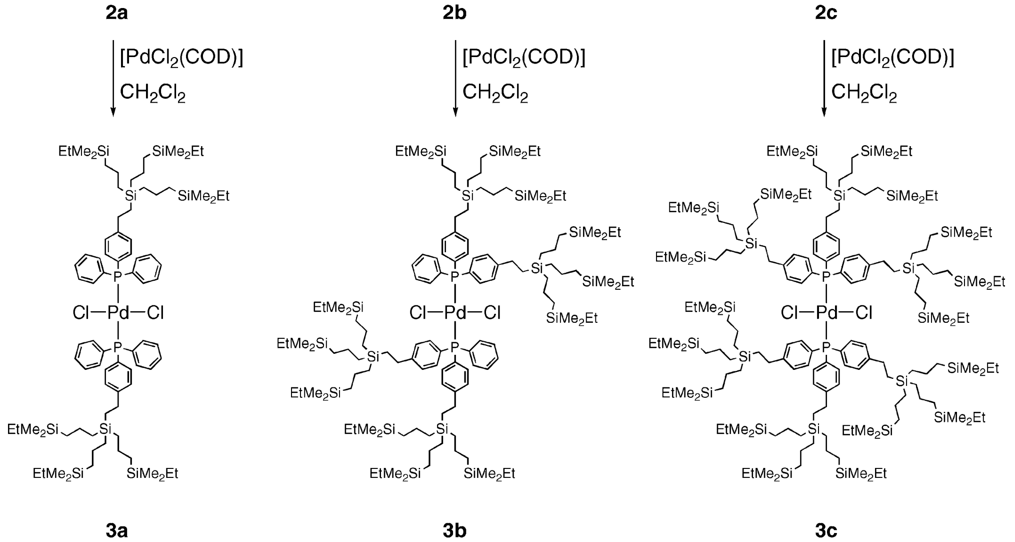

Table 1. Relative Energy (kcal·mol^{-1}) for the *cis* and *trans* Isomers of 3c

	cis		*trans*	
	charges Qeq	no charges	charges Qeq	no charges
$\Delta E_{\text{MM model}}$	0.0	0.0	10.3	−2.2
$\Delta E_{\text{DFT model}}$	0.0	0.0	−14.7	−13.3
$\Delta E_{\text{MM real}}$	0.0	0.0	37.0	42.5
ΔE_{ONIOM}	0.0	0.0	32.6	31.4

Theoretical Study of the *cis* and *trans* Isomers of Compound [PdCl$_2$(2c)$_2$], 3c. The *cis*/*trans* isomerism in [MX$_2$L$_2$] (M = Pd, Pt; X = Cl, Br, I, Me; L = PH$_3$, PMe$_3$, PPh$_3$) complexes was recently discussed in detail by Harvey et al.[20] by using a DFT method including solvent effects. Those authors found an intrinsic energetic preference for the *trans* configuration in the gas phase regardless of the nature of the complex, but that preference was reversed, in general, when solvent effects were included. In any case, monodentate phosphines form both *cis* and *trans* diphosphine complexes as the free energies may be very similar.[20] Stronger phosphorus donors and polar solvents are more likely to yield *cis* complexes. On the other hand, large bite angle bidentate phosphines, such as BISBI[21] and SPANphos,[2] may give *trans* complexes only, but the preparative method can direct the synthesis toward *cis*. Therefore, we wondered here if it is understandable that the carbosilane dendron complex [PdCl$_2$(**2c**)$_2$], **3c**, can be obtained as a *trans* or *cis* isomer depending on the solvent. An extensive search for conformers of low energy was performed (see Experimental Section), and the lowest energy structure for each isomer was reoptimized again using the ONIOM hybrid QM/MM method, in which the [PdCl$_2$(PH$_3$)$_2$] moiety was treated at the DFT level and the carbosilane dendron at the MM level. As Table 1 shows, the *cis* isomer was more stable than the *trans* by about 30 kcal·mol^{-1}, including or not electrostatic effects. Note that for the model system at the DFT level the *trans* isomer was favored, in nice agreement with previous findings.[20] The relative stability of both structures is dominated by the stabilizing interactions in the carbosilane dendron itself, which are larger in the *cis* than in the *trans* structure. Therefore, although the *trans* isomer may be obtained, it evolves toward the most stable *cis* isomer, as actually observed experimentally. These results reflect that these dendritic substituents, located far away from the metal center, have a high degree of conformational freedom. They can easily adopt a conformation that minimizes steric repulsions, or in other words, that maximizes the nonbonding attractive interactions.

