(Perfluoro)alkylsilyl-Substituted 2-[Bis(4-aryl)phosphino]pyridines: Synthesis and Comparison of Their Palladium Complexes in Methoxycarbonylation of Phenylacetylene in Regular Solvents and Supercritical CO_2

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The synthesis and characterization of three new 2-[bis{4-(bromo)phenyl}phosphino]-pyridine (**8**), 2-[bis{4-(trimethylsilyl)phenyl}phosphino]pyridine (**9**), and 2-[bis{4-((2-(perfluorohexyl)ethyl)dimethylsilyl)phenyl}phosphino]pyridine (**10**) ligands (L) is reported. The corresponding compounds *trans-/cis*-[$PdCl_2(L)_2$] **11**−**13**, *trans*-[PdCl(Me)$(L)_2$] **14**−**16**, and maleic anhydride complexes [$Pd(L)_2$(*cyclo*-(−CH=CHC(O)OC(O)−)] **17** and **18** were synthesized and characterized. In the methoxycarbonylation of phenylacetylene in methanol catalysts derived from [$Pd(OAc)_2$] as the palladium source with either **9** or **10** as ligand showed the same activity (TON = 4000, 50 min reaction time) and selectivity (about 98% for the *branched* product) as the catalyst obtained from [$Pd(OAc)_2$] and 2-[diphenylphosphino]-pyridine (**2**). Both **2** and **10** were also tested in this reaction using a 1:1 mixture of methanol and α,α′,α″-trifluorotoluene as solvent system: fluorous **10** generated a more active catalyst (TON = 3400 for **10** vs 3000 for **2**). In supercritical CO_2 the use of **10** as ligand (with [Pd-$(OAc)_2$]) in this reaction gave a TON of 2000 (50 min reaction time) and a selectivity of >99% for the *branched* product. Nonfluorous [$Pd(\mathbf{2})_2$(*cyclo*-(CH=CHC(O)OC(O)−)] gave a particularly active catalyst for the methoxycarbonylation of phenylacetylene (TON of about 8000, 50 min reaction time, TOF_{50} of about 30 000 mol phenylacetylene per mol Pd per hour in methanol) with no loss in selectivity (98% selectivity toward the *branched* product).

Introduction

The synthesis and application of phosphorus ligands that besides the phosphorus atom contain a second coordinating functionality is of considerable interest. For instance, in the Shell Higher Olefin Process (SHOP) the use of a bifunctional phosphine is necessary to obtain high activity and selectivity.[1] By introducing a second donor atom in the ligand, it is possible to obtain bidentate ligands that contain functionalities with different donor strengths and steric requirements. In this way the reactivity and accessibility of the metal center can be tuned. For instance, when in a bidentate ligand the second donor atom coordinates weaker than the first one, it can be replaced by incoming molecules and substrates during a catalytic reaction while the ligand remains monodentate-coordinated to the metal site. In this way, it serves as a stabilizing co-ligand by occupying a vacant site on the metal in the absence of substrate, preventing decomposition of the metal catalyst. Although several different donor atoms, such as O, S, C, and N, have been used, especially the latter has been employed extensively to make a variety of P,N-bidentate ligands and transition metal complexes derived thereof (Chart 1).[2−5]

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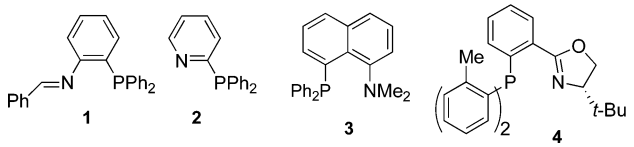
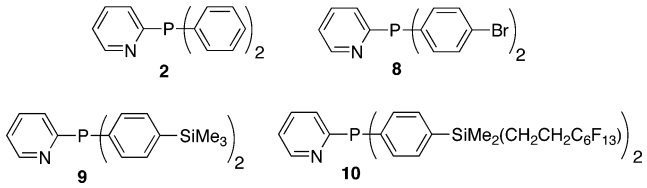
Chart 1



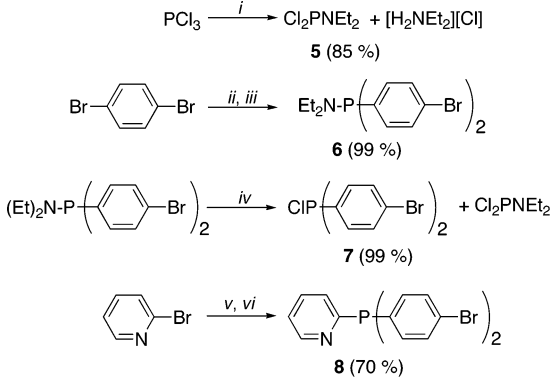
Drent and co-workers have developed a palladium system based on [Pd(OAc)$_2$] and 2-[bis(aryl)phosphino]-pyridine ligands, which shows high activity and selectivity in the methoxycarbonylation of alkynes.[3,6−8] In particular the methoxycarbonylation of propyne, which gives economically important products such as methyl methacrylate, was studied in detail. This initial research was followed by other studies by different authors directed to the development of new ligands,[9−12] the elucidation of mechanistic details of the catalytic cycle,[13−15] and the use of well-defined precursor complexes based on zerovalent palladium alkene complexes.[16] In these studies phenylacetylene was used as the substrate, which showed a high selectivity (>98%) toward the *branched* product. Therefore, the use of such catalysts in the methoxycarbonylation of 4-(isobutyl)-phenylacetylene and 2-ethynyl-6-methoxynaphthalene is of high interest because it provides a short route to Ibuprofen and Naproxen, respectively.

Recently, we have become interested in developing fluorous palladium complexes that can be used to perform methoxycarbonylation reactions in uncommon media such as fluorous biphasic systems (FBS) and supercritical carbon dioxide (scCO_2). In scCO_2 beneficial effects on activity are expected, because of the possibility to achieve complete miscibility of all reaction components involved, including in this case gases such as CO and H_2. Indeed improved activities and selectivities have been observed recently for several catalytic reactions in scCO_2, e.g., the Rh-catalyzed hydroformylation of alkenes[17−19] and the selective hydrogenation of alkynes to *Z*-alkenes.[20] Moreover, ample evidence exists that the introduction of fluorous tails in known ligand systems considerably increases the solubility of both ligands and derived metal catalysts in fluorous solvents and scCO_2.

Chart 2. Ligands Studied in This Paper.



Scheme 1. Synthetic Route for 2-[Bis{4-(bromo)phenyl}phosphino]pyridine 8[a]



[a] Legend: (i) 2 equiv Et_2NH, Et_2O, −75 °C; (ii) 1 equiv *n*-BuLi, hexane/Et_2O, 3:1, 20 °C; (iii) 0.5 equiv **5**, Et_2O, −75 °C; (iv) excess PCl_3, reflux, 1 h; (v) 1 equiv *n*-BuLi, Et_2O, −75 °C; (vi) 1 equiv **7**, −75 °C.

In recent years some of us have successfully applied the $SiMe_{3-x}(CH_2CH_2)_x$ group as a useful spacer to attach perfluoroalkyl chains to several mono- and bidentate phosphine ligands.[21,22] We report here the synthesis of a fluorous 2-[bis(4-aryl)phosphino]pyridine ligand, which is functionalized with $SiMe_2(CH_2CH_2C_6F_{13})$ groups, and derived palladium complexes. For comparison also the −$SiMe_3$-substituted ligand and palladium complexes thereof were prepared. The catalytic activity of the palladium complexes, derived from these new ligands, has been compared with the catalytic activity of the palladium complex derived from the nonfunctionalized ligand **2** in the methoxycarbonylation of phenylacetylene in both regular solvents and apolar solvents such as scCO_2.

Results

Synthesis of 2-[Bis{4-(trialkylsilyl)phenyl}phosphino]pyridines. In principle, the 2-[bis(aryl)phosphino]pyridine ligand can be functionalized with perfluoroalkylsilyl chains in three ways, at either the phenyl rings, the 2-pyridyl ring, or both. Following previously developed routes we decided to explore the functionalization of the phenyl rings. In this paper the following ligands were therefore considered (Chart 2). Ligand **2** is known, whereas **8**, **9**, and **10** are newly reported.