Solubility Measurements of Palladium Complexes 3 in scCO$_2$. The solubility measurements in scCO$_2$ of [PdCl$_2$(L)$_2$], **3a−c**, and [PdCl$_2$(PPh$_3$)$_2$] compounds were performed in a simple stainless steel high-pressure cell (28 mL), as described elsewhere.[23] For each solubility determination, a sufficient amount of palladium compound was put into the cell, to give a saturated solution in scCO$_2$ at 40 °C and at 165 bar of pressure. Previously, some experiments were performed in a stainless steel high-pressure cell equipped with two sapphire windows (4.4 mL) in order to see the saturated solution in those conditions. Before performing any measurement, the mixtures were efficiently stirred for several hours in order to guarantee that the saturation of the complex in the supercritical phase had been achieved. Samples were taken through a high-pressure sample loop (with a calibrated volume of 0.177 mL), by filling it with the supercritical fluid mixture. Subsequently, the sample loop was depressurized into a sample vial and was efficiently rinsed with Cl$_2$CH$_2$. The concentration of the resulting Cl$_2$CH$_2$ solutions was determined by analyzing them by UV spectroscopy and comparing the absorptions with a calibration plot. These experiments were performed for each compound at least three times, and the final value was taken as the average of all of the measurements. The average solubility values of 0.12, 0.57, and 0.87 g·L^{-1} were obtained for compounds **3a**, **3b**, and **3c**, respectively.

The solubility of the [PdCl$_2$(L)$_2$] complexes, **3**, in scCO$_2$ is moderate, but the effect of the number of carbosilane dendrons tethered to the phenyl groups of phosphine on this parameter is noticeably important. In fact, in agreement with other authors,[6] negligible solubility in scCO$_2$ was observed for the [PdCl$_2$(PPh$_3$)$_2$] complex, but the formal introduction of one dendron (**3a**) increases the solubility from practically zero to a low, but

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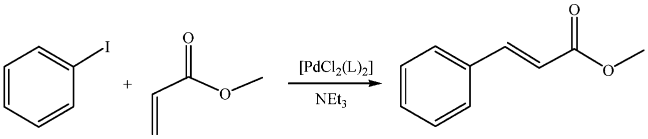
Table 2. Heck Coupling Reaction of Iodobenzene in $scCO_2$[a]



entry	Pd precatalyst	pressure (bar)	time (h)	yield (%)[b]
1	$[PdCl_2(\mathbf{2a})_2]$, **3a**	170	18	38
2	$[PdCl_2(\mathbf{2b})_2]$, **3b**	170	18	42
3	$[PdCl_2(\mathbf{2c})_2]$, **3c**	170	18	38
4	$[PdCl_2(PPh_3)_2]$	170	18	no reaction

[a] Reaction conditions: 1.0 equiv of iodobenzene, 5.0 equiv of methyl acrylate, 1.8 equiv of Et_3N, Pd precatalyst 2.5% mol, $T = 100$ °C. [b] Isolated yield after chromatographic purification.

Table 3. Heck Coupling Reaction of Iodobenzene in Conventional Solvents[a]

entry	Pd precatalyst	solvent	time	yield (%)[b]
5	$[PdCl_2(\mathbf{2a})_2]$, **3a**	toluene	18 h	66
6	$[PdCl_2(PPh_3)_2]$	toluene	18 h	48
7	$[PdCl_2(\mathbf{2a})_2]$, **3a**	DMF	75 min	19
8	$[PdCl_2(PPh_3)_2]$	DMF	75 min	99

[a] Conditions similar to those of Table 2. [b] Isolated yield after chromatographic purification.

significant, value. Moreover, the solubility was observed to increase from **3a** to **3c** with the increasing number of carbosilane dendrons attached to the phosphine.

Catalytic Reactions in $scCO_2$ and Comparison of the Results in this Medium with Conventional Solvents. The homogeneous palladium-catalyzed Heck reaction[24] was chosen in order to investigate the potential for catalysis in $scCO_2$ of the palladium compounds bearing carbosilane dendrons as substituents in the arylphosphine ligands. We selected as test reaction the coupling of iodobenzene and methyl acrylate. The corresponding catalytic experiments were carried out in $scCO_2$, with triethylamine present as a base and complexes **3a**−**c** as precatalysts, employing the same cell used for the solubility measurements. To compare the catalytic activity of these complexes, the reaction was repeated using the same conditions with the unsubstituted PPh_3 derivative. The results are summarized in Table 2. Conversions close to 40% to the coupled product were observed after 18 h using any of the palladium complexes **3a**−**c** as precatalyst (entries 1−3). Conversely, negligible reaction was observed under identical conditions using $[PdCl_2(PPh_3)_2]$ (entry 4). The higher conversions in $scCO_2$ for the compounds containing the dendritic phosphine in comparison with that with PPh_3 appear to arise from the enhanced solubility of the catalytically active palladium species. Therefore, this result confirms that the inclusion of the carbosilane dendron is essential for acquiring activity in $scCO_2$. Other factors, such as the lower accessibility of the catalytic site in **3c** compared to **3a**, should be considered in order to explain the same observed yields.

To compare the activity in the supercritical medium with that in conventional solvents, the reaction was repeated with complexes **3a** and $[PdCl_2(PPh_3)_2]$, under identical conditions, in two solvents of quite different polarity, toluene and DMF. The results are collected in Table 3.

We observed that the reaction carried out in toluene, a solvent of low polarity similar to $scCO_2$, afforded the coupled product with comparable conversions for **3a** (entry 5) and $[PdCl_2(PPh_3)_2]$ (entry 6) (yields of 66% and 48%, respectively). The activity of the latter compound in such a medium in comparison with the lack of activity in $scCO_2$ suggests that the catalyst's solubility is crucial for the progress of the reaction in the supercritical medium. It is worth noting that the activity of the palladium catalysts totally changes in a polar aprotic solvent. For instance, using complex **3a** and DMF as solvent, a conversion of 19% was observed after 75 min of reaction (entry 7). However, using the nondendritic analogous Pd−PPh_3 complex, the reaction was complete under identical conditions (entry 8). It has been proposed for the mechanism of the Heck reaction that under these reaction conditions coordinatively unsaturated anionic Pd(0) species are formed.[25] The formation of these catalytically active species is favored in polar solvents, which could explain the higher conversions observed in DMF compared with less polar solvents such as $scCO_2$ or toluene. The divergent reactivity observed in DMF between the dendritic and nondendritic systems can be ascribed to the local apolar environment originating from the dendritic carbosilane shell or to the lower accessibility of the catalytic site located at the core of the dendrimer.[15] The second explanation is in apparent contradiction with the behavior observed in toluene, where **3a** shows comparable activity with respect to the PPh_3 complex, if the conformational flexibility of the dendritic wedges is not taken into account. Thus, the encapsulation of the catalytic site by the dendritic wedges can be affected by the solvent polarity, the apolar branches being spread out in apolar solvents, opening the shell, but folded in polar solvents, restricting the accessibility of the metal center. Evidently, much more effort must be addressed to the search for specific conditions in which the results obtained in the supercritical medium improves upon those well established in conventional media. Work is in progress in this direction.