The starting compound, 2-[bis{4-(bromo)phenyl}phosphino]pyridine (**8**), was synthesized according to a four-step route (Scheme 1). For **7** excess PCl_3 instead of HCl(g) was used. This modified method had been reported for the conversion of diisopropylamide-protected phosphines into chlorophosphines in high yields and purity.[23]

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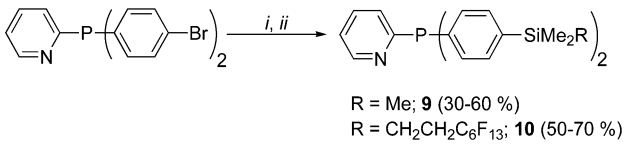
Scheme 2[a]



R = Me; **9** (30-60 %)
R = $CH_2CH_2C_6F_{13}$; **10** (50-70 %)

[a] Legend: (i) 2 equiv *n*-BuLi, THF, −78 °C; (ii) 2 equiv $ClSiMe_2R$, THF, −78 °C.

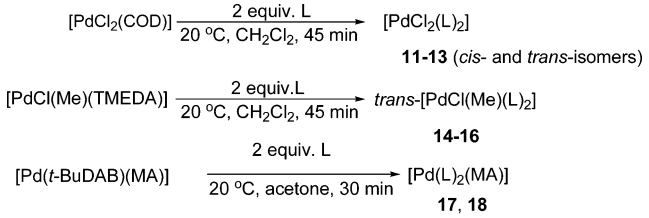
All compounds were obtained pure after workup with **6** as a yellow oil, **7** as a light yellow solid, and **8** as a yellow viscous oil, which slowly solidified upon standing. They were characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy as well as elemental analyses. The $^{31}P\{^1H\}$ NMR resonance of **8** showed an upfield shift ($\delta = -5.35$ ppm) as compared to the resonance of parent 2-[diphenylphosphino]pyridine ($\delta = -2.89$ ppm).

The key step in the synthesis of **8** is the last step in Scheme 1. Both the lithiation of the 2-bromopyridine and the addition of **7** have to be carried out at temperatures lower than −75 °C (preferentially between −75 and −80 °C). If the temperature is higher, especially during the lithiation of 2-bromopyridine, formation of large amounts of bi- and polypyridine compounds are observed as a result of reaction of 2-lithiopyridine with unreacted 2-bromopyridine or with another molecule of 2-lithiopyridine. This results in a significantly lower yield of the final product. Furthermore both *n*-BuLi and **7** have to be slowly added to avoid excessive heating of the solution, leading to the above-mentioned problems.

The functionalization of **8** with alkylsilyl groups was carried out via the method shown in Scheme 2. This synthetic route afforded both **9** and **10** in acceptable yields (**9**, 30−60%; **10**, 50−70%). NMR spectroscopic analyses as well as their correct elemental analyses confirmed the identity of **9** and **10**. Their ^1H NMR spectra showed the same chemicals shifts for the signals corresponding to the various pyridyl and phenyl protons, as well as the expected resonance patterns for the perfluoroalkyl chains for **10** in both its $^{13}C\{^1H\}$ and ^{19}F NMR spectra. Likewise the chemical shifts in the $^{31}P\{^1H\}$ NMR spectra were almost identical (**9**, $\delta = -2.89$ ppm; **10**, $\delta = -2.85$ ppm) and in good agreement with the value found for parent 2-[diphenylphosphino]pyridine ($\delta = -2.89$ ppm). This also indicates that the introduction of a *p*-silyl (either fluorous or nonfluorous) substituent in the phenyl phosphino grouping has little electronic influence on the phosphorus atom. This is desired indeed and is in agreement with previously reported results for derivatives of PPh_3 that employ the perfluoroalkylated ethylsilyl spacer.[21]

The physical properties of **9** and **10** were quite different from each other though. Whereas **9** was initially isolated as a yellow oil, which only solidified on prolonged standing, **10** was obtained as a light yellow solid after washing with *n*-pentane. This difference in appearance at ambient temperature also affected the workup and final yield of both products. Because **10** is a solid, it was quite easy to isolate this fluorous compound in pure form and high yield by repeated washing with *n*-pentane. Compound **9**, however, displayed good to excellent solubility in a broad range of solvents, both polar (MeOH and acetone) and apolar (*n*-pentane, *n*-hexane, and Et_2O). Removal of impurities, such as traces of phosphine-oxide, free pyridine, and only partly substituted phosphine, could be achieved only by washing at low temperatures. This meant that the yield for **9** varied significantly from one reaction to the other.

Scheme 3. Synthetic Routes for the Various Palladium Complexes[a]



11: L = **2**; **12**: L = **8**; **13**: L = **9**;
14: L = **2**; **15**: L = **8**; **16**: L = **10**
17: L = **2**; **18**: L = **10**

[a] Legend: COD = 1,5-cyclo-octadiene, TMEDA = *N,N,N′,N′*-tetramethylethylenediamine, *t*-BuDAB = 1,4-bis(*tert*-butyl)-1,4-diaza-1,3-butadiene, MA = *cyclo*-(−CH=CHC(O)OC(O)−).

Synthesis of Palladium Complexes. To further assess the properties of the new ligands **8**−**10**, we synthesized several of their palladium complexes (Scheme 3).

The $[PdCl_2(L)_2]$ complexes **11**−**13** were obtained as yellow solids in good yields. Complex **11** had already been synthesized using $[PdCl_2(PhCN)_2]$ as the palladium precursor.[24] The compounds showed the expected resonance patterns in the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra. All complexes were obtained as a mixture of *cis*- and *trans*-isomers, with the *trans*-isomer being the major isomer (*trans*:*cis* ratio is ca. 90:10), as was evident from the distinctive signals observed in the $^{31}P\{^1H\}$ NMR spectra for compounds **11**−**13** (singlet at about 23 ppm, indicative for a *trans* bis-phosphine complex, and a second singlet at about 28 ppm, indicative for a *cis* bis-phosphine complex). For compound **12** (with **8** as the ligand) crystals suitable for X-ray diffraction were obtained by slow distillation of *n*-pentane into a solution of the complex in $CDCl_3$ in a standard 5 mm NMR tube at −20 °C. In the crystal structure of **12** the Pd atoms are located on inversion centers of space group $P2_1/c$. The molecular structure of **12** in the crystal and the relevant bond lengths and angles are given in Figure 1 and Table 1, respectively.

Only the *trans*-isomer of **12** was observed in the solid-state structure. The palladium has a square-planar coordination geometry with angles Cl(1)−Pd(1)−P(1) (89.20(3)°) and Cl(1)−Pd(1)−P(1)^i (90.80(4)°) close to 90°. In the crystal structure of the related complex *trans*-$[PdCl_2(PPh_3)_2]$[25,26] these values are 92.03° and 87.97°, respectively. The bond lengths Pd(1)−Cl(1) (2.2828(9) Å) and Pd(1)−P(1) (2.3240(10) Å) are slightly shorter than the values reported for the complex $[PdCl_2(PPh_3)_2]$

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(26) Although in the Cambridge Crystal Structure Database an entry is present for the complex *trans*-[$PdCl_2$[2-(diphenylphosphino]-pyridine)$_2$], no 3D coordinates were reported.

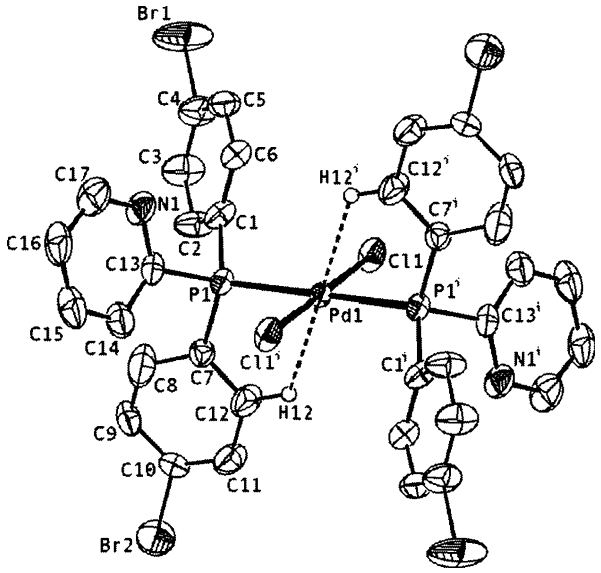

Figure 1. Displacement ellipsoid plot of **12**, drawn at the 50% probability level. All hydrogen atoms, except H(12) and H(12)^i, have been omitted for clarity. Only one orientation of the disordered bromophenyl groups is shown. Symmetry operation i: $-x, -y, -z$.