Conclusions

The incorporation of carbosilane dendritic wedges to arylphosphines, according to conventional synthetic procedures, allows the preparation of the functionalized phosphines $L = [P(C_6H_5)_n((C_6H_4CH_2CH_2Si(CH_2CH_2CH_2SiEtMe_2)_3)_{3-n})]$ ($n = 2$, **2a**; 1, **2b**; 0, **2c**), which are used to synthesize palladium complexes of general formula $[PdCl_2(L)_2]$, **3a**−**c**. As result of the inclusion of the carbosilane dendrons, the solubility of the corresponding metal complexes in $scCO_2$ increased in comparison with the palladium complex containing the PPh_3 ligand, which shows negligible solubility. The improved solubility makes possible the employment of the palladium complexes **3** as precatalysts in Heck coupling reactions in $scCO_2$, a medium in which the palladium complex containing PPh_3 shows no activity. The comparison of the catalytic activity of these compounds in the supercritical medium and in conventional solvents recommends that further research is necessary in order to improve the results.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques or a drybox. Solvents were previously dried and freshly distilled under argon: tetrahydrofuran from sodium benzophenone ketyl; toluene from sodium; hexane from sodium-potasium; and dichloromethane over P_4O_{10}. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $[PdCl_2(COD)]$[26] and

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$[BrC_6H_4CH_2CH_2Si(CH_2CH{=}CH_2)_3]$[13a] were prepared according to reported methods. UV/visible spectra were recorded using a Perkin-Elmer Lambda 25 UV/vis spectrometer. ^1H, ^{13}C, and ^{31}P spectra were recorded on a Varian Unity VXR-300 or Varian 500 plus instrument. Chemical shifts (δ, ppm) are relative to $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P) and were measured relative to ^{13}C and residual ^1H resonances of the deuterated solvents, or by the substitution method in the ^{31}P case. Coupling constants (J) are given in Hz. In ^{13}C NMR, $J_{P\ virtual}$ of pseudotriplets corresponds to $J(^{13}C-^{31}P_A) + J(^{13}C-^{31}P_{A'})$. The Analytical Services of the Universidad de Alcalá performed the C and H analyses with a Heraeus CHN-O-Rapid microanalyzer.

Synthesis of $[BrC_6H_4CH_2CH_2Si(CH_2CH_2CH_2SiEtMe_2)_3]$, 1. An excess of dimethylchlorosilane (2.5 mL, 23.0 mmol), used as reagent and solvent, was added to $[BrC_6H_4CH_2CH_2Si(CH_2CH{=}CH_2)_3]$ (1.4 g, 4.2 mmol) in the presence of a 2×10^{-3} M solution of H_2PtCl_6 catalyst in 2-propanol (4 drops). The solution was stirred at room temperature until the reaction was completed (ca. 4 h, monitored by ^1H NMR), and then the excess silane and other volatiles were removed under vacuum. The crude product was dissolved in diethyl ether (25 mL) and added dropwise (30 min) to an ice-cooled 2.0 M THF solution of ethylmagnesium chloride (7.0 mL, 14.0 mmol) diluted in THF (100 mL). After the addition was finished, the reaction mixture was allowed to reach room temperature and the stirring was continued overnight. The excess ethylmagnesium chloride was hydrolyzed with a concentrated aqueous solution of NH_4Cl (100 mL). The organic phase was separated by decantation, and the aqueous solution was washed twice with diethyl ether (2 × 50 mL). The combined organic extracts were dried with anhydrous $MgSO_4$, filtered off, and evaporated in vacuo to yield compound **1** as a colorless liquid (2.3 g, 92%). Anal. Calcd for $C_{29}H_{59}BrSi_4$ ($M = 600.03$ g/mol): C, 58.05; H, 9.91. Found: C, 57.88; H, 9.82. ^1H NMR ($CDCl_3$): δ 7.38 (d, 2H, C_6H_4, $J_{HH} = 7$), 7.04 (d, 2H, C_6H_4), 2.55 (m, 2H, $PhCH_2CH_2Si$), 1.30 (m, 6H, $CH_2CH_2CH_2$) 0.90 (t, 9H, CH_2CH_3, $J_{HH} = 8$), 0.80 (m, 2H, $PhCH_2CH_2Si$), 0.60 (m, 12H, $CH_2CH_2CH_2$), 0.45 (q, 6H, CH_2CH_3), −0.06 (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 144.5 (C_6H_4, C bonded to Br), 131.2 (C_6H_4, C *ortho* to Br), 129.4 (C_6H_4, C *meta* to Br), 119.0 (C_6H_4, C *para* to Br), 29.7 ($PhCH_2CH_2Si$), 19.9, 18.5, and 17.4 ($CH_2CH_2CH_2$), 15.0 ($PhCH_2CH_2Si$), 7.4 ($SiCH_2CH_3$), 7.0 ($SiCH_2CH_3$), −3.8 ($SiCH_3$).

Synthesis of $[P(C_6H_5)_n((C_6H_4CH_2CH_2Si(CH_2CH_2CH_2SiEtMe_2)_3)_{3-n})]$ ($n = 2, 1, 0$), 2a−c. Phosphines **2a**−**c** were obtained by reaction of the corresponding chlorophosphine $P(C_6H_5)_nCl_{3-n}$ with the phenyllithium derivative of **1** in THF, as exemplified by the preparation of **2a** here described. A 2.5 M hexane solution of *n*-BuLi (0.25 mL, 0.61 mmol) was dropwise added to 10 mL of a THF solution of **1** (0.37 g, 0.61 mmol) previously cooled at −78 °C. The stirring was continued at this temperature for 30 min, and then PPh_2Cl (0.11 mL, 0.61 mmol) was added via a syringe. The reaction mixture was allowed to slowly warm to room temperature overnight. Afterward, the solvent was removed under vacuum, the residue was extracted twice with pentane (2 × 10 mL), and the solution was filtered. The solvent was evaporated under vacuum to yield **2a** as a colorless oil (0.43 g, 89%). **2b** and **2c** were obtained by the same procedure in a similar molar scale (83% and 86% yields, respectively).

Data for **2a**: Anal. Calcd for $C_{41}H_{69}PSi_4$ ($M = 705.30$ g/mol): C, 69.82; H, 9.86. Found: C, 69.70; H, 9.54. ^1H NMR ($CDCl_3$): δ 7.30 (m, 10H, C_6H_5), 7.19 (m, 4H, C_6H_4), 2.57 (m, 2H, $PhCH_2CH_2Si$), 1.34 (m, 6H, $CH_2CH_2CH_2$), 0.91 (t, 9H, CH_2CH_3), 0.84 (m, 2H, $PhCH_2CH_2Si$), 0.58 (m, 12H, $CH_2CH_2CH_2$), 0.46 (q, 6H, CH_2CH_3), −0.06 (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.3 (s, C_6H_4, C *para* to P), 137.4 (d, C_6H_5, C bonded to P, $J_P = 9.9$), 135.0 (d, C_6H_4, C bonded to P, $J_P = 9.9$), 133.8 (d, C_6H_4, C *ortho* to P, $J_P = 19.9$), 133.5 (d, C_6H_5, C *ortho*, $J_P = 19.3$), 128.4 (s, C_6H_5, C *para*), 128.3 (d, C_6H_5, C *meta*, $J_P = 6.8$), 127.9 (d, C_6H_4, C *meta* to P, $J_P = 7.5$), 30.1 (s, $PhCH_2CH_2Si$), 19.9, 18.6, and 17.5 (s, $CH_2CH_2CH_2$), 14.9 (s, $PhCH_2CH_2Si$), 7.5 (s, $SiCH_2CH_3$), 7.1 (s, $SiCH_2CH_3$), −3.6 (s, $SiCH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.02.