(2.2905 and 2.3366 Å respectively). A large anisotropy was observed for the 4-(bromo)phenyl rings, but not for the pyridyl ring. In the crystal structure of **12** the distance H(12)−Pd(1) (2.87 Å) is significantly shorter than the sum of the van der Waals radii (3.50 Å), indicating an additional interaction with the d_{z^2} orbital of palladium. Such an interaction has also been observed in the complex *trans*-[$PdCl_2(PPh_3)_2$] (a distance of 2.91 Å was reported).[25] In the latter complex also a short intramolecular Cl−H_{aryl} interaction (2.81 Å) was observed, which is not present in the structure of **12** (Cl(1)−H(12) is 3.36 Å). This therefore leads to a situation for **12** where one of the phenyl rings (C(7)−C(8)−C(9)−C(10)−C(11)−C(12)) is almost perpendicular to the P(1)−P(1)^i−Pd(1)−Cl(1)−Cl(1)^i coordination plane, as was evident from the value of 88.2(3)° for the angle between the least-squares planes of P(1)−P(1)^i−Cl(1)−Cl(1)^i and C(7)−C(8)−C(9)−C(10)−C(11)−C(12). For *trans*-[$PdCl_2(PPh_3)_2$] the angle between the least-squares plane of P(1)−P(1)^i−Cl(1)−Cl(1)^i and C(7)−C(8)−C(9)−C(10)−C(11)−C(12) has a value of 69.99° (Figure 2). Furthermore, in complex **12** an *intermolecular* hydrogen bond is present between H(16) and the chloride of a neighboring palladium complex (2.76 Å, angle of 132°).

The palladium methyl chloride complexes **14**−**16**, which were synthesized following the same route as reported for the triphenylphosphine complex,[27] were isolated as light yellow solids. They were characterized by their ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopic data and elemental analysis and, for **16**, also by ^{19}F NMR, which showed the expected signals for the C_6F_{13} tail. Unfortunately, for complex **15** no good elemental analyses could be obtained, due to the presence of impurities, which could not be removed. In all ^{1}H NMR spectra at ambient temperature, the signal for Pd-*Me* was observed as a broad singlet instead of the expected triplet, arising from coupling to both ^{31}P nuclei. For all complexes, however, cooling of the samples to −10 °C led to the appearance of the expected triplet for the Pd-*Me* signal ($^3J_{H,P}$ = 6.2 Hz), due to coupling with the two P atoms. The appearance of this triplet, along with only one signal in the ^{31}P{^{1}H} NMR spectra, also showed that complexes **14**−**16** have the *trans* bis-phosphine configuration. These results point to the presence of an exchange process at ambient temperature. One possibility could be the displacement of the chloride by the nitrogen of the pyridyl ring, which has been shown to occur by others in complexes such as [PdCl(Me)(N−N−N)] (N−N−N = 2-(2-((2′-pyridylmethylene)amino)ethyl)-pyridine (MAP)[28] or 2,6-bis(pyrimidin-2-yl)pyridine (bppy)[29]). We therefore performed ^{15}N NMR measurements (using the DEPT sequence) with both the free ligand **2** and complex **14** in order to study this process in more detail. For **2**, a triplet at −51 ppm (relative to nitromethane) was observed.[30] Unfortunately, for complex **14** no signal could be observed, despite several attempts and variation of several parameters.[31] Apparently, the N−H coupling, needed for the DEPT measurement, is lost upon coordination of the ligand to palladium. This has also been reported for complexes of the type [PdCl(Me)(N−N−N)].[28]

The zerovalent palladium complex **17** was obtained as a yellow solid in good yield following a literature method published for the corresponding triphenylphosphine complex.[32] In its room-temperature ^{1}H NMR spectrum (in CD_2Cl_2) the signal for the olefinic CH of MA was observed as a broad singlet instead of the expected doublet. In the aromatic region some signals for the pyridyl protons as well as the aryl protons were overlapping. The ^{13}C{^{1}H} NMR spectrum (20 °C) showed broad signals in the aromatic region. When the sample was cooled to −30 °C, the signal in the ^{1}H NMR spectrum for the CH's of MA became a doublet with a ^3J(^{1}H−^{31}P) of 5.5 Hz. Also the overlapping signals in the aromatic region for the pyridyl protons sharpened into distinct doublets and triplets.

The ^{13}C{^{1}H} NMR spectrum at −40 °C revealed the =*C*H resonance of maleic anhydride as a multiplet pattern (Figure 3, top left), similar to that observed for [$Pd(PPh_3)_2$(*cyclo*-(−CH=CHC(O)OC(O)−))].[33] As was shown for that complex also for **17** the observed pattern is the X part of an AA′X pattern (A = ^{31}P, A′ = ^{31}P, for the simulated spectrum (using WINDNMR[34]) see Figure 3, bottom left[35]) with exchange between the A and A′ nuclei.

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(30) For the ^{15}N NMR measurement of **2** a value of ^2J(^{15}N−^{1}H) of 11 Hz was used.

(31) Measurements with **14** were carried out at −15 °C. Different values of ^2J(^{15}N−^{1}H), namely, 3, 9, and 11 Hz, were tried, as well as longer delay times (d1) and longer acquisition periods (up to 72 h).

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(35) The following values were used in the simulation of this pattern: $V_{AA'}$ = 0.3 Hz, $J_{AA'}$ = 12.0 Hz, J_{AX} = −7.5 Hz (*cis*-phosphine), $J_{A'X}$ = 29.4 Hz (*trans*-phosphine), $K_{AA'}$ = 5.0.

Table 1. Selected Bond Lengths, Bond Angles, and Torsion Angles for *trans*-[PdCl$_2$(P{C$_6$H$_4$-*p*-Br}$_2${C$_5$H$_4$N-2})$_2$] (12)[a]

Bond Lengths (Å)			
Pd(1)−P(1)	2.3240(8)	Pd(1)−Cl(1)	2.2827(8)
Bond Angles (deg)			
Cl(1)−Pd(1)−P(1)^i	90.80(3)	Cl(1)−Pd(1)−P(1)	89.20(3)
Torsion Angles (deg)			
Cl(1)−Pd(1)−P(1)−C(1)	−32.15(13)	Cl(1)−Pd(1)−P(1)−C(7)	88.70(13)
Cl(1)−Pd(1)−P(1)−C(13)	−152.36(15)	Cl(1)^i−Pd(1)−P(1)−C(1)	147.85(13)
Cl(1)^i−Pd(1)−P(1)−C(7)	−91.30(13)	Cl(1)^i−Pd(1)−P(1)−C(13)	27.64(15)

[a] Symmetry operation *i*: $-x, -y, -z$.

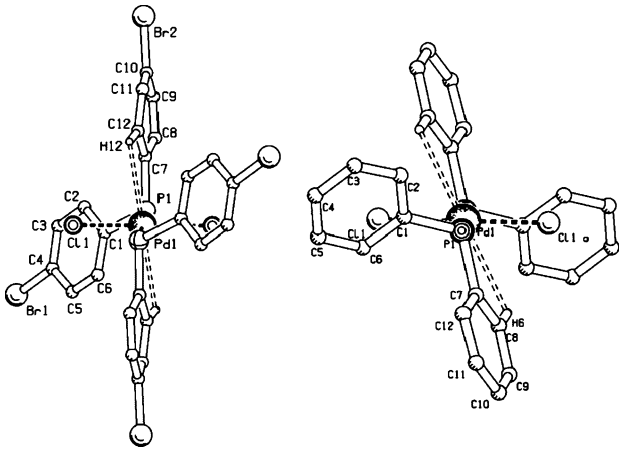


Figure 2. Crystal structure of **12** (left) and *trans*-[PdCl$_2$(PPh$_3$)$_2$] (right), showing the tilting of one of the phenyl rings. For **12** the pyridyl ring and all hydrogen atoms not involved have been omitted; for *trans*-[PdCl$_2$(PPh$_3$)$_2$] one of the phenyl rings and all hydrogen atoms not involved have been omitted.

In the aromatic region, multiplet signals corresponding to the carbon atoms of the phenyl ring as well as the *ipso*-C of the pyridyl ring were observed. For the *ortho*- and *meta*-PPh$_2$ carbon atoms the expected virtual triplet pattern was observed,[36,37] but they were observed as two sets of separate signals. For the *ipso*-C PPh$_2$ carbon atom a more complicated multiplet pattern was observed (see Figure 3, top right). This multiplet pattern could be simulated (using WINDNMR[34]), which showed that this pattern is the X-part of an AA′X pattern (A = ^{31}P, A′ = ^{31}P, Figure 3, bottom right).[38] When the ^{13}C NMR spectrum was measured with simultaneous decoupling of ^{1}H and ^{31}P, the spectrum simplified. The resonance for =*C*H (MA) became a singlet, while the multiplets in the aromatic region became two sets of singlets. This proves that the multiplet structure was caused by coupling to ^{31}P, while the observation of two sets of signals for the phenyl rings under simultaneous ^{1}H and ^{31}P decoupling indicates that the phenyl rings of the phosphorus ligand are nonequivalent. The ^{31}P-{^{1}H} NMR spectra showed in the whole temperature range a singlet at 30.06 ppm.

We also attempted the synthesis of complex **18**, based on the fluorous ligand **10**. Although complex formation did indeed take place, as confirmed by the expected ^{1}H and ^{31}P{^{1}H} NMR resonance patterns, purification of **18** was not possible due to the presence of free *tert*-butyl DAB. For **17**, this ligand could be removed by washing with Et$_2$O at room temperature, but for **18** the complex and the free *tert*-butyl DAB have similar solubility properties, making separation difficult. Other methods, such as removal of *tert*-butyl DAB at low temperature or by sublimation, did indeed lower the amount of free DAB in the final product. This procedure led to very low product yields and did not result in a completely pure product.

Catalysis. We applied in situ prepared palladium catalysts based on [Pd(OAc)$_2$] with **2** and the new ligands **9** and **10** as well as the zerovalent palladium complex **17** in the methoxycarbonylation of phenylacetylene. The in situ catalysts were prepared according to the conditions as described by Scrivanti (Scheme 4).[10] The results are presented in Table 2.

All in situ prepared catalysts afforded complete conversion of the substrate (Pd:substrate = 1:4000, 50 min reaction time, 50 °C) when the solvent used was pure methanol. If a 1:1 mixture of methanol and α,α′,α″-trifluorotoluene was used, the catalyst derived from the new ligand **10** showed a higher activity than the one with **2**. In both solvents catalyst systems with **10** also gave a selectivity toward the *branched* product similar to those with **2**, indicating that *para*-substitution of the phenyl rings with either a fluorous or a nonfluorous alkylsilyl moiety did not affect the catalysis. For **2** and **10** it was observed that when a 1:1 mixture of MeOH and α,α′,α″-trifluorotoluene was used, a slight decrease in the selectivity toward the *branched* product was obtained.

The catalytic system with ligand **10** was also tested in the methoxycarbonylation of phenylacetylene in scCO$_2$. A slight modification of the above experiments was adopted to ensure that the total volume of the organic phase was approximately 5 mL (note that the total volume of the autoclave used is 50 mL). Therefore, phenylacetylene and methanol were added in a 1:2 ratio, whereas all other ratios were the same as given in Scheme 4 and Table 2. Confirmation that the mixture was indeed supercritical and homogeneous was achieved by visual inspection of the autoclave interior after heating and pressurization.[39] It was observed that a

(36) The appearance of these triplets is due to virtual ^{31}P-coupling. Such a resonance pattern is observed for AA′X spins systems when $J_{AA'} \gg (V_A - V_{A'}) + (J_{AX} + J_{A'X})/2$, see: Wiberg, K. B., Nist, B. J., Eds. *Interpretation of NMR Spectra*; W. A. Benjamin, Inc.: New York, 1962; pp 21−27. The appearance of such virtual triplets is not uncommon for PPh$_3$ ligands when coordinated to metal centers. It has for instance been observed for [Pt(PPh$_3$)$_2$(*trans*-CH(CO$_2$Et)=CH(CO$_2$Et))], see: Guedes da Silva, M. F. C.; Fraústo, J. J. R.; Pombeiro, A. J. L.; Betani, R.; Michelin, R. A.; Mozzon, M.; Benetollo, F.; Bombieri, G. *Inorg. Chim. Acta* **1993**, *214*, 85.

(37) Verkade, J. G. *Coord. Chem. Rev.* **1972/73**, *9*, 1.

(38) The following values were used in the simulation of this pattern: $V_{AA'} = 3.4$ Hz, $J_{AA'} = 17.2$ Hz, $J_{AX} = 2.3$ Hz (*cis*-phosphine), $J_{A'X} = 34.1$ Hz (*trans*-phosphine), $K_{AA'} = 2.2$.

(39) This autoclave was built in-house at the University of Amsterdam. For a detailed technical description, see ref 20, chapter 2.

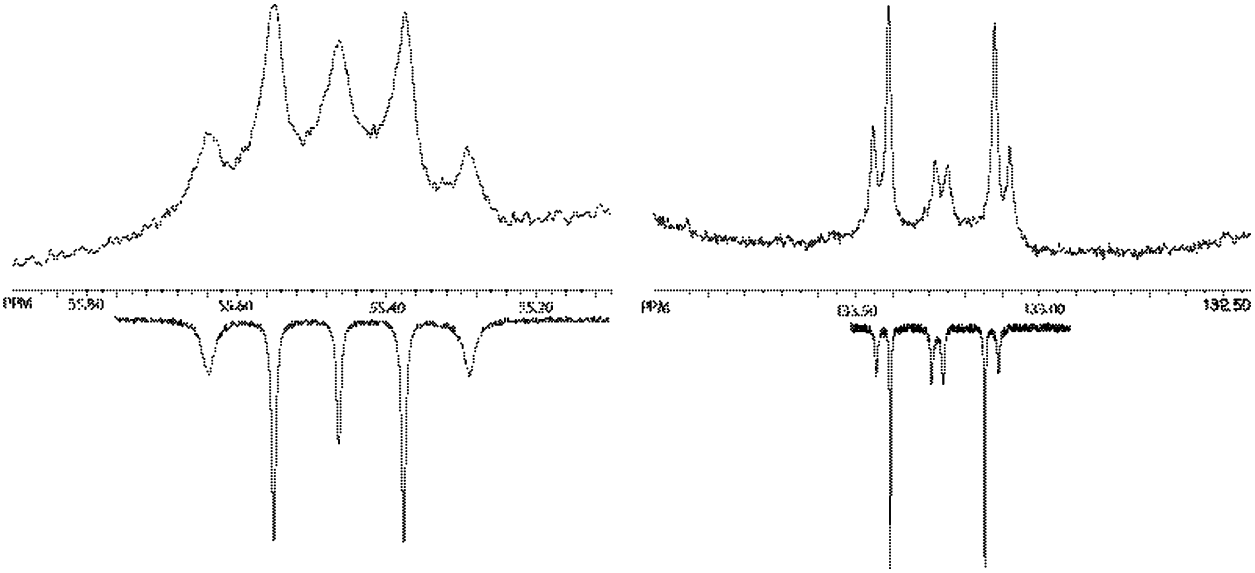


Figure 3. $^{13}C\{^1H\}$ NMR spectrum, alkene region (top left) and part of the aromatic region (top right) of complex **17**, in CD_2Cl_2 at −40 °C. Bottom left and right are simulations of these patterns.

Scheme 4. Palladium-Catalyzed Methoxycarbonylation of Phenylacetylene

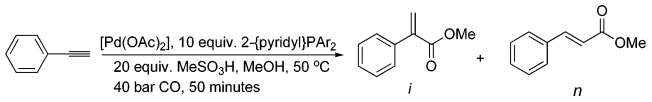


Table 2. Results for Methoxycarbonylation of Phenylacetylene with Catalysts Derived from 2, 9, or 10[a]

entry	ligand	solvent	conversion (%)	*i*:*n*[b]
1	**2**	MeOH	100	97.8:2.2
2	**9**	MeOH	100	98.2:1.8
3	**10**	MeOH	100	98.3:1.7
4	**2**	MeOH/BTF[c]	75	96.5:3.5
5	**10**	MeOH/BTF[c]	85	96.8:3.2

[a] General conditions: Pd:substrate = 1:4000, [phenylacetylene] = 1.4 mmol/mL, stirrer = 400 rpm. [b] Estimated error in the *i*- and *n*-values: ±0.1. [c] BTF = $C_6H_5CF_3$.

Scheme 5. Conditions for Methoxycarbonylation of Phenylacetylene with [Pd(2)$_2$(*cyclo*-(CH=CHC(O)OC(O)−))] (17)

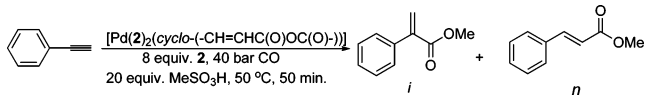


Table 3. Results for the Methoxycarbonylation of Phenylacetylene with 17 as the Precursor[a]

entry	Pd:substrate	solvent	conversion (%)	*i*:*n*[b]
1	1:4000	MeOH	100	98.4:1.6
2	1:8000	MeOH	99	98.5:1.5
3	1:20000	MeOH	40	98.2:1.8
4	1:4000	MeOH/BTF[c]	100	98.8:1.2
5	1:8000	MeOH/BTF[c]	75	97.6:2.4

[a] General conditions: [phenylacetylene] = 1.4 mmol/mL, stirrer = 400 rpm, Pd:ligand = 1:10. [b] Estimated error in the *i*- and *n*-values: ±0.1. [c] BTF = $C_6H_5CF_3$.

homogeneous solution was obtained at *P*(total) = 140 bar (*P*(CO) = 40 bar). Initial catalytic tests performed at *P*(total) = 150 bar gave a conversion of 50% (turnover number (TON) = 2000) in 50 min and a selectivity for the *branched* product of more than 99%. The presence of perfluoroalkyl chains in the palladium catalyst provided an enormous improvement, since application of nonfluorous **2** as ligand under identical conditions gave a suspension and only 3% conversion (TON = 120) in 50 min time.