Data for **2b**: Anal. Calcd for $C_{64}H_{123}PSi_8$ ($M = 1148.32$ g/mol): C, 66.94; H, 10.80. Found: C, 66.67; H, 10.68. ^1H NMR ($CDCl_3$): δ 7.28 (m, 5H, C_6H_5), 7.18 (m, 8H, C_6H_4), 2.56 (m, 4H, $PhCH_2CH_2Si$), 1.32 (m, 12H, $CH_2CH_2CH_2$), 0.90 (t, 18H, CH_2CH_3), 0.81 (m, 4H, $PhCH_2CH_2Si$), 0.55 (m, 24H, $CH_2CH_2CH_2$), 0.44 (q, 12H, CH_2CH_3), −0.08 (s, 36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.5 (s, C_6H_4, C *para* to P), 137.5 (d, C_6H_5, C bonded to P, $J_P = 9.9$), 133.8 (d, C_6H_4, C *ortho* to P, $J_P = 19.8$), 133.4 (d, C_6H_5, C *ortho* to P, $J_P = 19.4$), 128.4 (s, C_6H_5, C *para*), 128.3 (d, C_6H_5, C *meta*, $J_P = 7.0$), 127.9 (d, C_6H_4, C *meta* to P, $J_P = 7.2$), 30.2 (s, $PhCH_2CH_2Si$), 20.0, 18.6, and 17.4 (s, $CH_2CH_2CH_2$), 14.9 (s, $PhCH_2CH_2Si$), 7.5 (s, $SiCH_2CH_3$), 7.2 (s, $SiCH_2CH_3$), −3.6 (s, $SiCH_3$), not found C bonded to P in C_6H_4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.77.

Data for **2c**: Anal. Calcd for $C_{87}H_{177}PSi_{12}$ ($M = 1591.34$ g/mol): C, 65.66; H, 11.21. Found: C, 65.04; H, 10.10. ^1H NMR ($CDCl_3$): δ 7.19 (m, 2H, C_6H_4), 7.12 (m, 2H, C_6H_4), 2.56 (m, 2H, $PhCH_2CH_2Si$), 1.30 (m, 6H, $CH_2CH_2CH_2$), 0.87 (t, 9H, CH_2CH_3), 0.80 (m, 2H, $PhCH_2CH_2Si$), 0.55 (m, 12H, $CH_2CH_2CH_2$), 0.43 (q, 6H, CH_2CH_3), −0.08 (s, 18H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.8 (s, C_6H_4, C *para* to P), 134.0 (d, C_6H_4, C *ortho* to P, $J_P = 20.0$), 128.1 (d, C_6H_4, C *meta* to P, $J_P = 7.5$), 30.2 (s, $PhCH_2CH_2Si$), 20.1, 18.5, and 17.3 (s, $CH_2CH_2CH_2$), 14.9 (s, $PhCH_2CH_2Si$), 7.4 (s, $SiCH_2CH_3$), 7.2 (s, $SiCH_2CH_3$), −3.6 (s, $SiCH_3$), not found C bonded to P in C_6H_4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −6.52.

Synthesis of $[PdCl_2(P(C_6H_5)_n(C_6H_4CH_2CH_2Si(CH_2CH_2CH_2SiEtMe_2)_3)_{3-n})_2]$ ($n = 2, 1, 0$), 3a−c. The *trans* phosphine complexes were obtained from reaction of the appropriate phosphine **2** and $[PdCl_2(COD)]$ in dichloromethane. The preparation of **3a** is here described as representative. A solution of $[PdCl_2(COD)]$ (0.090 g, 0.32 mmol) and **2a** (0.45 g, 0.64 mmol) in dichloromethane (10 mL) was stirred for 1 h at room temperature. Then, the solvent was removed under vacuum and the resulting orange oil purified by flash chromatography, using pentane as an eluent to separate the organic residues and, subsequently, dichloromethane. The dichloromethane solution was evaporated to dryness to give **3a** as an orange oil (0.39 g, 74%). Complexes **3b** and ***trans*-3c** were obtained by the same procedure in a similar molar scale (76% and 71% yields, respectively). Complex ***cis*-3c** (73% yield) was obtained instead of ***trans*-3c** when the reaction was carried out in THF.