It has been reported that for the in situ prepared catalysts a certain ligand-to-palladium ratio is needed to convert the palladium precursor into the actual catalytic species.[13,14] In this process some ligand is sacrificed and oxidized to the corresponding phosphine oxide. Furthermore, only a small amount (15−20%) of the starting palladium compound is transformed into an active species, the bulk being present as unidentified polynuclear species.[13] We were therefore interested to see if we could apply a more well-defined palladium(0) complex as a catalyst precursor for the methoxycarbonylation of phenylacetylene. The use of palladium(0)-alkene complexes as precursors for this reaction has been reported.[16] We therefore applied **17** as a precursor complex using the conditions given in Scheme 5. The results of these catalytic reactions using **17** are given in Table 3.

From this table one can see that the zerovalent complex **17** is an excellent precursor for the methoxycarbonylation reaction, giving complete conversion for substrate-to-palladium ratios of 4000:1 and 8000:1 in MeOH. At higher substrate-to-palladium ratios incomplete conversion is observed in 50 min. A conversion of 40% (corresponding to a TON of 8000, see entry 3 in Table 3) is then reached. In a 1:1 mixture of methanol and α,α′,α″-trifluorotoluene the activity is somewhat lower (TON of ca. 6000), although it is still about twice as high when compared to the in situ prepared catalyst from $[Pd(OAc)_2]$ and **2** (compare entry 5 in Table 3 with entry 4 in Table 2). Furthermore, the selectivity to the *branched* ester is not affected and remained in all experiments above 97%. For **17** in MeOH a time-versus-conversion profile was established by sampling the reaction at regular intervals and plotting the results (Figure 4). As is clearly seen, the activity is very high in the first 5 to 10 min and then starts to level off. Using the data from Figure 4 we can see that after about 10 min 50% of the substrate has been consumed. This

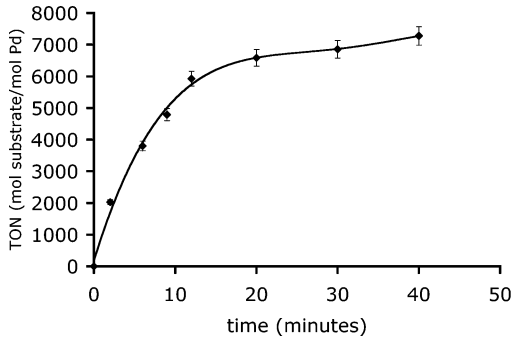


Figure 4. Conversion (TON) versus time plot for complex **17**. General conditions: Pd:substrate = 1:10173, [phenylacetylene] = 1.4 mmol/mL, 50 °C, 40 bar CO, solvent = MeOH.

Table 4. Influence of Ligand-to-Palladium Ratio on Activity of 17 in Methoxycarbonylation of Phenylacetylene[a]

entry	ligand:palladium	conversion (%)	*i*:*n*[b]
1	10	98	98.0:2.0
2	8	99	98.5:1.5
3	6	>99	98.3:1.7
4	4	>99	98.4:1.6
5	3	85	98.5:1.5
6	2	35	98.5:1.5

[a] General conditions: Pd:substrate:$MeSO_3H$ = 1:8000:20, 40 bar CO, 50 °C, 50 min, stirrer = 400 rpm, [phenylacetylene] = 1.4 mmol/mL, solvent = MeOH. [b] Estimated error in the *i*- and *n*-values: ±0.1.

corresponds to a TOF_{50} value of about 30 000 mol substrate per mol palladium per hour.

Furthermore, application of a zerovalent palladium alkene complex as a precursor might allow lower ligand-to-palladium ratios, since in principle no ligand will be sacrificed to form the catalytically active species.[14] To study the best ligand-to-palladium ratio without lowering the activity and selectivity of the catalyst, the experiments shown in Table 4 were performed. For a ligand:Pd(0) ratio of 2, i.e., when complex **17** itself was used, the conversion was only 35% after 50 min (entry 6, Table 4). Addition of one extra equivalent of ligand (entry 5 in Table 4) gave a dramatic increase in the catalytic activity to 85% conversion in the same time. With two extra equivalents added (total ligand-to-palladium ratio is 4, entry 4 in Table 4) complete conversion is observed within the reaction time (50 min). Further increase of the ligand:Pd(0) ratio had no further beneficial effect and beyond a certain point appeared to cause a small decrease in catalyst activity.

Discussion

The new ligands **9** and **10** display a coordination behavior similar to that of the unsubstituted ligand 2-[diphenylphosphino]pyridine (**2**). This was not unexpected, since the introduced funtionalities at the *para*-positions are expected not to introduce significant steric hindrance at the metal center. Moreover, the $^{31}P\{^1H\}$ NMR chemical shifts observed for the different complexes showed similar values, which indicated that the electron-withdrawing effect of the perfluoroalkyl chains on the phosphorus atom is attenuated by the silicon atom.

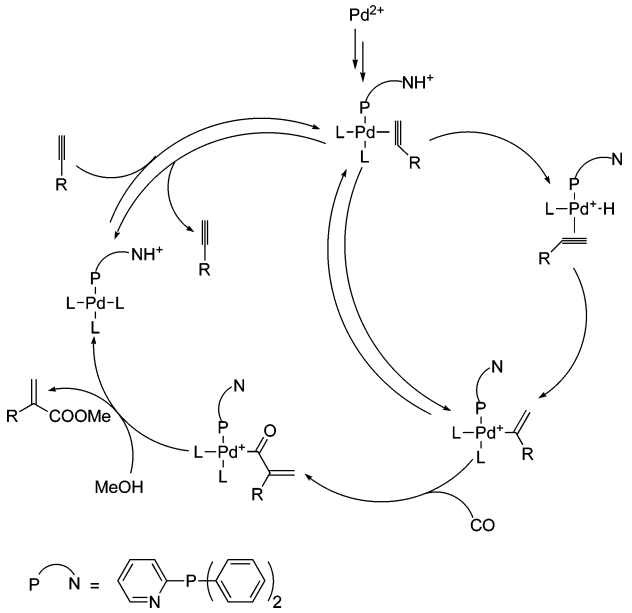
The $^{13}C\{^1H\}$ NMR spectrum of **17** at −40 °C showed some very special features in the aromatic region. Not only were the signals for the *ipso*-C PPh_3 carbon atoms observed as complicated multiplet patterns instead of the expected virtual triplets, but also all the signals for the PPh_2 carbon atoms were split into two sets. The presence of these multiplet signals for the *ipso*-C as well as the observed multiplet for the alkene carbon atoms are the result of an AA′X spin system with exchange between A and A′, as was shown when these patterns were simulated. Since simultaneous decoupling of ^1H and ^{31}P resulted in the disappearance of the multiplet patterns, but not the splitting of the aromatic signals into two sets, this provides evidence that the phosphorus centers are diastereotopic; that is, the molecule does not have an apparent symmetry plane containing the phosphorus centers. This can be caused by the fact that there is no free rotation around the Pd−P bond at this low temperature. When the $^{13}C\{^1H\}$ NMR spectrum of **17** was measured at ambient temperature, we observed that these multiplet patterns had disappeared and that all signals were observed as broad singlets. Apparently the interchange process between two different isomers of the complex, possibly caused by alkene rotation around the palladium(C=C) bond, dissociation/reassocation reaction of the alkene, or Pd−P rotation, becomes fast at room temperature.[40]

Catalytic methoxycarbonylation of phenylacetylene using the in situ prepared catalysts has demonstrated that the influence of funtionalization of the P,N-ligand with a fluoroalkyl group is especially evident when catalysis was performed in a 1:1 (v/v) mixture of methanol and α,α′,α″-trifluorotoluene, where the use of **10** led to a higher conversion compared to **2**. A possible explanation might be that the actual catalyst is formed with different rates and efficiency. Ligand **10**, with its perfluoroalkyl silyl groups attached, might be more compatible with the more apolar medium. Subtle influences such as more favorable formation of mononuclear species of the type $[Pd(OAc)_2(\{2\text{-pyridyl}\}PAr_2)_2]$ might play a role here. The effect of perfluoralkyl functionalization was even more pronounced when the reaction was performed in $scCO_2$. An in situ prepared catalyst that has **10** as the ligand gave a homogeneous solution and a good activity, whereas with **2** a suspension was obtained and only a low activity. In $scCO_2$ also a higher selectivity toward the *branched* product was observed when compared with the reactions in methanol and methanol:α,α′,α″-trifluorotoluene 1:1 (v/v). These results therefore show that the methoxycarbonylation of phenylacetylene and other alkynes in $scCO_2$ clearly has potential, which warrants further investigations.