Data for **3a**: Anal. Calcd for $C_{82}H_{138}Cl_2P_2PdSi_8$ ($M = 1587.93$ g/mol): C, 62.02; H, 8.76. Found: C, 61.65; H, 8.31. ^1H NMR ($CDCl_3$): δ 7.65 (overlapped m, 12H, C_6H_5 and C_6H_4), 7.37 (m, 12H, C_6H_5), 7.18 (m, 4H, C_6H_4), 2.56 (m, 4H, $PhCH_2CH_2Si$), 1.32 (m, 12H, $CH_2CH_2CH_2$), 0.89 (t, 18H, CH_2CH_3), 0.83 (m, 4H, $PhCH_2CH_2Si$), 0.58 (m, 24H, $CH_2CH_2CH_2$), 0.45 (q, 12H, CH_2CH_3), −0.07 (s, 36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.3 (s, C_6H_4, C *para* to P), 135.1 (pseudo t, C_6H_5, C *ortho*, $J_{P\ virtual} = 12.4$), 134.8 (pseudo t, C_6H_4, C *ortho* to P, $J_{P\ virtual} = 12.5$), 130.2 (s, C_6H_5, C *para*), 127.8 (pseudo t, C_6H_5, C *meta*, $J_{P\ virtual} = 11.0$), 127.4 (pseudo t, C_6H_4, C *meta* to P, $J_{P\ virtual} = 11.2$), 30.3 (s, $PhCH_2CH_2Si$), 20.0, 18.7, and 17.5 (s, $CH_2CH_2CH_2$), 14.7 (s, $PhCH_2CH_2Si$), 7.5 (s, $SiCH_2CH_3$), 7.2 (s, $SiCH_2CH_3$), −3.6 (s, $SiCH_3$), not found C bonded to P. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.74.

Data for **3b**: Anal. Calcd for $C_{128}H_{246}Cl_2P_2PdSi_{16}$ ($M = 2473.96$ g/mol): C, 62.14; H, 10.02. Found: C, 61.74; H, 9.81. ^1H NMR ($CDCl_3$): δ 7.65 (overlapped m, 12H, C_6H_5 and C_6H_4), 7.37 (m, 8H, C_6H_5), 7.17 (m, 8H, C_6H_4), 2.59 (m, 8H, $PhCH_2CH_2Si$), 1.33 (m, 24H, $CH_2CH_2CH_2$), 0.90 (t, 36H, CH_2CH_3), 0.83 (m, 8H, $PhCH_2CH_2Si$), 0.58 (m, 48H, $CH_2CH_2CH_2$), 0.45 (q, 24H, CH_2CH_3), −0.07 (s, 72H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.1 (s, C_6H_4, C *para* to P), 135.1 (pseudo t, C_6H_5, C *ortho*, $J_{P\ virtual} = 12.4$), 134.9 (pseudo t, C_6H_4, C *ortho* to P, $J_{P\ virtual} = 12.5$), 130.1

(s, C_6H_5, C *para*), 127.7 (pseudo t, C_6H_5, C *meta*, $J_{\mathrm{P\ virtual}} = 11.1$), 127.4 (pseudo t, C_6H_4, C *meta* to P, $J_{\mathrm{P\ virtual}} = 11.2$), 30.2 (s, $PhCH_2CH_2Si$), 19.8, 18.5, and 17.3 (s, $CH_2CH_2CH_2$), 14.9 (s, $PhCH_2CH_2Si$), 7.4 (s, $SiCH_2CH_3$), 7.2 (s, $SiCH_2CH_3$), −3.6 (s, $SiCH_3$), not found C bonded to P. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.12.

Data for ***trans*-3c**: Anal. Calcd for $C_{174}H_{354}Cl_2P_2PdSi_{24}$ (M = 3360.00 g/mol): C, 62.20; H, 10.62. Found: C, 61.74; H, 10.31. ^1H NMR ($CDCl_3$): δ 7.58 (m, 12H, C_6H_4), 7.15 (m, 12H, C_6H_4), 2.56 (m, 12H, $PhCH_2CH_2Si$), 1.32 (m, 36H, $CH_2CH_2CH_2$), 0.89 (t, 54H, CH_2CH_3), 0.83 (m, 12H, $PhCH_2CH_2Si$), 0.57 (m, 72H, $CH_2CH_2CH_2$), 0.45 (q, 36H, CH_2CH_3), −0.07 (s, 108H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 148.2 (s, C_6H_4, C *para* to P), 135.1 (pseudo t, C_6H_4, C *ortho* to P, $J_{\mathrm{P\ virtual}} = 12.4$), 127.3 (pseudo t, C_6H_4, C *meta* to P, $J_{\mathrm{P\ virtual}} = 11.0$), 30.2 (s, $PhCH_2CH_2Si$), 19.0, 18.5, and 17.4 (s, $CH_2CH_2CH_2$), 14.6 (s, $PhCH_2CH_2Si$), 7.4 (s, $SiCH_2CH_3$), 7.1 (s, $SiCH_2CH_3$), −3.8 (s, $SiCH_3$), not found C bonded to P. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.47.