The distinct difference in activity when zerovalent palladium complex **17** is used instead of the in situ prepared catalyst can be explained by considering the crucial steps in the proposed catalytic cycle (Scheme 6).[13] As mentioned earlier, the in situ catalyst first proceeds through several steps before the actual catalytically

(40) These processes have been observed in other palladium(0)-alkene complexes as well, see: (a) Gómez-de la Torre, F.; Jalón, F. A.; López-Agenjo, A.; Manzano, B. R.; Rodríguez, A.; Sturm, T.; Wassensteiner, W.; Martínez-Ripoll, M. *Organometallics* **1998**, *17*, 4634. (b) Manzano, B. R.; Jalón, F. A.; Gómez-de la Torre, F.; López-Agenjo, A. M.; Rodríguez, A. M.; Mereiter, K.; Weissensteiner, W.; Sturm, T. *Organometallics* **2002**, *21*, 789. (c) van Asselt, R.; Elsevier, C. J. *Inorg. Chem.* **1994**, *33*, 1521.

Scheme 6. Proposed Catalytic Cycle for the Methoxycarbonylation of Alkynes[a]



[a] R = methyl or phenyl.

active species, presumably a palladium(0) complex, is formed. In this process only a small part of the starting compound is converted into a catalytically active species.[13,14] When the zerovalent palladium complexes are used, these initial reactions are not required, because the catalyst precursor in this case will closely resemble the actual catalytically active species. The only step required is a replacement of the coordinated alkene by an alkyne, which is a facile process. It can be assumed that a larger part of the precursor complex is directly available to play a role in the catalytic cycle.

Variation of the ligand-to-palladium ratio with the zerovalent palladium complex as precursor showed that a certain excess of ligand is needed to obtain good conversions. This can be explained in the following manner. It has been proposed that one of the key steps in the catalytic cycle of Scheme 6 is the transfer of H^+ from the N atom of the pyridine ring to the coordinated alkyne (whether this goes via a palladium hydride will not be discussed here[41]). When a low ligand-to-palladium ratio is used (lower than 4), we can assume that there is a competition between the phosphine ligand, CO, and also methanol to coordinate to the palladium center. This might lead to a situation where only one phosphine ligand is coordinated to palladium and in the *trans*-position to the alkyne. Furthermore, it is known in the literature that with this type of ligand formation of polynuclear species is a feasible process,[13,42] and we expect that this is especially favorable at low ligand-to-palladium ratios. When more than 2 equiv of ligand is present, this formation of polynuclear species will be disfavored and the concentration of mononuclear species, with at least two phosphines coordinated to the palladium center and in the right geometry, will be increased, thus enhancing the activity. When the ligand-to-palladium ratio is too high, on the other hand, the phosphine ligand competes with CO and/or methanol for coordination to the metal center, thus slowing down the catalyst somewhat. In the range of ligand-to-palladium ratio we studied, however, this is only a marginal effect.

Conclusions

In conclusion, we have developed a new route toward 2-[bis(4-substituted aryl)phosphino]pyridines. These compounds were readily made from a convenient starting compound, the *p*-bromo-functionalized phosphine **8**, which itself was obtained in high yield via a four-step route. A number of palladium complexes were made with these new P,N-ligands and it was shown that they displayed a coordination behavior similar to that of the nonfunctionalized ligand **2**.

Testing of the new ligands **9** and **10** in both methanol and a 1:1 (v/v) mixture of methanol and α,α′,α″-trifluorotoluene showed that 4-(perfluoroalkyl)ethylsilyl functionalization has a beneficial effect on activity when compared with **2** (a TON of about 3400 was reached with **10** in MeOH/α,α′,α″-trifluorotoluene, 1:1, compared to 3000 with **2** as the ligand), while selectivity was not affected (about 97−98% toward the *branched* ester). For the methoxycarbonylation of phenylacetylene in $scCO_2$ the use of [$Pd(OAc)_2$] with **10** as the ligand afforded an active catalyst (TON of about 2000), which showed a significantly higher selectivity (>99%) for the *branched* ester than in regular solvents. The use of complex **17** afforded a catalyst that is twice as active (TON of about 6000 in MeOH/α,α′,α″-trifluorotoluene, 1:1, 8000 in MeOH) as the in situ prepared catalysts in regular solvents. These results allow the further development of new catalysts that combine high activity and selectivity with excellent compatibility with apolar solvents such as $scCO_2$.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk techniques under N_2 atmosphere. Diethyl ether and THF were distilled from Na/benzophenone, acetone was distilled from B_2O_3, benzene, *n*-pentane, and *n*-hexane were distilled from sodium wire, methanol was distilled from $Mg(OMe)_2$, and CH_2Cl_2 was distilled from CaH_2. α,α′,α″-Trifluorotoluene was degassed via freeze−pump−thaw cycles (3 times) and stored on molecular sieves. C_6D_6 (Cambridge Isotopes Laboratories, CIL) was degassed and stored under nitrogen on Na. $CDCl_3$ and CD_2Cl_2 (CIL) were degassed and stored under nitrogen on molecular sieves. PCl_3 was refluxed to expel dissolved HCl and subsequently distilled.[43] Phenylacetylene (98%, Acros) was flashed over a short column (neutral alumina (Merck)) prior to use. All other reagents (Acros, Aldrich, Lancaster) were used as received. ^1H, $^{13}C\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Unity-INOVA 300 MHz, a Varian Unity-INOVA 500 MHz, a Varian Mercury-VxWorks 300 MHz, or a Varian Mercury 200 MHz spectrometer at 25 °C unless stated otherwise. Additional $^1H-^1H$ COSY-45 and $^{13}C-^1H$ HETCOR spectra were recorded on a Varian Unity-INOVA 500 MHz to assign ^1H and ^{13}C signals for compounds **8**, **9**, **10**, and **17**. The COSY measure-

(41) The route where a direct transfer of the H^+ from the pyridyl N atom to the coordinated alkyne takes place seems more plausible, since this route can explain all the results acquired from several experiments as described in the literature. See: (a) Ref 13. (b) Trost, B. M.; Schmidt, T. *J. Am. Chem. Soc.* **1988**, *110*, 2301.

(42) Newkome, G. R. *Chem. Rev.* **1993**, *93*, 2067, and references therein.

(43) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988; p 336.

ments were performed with a relaxation delay of 1 s, an acquisition time of 193 ms, 8 scans per FID, and 512 increments. This gave a 2K × 2K data matrix, which was further processed with the VNMR software package. For the HETCOR measurements a relaxation delay of 2 s and an acquisition time of 81 ms were used. Per FID 48 scans were performed and a total of 128 increments were used. This gave a 4K × 1K data matrix, which was further processed with the VNMR software package. ^{15}N NMR measurements were performed using the DEPT sequence on a Bruker DRX-300 spectrometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the residual solvent peak (^{1}H: $CHCl_3$ $\delta = 7.26$ ppm, C_6HD_5 $\delta = 7.16$ ppm, $CHDCl_2$ $\delta = 5.35$ ppm; ^{13}C: $CDCl_3$ $\delta = 77.16$ ppm, C_6D_6 $\delta = 128.06$ ppm, CD_2Cl_2 $\delta = 54.00$ ppm), ^{31}P{^{1}H} NMR spectra externally to H_3PO_4 (85%), ^{19}F NMR spectra externally to $CFCl_3$, and ^{15}N NMR spectra externally to nitromethane. Abbreviations used: s = singlet, d = doublet, t = triplet, vt = virtual triplet, q = quartet, m = multiplet. Elemental analyses were carried out by H. Kolbe Mikroanalytisch Laboratorium, Müllheim an der Ruhr. GC analyses were performed on a Varian 3300 gas chromatograph, equipped with J&W Scientific Inc. DB-5 column (30 m, 0.320 mm internal diameter) and a FID detector (280 °C), using N_2 as the carrier gas and attached to a Varian 4400 integrator. The compounds [$RhCl(PPh_3)_3$],[44] 2-[diphenylphosphino]pyridine (**2**),[45] Et_2NPCl_2 (**5**),[46] [$PdCl_2$(COD)],[47] [PdCl(Me)(TMEDA)],[27] and [Pd(*t*-BuDAB)(*cyclo*-(−CH═CHC(O)OC(O)−))][32] were synthesized as reported.