Data for ***cis*-3c**: Anal. Calcd for $C_{174}H_{354}Cl_2P_2PdSi_{24}$ (M = 3360.00 g/mol): C, 62.20; H, 10.62. Found: C, 61.68; H, 10.26. ^1H NMR ($CDCl_3$): δ 7.58 (m, 12H, C_6H_4), 7.17 (m, 12H, C_6H_4), 2.56 (m, 12H, $PhCH_2CH_2Si$), 1.32 (m, 36H, $CH_2CH_2CH_2$), 0.89 (t, 54H, CH_2CH_3), 0.83 (m, 12H, $PhCH_2CH_2Si$), 0.57 (m, 72H, $CH_2CH_2CH_2$), 0.44 (q, 36H, CH_2CH_3), −0.07 (s, 108H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 149.5 (s, C_6H_4, C *para* to P), 134.7 (d, C_6H_4, C *ortho* to P, $J_P = 11.1$), 127.7 (d, C_6H_4, C *meta* to P, $J_P = 12.9$), 30.2 (s, $PhCH_2CH_2Si$), 18.7, 18.5, and 17.3 (s, $CH_2CH_2CH_2$), 14.4 (s, $PhCH_2CH_2Si$), 7.4 (s, $SiCH_2CH_3$), 7.0 (s, $SiCH_2CH_3$), −3.8 (s, $SiCH_3$), not found C bonded to P. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.66.

General Catalytic Procedure. The catalytic experiments were carried out with compounds $[PdCl_2(L)_2]$, **3**, and $[PdCl_2(PPh_3)_2]$ under identical experimental conditions. A typical experimental run is the following: complex $[PdCl_2(L)_2]$ (0.012 mmol) was placed into the autoclave, and then iodobenzene (55 μL, 0.5 mmol), methyl acrylate (230 μL, 2.5 mmol), and Et_3N (130 μL, 0.9 mmol) were added. The reactor was heated to 100 °C and pressurized with CO_2 using a cooled hplc pump. After reaction, the autoclave was allowed to cool in ice, then the CO_2 was slowly vented and the resulting product was extracted with Et_2O. The crude product obtained on evaporating the solvent was purified by column chromatography (silica gel 60, Et_2O). Conversions were determined by ^1H NMR analysis (using hexamethyldisiloxane as internal reference). Reactions in conventional organic solvents were performed as described above, but using degassed organic solvent (10 mL) instead of $scCO_2$.

Computational Details. To find low-energy structures for the *cis* and *trans* complexes, a classical molecular dynamics strategy was followed. The UFF force field[27] in conjunction with Qeq atomic charges,[28] as implemented in the Forcite module of the MS Modeling package,[29] was used. The protocol consisted in a molecular dynamics simulation of 300 ps, with 0.5 fs time step at 500 K, quenching each 5000 steps and followed by a geometry optimization process. For nonbonded interactions (electrostatics and van der Waals) a cutoff distance of 18.5 Å was applied. The lowest energy structure was selected and subsequently reoptimized using the two-layer ONIOM[30] method as implemented in Gaussian.[31] The B3LYP[32] DFT-based method was used to describe the high-level layer atoms $[PdCl_2(PH_3)_2]$ (LANL2DZ basis set), while the bulky phosphine substituents were included in the low-level layer and described using the UFF force field.

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Supporting Information Available: Figures showing several views of the optimized structures and details of the molecular dynamics calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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