Autoclaves. Standard catalytic runs were performed by using two different autoclaves, except for the experiments in $scCO_2$, where only the second autoclave described was used. One was a stainless steel autoclave with a total volume of 100 mL, equipped with a pressure gauge, a rupture disk assembly, and a connection to the high-pressure system. To avoid contamination from the autoclave walls, a glass insert was used with this autoclave. The second autoclave was an in-house built stainless steel autoclave ($V = 50$ mL),[39] equipped with two borosilicate (Maxos 200) windows to allow visual inspection of the interior of the autoclave, a pressure transducer, temperature gauges inside the autoclave and the wall, a rupture disk assembly (set at 250 bar), and four heating elements in the wall for heating. For both autoclaves the contents were stirred via magnetic stirring bars at 400 rpm.

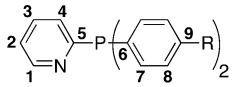
Synthesis of Chlorodimethyl(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl)silane. To a solution of [$RhCl(PPh_3)_3$] (0.19 g, 0.21 mmol) in benzene (20 mL) were added 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene (11.47 g, 33.1 mmol) and $HSiMe_2Cl$ (7.5 mL, 66.2 mmol). The resulting light yellow solution was refluxed for 2 h. After cooling the excess $HSiMe_2Cl$ and benzene were distilled off at ambient pressure. The final product was obtained by flame distillation at reduced pressure as a colorless liquid (12.47 g, 28.0 mmol, 85% based on 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene). All NMR data were in accordance with literature values.[48]

Synthesis of Bis(4-(bromo)phenyl) *N,N*-Diethylphosphoramidite (6). To a stirred solution of 1,4-dibromobenzene (9.11 g, 38.6 mmol) in a 3:1 (v/v) mixture of hexane and Et_2O was added a 1.6 M solution of *n*-BuLi in hexane (24.3 mL, 38.9 mmol). The mixture was stirred for 15 min at room temperature, during which a white suspension was formed. This suspension was cooled to −75 °C, and Et_2NPCl_2 (3.51 g, 21.9 mmol) was added. The resulting yellowish suspension was allowed to reach room temperature during overnight stirring. The suspension was centrifuged and all volatiles of the liquid layer were removed in vacuo, yielding the desired product as a yellow oil (7.90 g, 19.2 mmol, 99%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 0.96 (t, $^{3}J_{H,H} = 7.0$ Hz, 6 H, CH_3), 3.05 (dq, $^{3}J_{H,P} = 2.6$ Hz, $^{3}J_{H,H} = 7.0$ Hz, 4 H, CH_2), 7.25 (t, $^{3}J_{H,H} = 7.2$ Hz, H-aryl), 7.47 (d, $^{3}J_{H,H} = 6.9$ Hz, H-aryl). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 14.8 (d, $^{3}J_{C,P} = 3.2$ Hz, CH_3), 44.5 (d, $^{2}J_{C,P} = 15.7$ Hz, CH_2), 123.2 (d, $^{4}J_{C,P} = 1.2$ Hz, *p*-C C_6H_4), 131.5 (d, $^{3}J_{C,P} = 5.9$ Hz, *m*-C C_6H_4), 133.7 (d, $^{2}J_{C,P} = 20.7$ Hz, *o*-C C_6H_4), 139.2 (d, $^{1}J_{C,P} = 16.2$ Hz, *ipso*-C C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ 59.8 (s). Anal. Calcd for $C_{16}H_{18}Br_2NP$: C 46.29, H 4.37, N 3.37, P 7.46. Found: C 46.42, H 4.48, N 3.31, P 7.41.

Synthesis of Chlorobis(4-(bromo)phenyl)phosphine (7). To a sample of **6** (6.64 g, 16.0 mmol) was added 15 mL of PCl_3. The mixture was stirred at 75 °C for 2 h. After cooling to room temperature the excess PCl_3 and formed Et_2NPCl_2 were distilled off by flame distillation under reduced pressure. The yellow-orange solid residue was extracted twice with *n*-pentane and Et_2O. After removing the volatiles in vacuo a light yellow solid was obtained (5.86 g, 15.5 mmol, 99%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.43 (t, $J = 7.8$ Hz), 7.56 (t, $J = 8.4$ Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 125.8 (s, *p*-C C_6H_4); 132.3 (d, $^{3}J_{C,P} = 6.7$ Hz, *m*-C C_6H_4); 133.2 (d, $^{2}J_{C,P} = 24.6$ Hz, *o*-C C_6H_4); 137.3 (d, $^{1}J_{C,P} = 33.8$ Hz, *ipso*-C C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ 78.6 (s). Anal. Calcd for $C_{12}H_8Br_2ClP$: C 38.09, H 2.13, P 8.18. Found: C 38.15, H 2.04, P 8.28.



Numbering scheme for the 2-[bis(aryl)phosphino]pyridine ligands in compounds 8-17.

Synthesis of 2-[Bis{4-(bromo)phenyl}phosphino]pyridine (8). To a solution of 2-bromopyridine (1.42 g, 8.99 mmol) in Et_2O at −75 °C was added dropwise a 1.6 M solution of *n*-BuLi in hexane (5.8 mL, 9.28 mmol). The resulting dark red solution was stirred for 1 h at −75 °C, after which **7** (3.42 g, 8.99 mmol) in Et_2O was added dropwise. The resulting orange suspension was allowed to reach room temperature overnight. To the yellow-orange suspension was added degassed H_2O (20 mL). After phase separation the aqueous layer was extracted twice with Et_2O. The combined organic fractions were dried on $MgSO_4$ and filtered and the volatiles removed in vacuo. The resulting orange oil (crude product) was extracted twice with *n*-pentane. After combining the pentane layers the solvent was evaporated. The final product was obtained as a yellow solid (2.63 g, 6.29 mmol, 70%).

^{1}H NMR (C_6D_6, 300.1 MHz): δ 7.12 (d, $J = 7.5$ Hz, 2 H, H-*pyridyl*), 7.24 (m, H-*aryl* and H-*pyridyl*), 7.48 (d, $J = 8.4$ Hz, H-*aryl*), 7.58 (t, $J = 4.5$ Hz, H-*pyridyl*), 8.71 (d, $J = 3.9$ Hz, H-*pyridyl*). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 122.39 (s, C(2)); 124.16 (s, C(9)); 128.26 (d, $^{3}J_{C,P} = 23.9$ Hz, C(3)); 132.02 (d, $^{3}J_{C,P} = 7.2$ Hz, C(8); 135.41 (d, $^{2}J_{C,P} = 4.5$ Hz, C(4)); 135.96 (d, $^{1}J_{C,P} = 12.8$ Hz, C(6)); 136.06 (d, $^{2}J_{C,P} = 20.6$ Hz, C(7)); 150.62 (d, $^{3}J_{C,P} = 10.6$ Hz, C(1)); 163.13 (d, $^{1}J_{C,P} = 1.9$ Hz, C(5)). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ −5.34 (s). Anal. Calcd for $C_{17}H_{12}Br_2NP$: C 48.49, H 2.87, Br 37.95, N 3.33, P 7.36. Found: C 48.52, H 2.87, Br 37.69, N 3.26, P 7.39.

Synthesis of 2-[Bis{4-(trimethylsilyl)phenyl}phosphino]-pyridine (9). A solution of **8** (1.04 g, 2.47 mmol) in THF was cooled to −80 °C with an ethanol/liquid N_2 bath. Subsequently, a 1.6 M solution of *n*-BuLi in hexane (3.15 mL, 5.02 mmol) was added. The resulting red solution was stirred for 1 h at −80 °C, after which Me_3SiCl (0.58 g, 5.34 mmol) in THF (5 mL) was added. The mixture was slowly warmed to room temperature overnight, after which a saturated degassed $NaHCO_3$ solution (10 mL) was added to the light yellow suspension. The organic layer was separated, and the aqueous layer was extracted once with Et_2O. The organic layers were combined, dried on $MgSO_4$, and filtered, and the volatiles were

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removed in vacuo. The crude product was washed with *n*-pentane and MeOH at low temperatures to give the product as a yellow oil (0.60 g, 1.50 mmol, 60%), which slowly solidified to a yellow solid.

^{1}H NMR (C_6D_6, 499.8 MHz): δ 0.26 (s, 18 H, Si*Me*$_3$), 6.53 (m, 1H, H(2)), 6.87 (m, 1H, H(4)), 7.12 (m, 1 H, H(3)), 7.36 (d, $^3J_{H,H}$ = 7.5 Hz, 4 H, H(8)), 7.57 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, H(7)), 8.52 (d, $^3J_{H,H}$ = 4.0 Hz, 1 H, H(1)). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz): −0.83 (s, Si*Me*$_3$), 122.38 (s, C(2)), 128.72 (d, $^3J_{C,P}$ = 20.2 Hz, C(3)), 134.11 (d, $^3J_{C,P}$ = 6.4 Hz, C(8)), 134.44 (d, $^3J_{C,P}$ = 19.0 Hz, C(7)), 135.58 (d, $^2J_{C,P}$ = 3.5 Hz, C(4)), 138.52 (d, $^1J_{C,P}$ = 11.6 Hz, C(6)), 141.51 (s, C(9)), 150.85 (d, $^3J_{C,P}$ = 11.6 Hz, C(1)), 164.98 (d, $^1J_{C,P}$ = 2.3 Hz, C(5)). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ −2.89 (s). Anal. Calcd for $C_{23}H_{30}NPSi_2$: C 67.76, H 7.42, N 3.44, P 7.60. Found: C 67.95 H 7.56, N 3.12, P 7.80.

Synthesis of 2-[Bis{4-((2-(perfluorohexyl)ethyl)dimethylsilyl)phenyl}phosphino]pyridine (10). The procedure followed was the same as for compound **9**. To a solution of **8** (1.15 g, 2.73 mmol) in THF at −80 °C was added a 1.6 M solution of *n*-BuLi in hexane (3.4 mL, 5.46 mmol) and after 1 h tridecafluorooctyldimethyl chlorosilane (2.45 g, 5.50 mmol) in THF. After workup as described for **9** the crude product was washed with *n*-pentane at −40 °C to afford compound **10** as an off-white solid (1.48 g, 1.37 mmol, 51%).

^{1}H NMR (C_6D_6, 300.1 MHz): δ 0.02 (s, 12 H, Si(*Me*)$_2$), 0.84 (m, 4 H, SiC*H*$_2$CH$_2$), 1.90 (m, 4 H, SiCH$_2$C*H*$_2$), 6.56 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H(2)), 6.92 (tt, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,P}$ = 1.8 Hz, H(4)), 7.13 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, H(3)), 7.23 (d, $^3J_{H,H}$ = 6.5 Hz, 4 H, H(8)), 7.54 (t, $^3J_{H,H}$ = 7.5 Hz, 4 H, H(7)), 8.52 (d, $^3J_{H,H}$ = 4.8 Hz, H(1)). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz): δ −4.04 (s, Si(*Me*)$_2$), 5.04 (s, Si*C*H$_2$CH$_2$), 26.00 (t, $^2J_{C,F}$ = 20.7 Hz, SiCH$_2$*C*H$_2$), 120−107 (multiple m, C_6F_{13} tail), 122.10 (s, C(2)), 128.30 (d, $^3J_{C,P}$ = 22.6 Hz, C(3)), 133.64 (d, $^3J_{C,P}$ = 6.7 Hz, C(8)), 134.06 (d, $^2J_{C,P}$ = 19.5 Hz, C(7)), 135.13 (d, $^2J_{C,P}$ = 4.3 Hz, C(4)), 138.06 (s, C(9)), 138.71 (d, $^1J_{C,P}$ = 12.2 Hz, C(6)), 150.44 (d, $^3J_{C,P}$ = 10.3 Hz, C(1)), 163.78 (d, $^1J_{C,P}$ = 4.0 Hz, C(5)). ^{19}F NMR (C_6D_6, 282.4 MHz): δ −93.91 (s, 6 F, C*F*$_3$), −128.27 (m, 4 F, C*F*$_2$), −134.68 (s, 4 F, C*F*$_2$), −135.75 (s, 8 F, C*F*$_2$), −138.99 (s, 4 F, C*F*$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ −2.85 (s). Anal. Calcd for $C_{37}H_{32}F_{26}NPSi_2$: C 41.46, H 3.01, F 46.09, N 1.31, P 2.89. Found: C 41.26, H 2.88, F 45.98, N 1.29, P 2.81.

General Procedure for Synthesis of [PdCl$_2$(2-[bis(aryl)phosphino]pyridine)$_2$] Complexes 11−13. A procedure previously reported for **11** was followed,[25] but instead of [PdCl$_2$(PhCN)$_2$] [PdCl$_2$(COD)] was used as the palladium precursor complex.

[PdCl$_2$(2-[diphenylphosphino]pyridine)$_2$] (11). Starting from 2-[diphenylphosphine]pyridine (0.43 g, 1.62 mmol) and [PdCl$_2$COD] (0.23 g, 0.81 mmol) the desired compound was obtained as a yellow solid (0.57 g, 0.81 mmol, 99%). NMR spectroscopic data were in accordance with those reported in the literature.[25]

[PdCl$_2$(2-[bis{4-(bromo)phenyl}phosphino]pyridine)$_2$] (12). Starting from **8** (0.47 g, 1.12 mmol) and [PdCl$_2$(COD)] (158.5 mg, 0.56 mmol) after normal workup, the final product was obtained by recrystallization from CH_2Cl_2/Et_2O (0.50 g, 0.49 mmol, 88%). Crystals suitable for X-ray analysis were obtained after 2 weeks by slow distillation of *n*-pentane into a solution of **12** in $CDCl_3$ in a 5 mm NMR tube at −20 °C.

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.30−8.74 (br m, 24 H, H-*aryl* and *pyridyl*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 124.83 (br s, *p*-C *aryl*), 126.59 (br s, C-*pyridyl*), 127.77 (t, *ipso*-C *aryl*), 128.91 (s, *p*-C *pyridyl*), 131.69 (br s, C-*aryl*), 136.02 (br s, C-*pyridyl*), 136.84 (br s, C-*aryl*), 150.28 (br s, C-*pyridyl*). ^{31}P-{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ 22.39 (s, *trans*-isomer), 28.72 (s, *cis*-isomer). Anal. Calcd for $C_{34}H_{24}Br_4Cl_2N_2P_2Pd$: C 40.06, H 2.37, P 6.08, Pd 10.44. Found: C 39.70, H 2.52, P 6.18, Pd 10.49.

X-ray Crystal Structure Determination of Compound 12. Pertinent data for the structure determination are given in Table 5. Data were measured on a Nonius KappaCCD diffractometer with rotating anode and Mo Kα radiation (graphite monochromator, λ = 0.71073 Å) at a temperature of 150(2) K. An absorption correction based on multiple measured reflections was applied. The structure was solved with direct methods[49] and refined with SHELXL-97[50] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined as rigid groups. The bromophenyl groups were disordered over two positions in a 50% ratio, respectively, to avoid close intermolecular contacts. Geometry calculations, drawings, and checking for higher symmetry were performed with the PLATON package.[51]

Table 5. Crystallographic Data for the Crystal Structure Determination of 12

formula	$C_{34}H_{24}Br_4Cl_2N_2P_2Pd$
mol wt	1019.43
cryst syst	monoclinic
space group	$P2_1/c$ (no. 14)
a (Å)	13.5697(1)
b (Å)	7.5837(1)
c (Å)	19.7320(2)
β (deg)	117.1114(4)
V (Å^3)	1807.47(3)
D_{calcd} (g cm^{-1})	1.873
Z	2
F(000)	984
μ(Mo Kα) (mm^{-1})	5.199
cryst color	yellow
cryst size (mm)	0.15 × 0.15 × 0.15
θ_{min}, θ_{max} (deg)	1.69, 27.49
data set (hkl)	−17 to +17, −9 to +9, −25 to +25
abs corr range	0.42−0.46
total no. of data, no. of unique data	32 263, 4151
R_{int}	0.0444
no. of refined params, no. of restraints	295, 138
R1/wR2 ($I > 2\sigma(I)$)	0.0393, 0.0928
R1/wR2 (all data)	0.0509, 0.1000
goodness of fit	1.077
w^{-1} [a]	$\sigma^2(F_o^2) + (0.0372P)^2 + 4.0289P$
min., max. residual density (e/Å^3)	−1.51, 1.48

[a] $P = (F_o^2 + 2F_c^2)/3$.

[PdCl$_2$(2-[bis{4-(trimethylsilyl)phenyl}phosphino]pyridine)$_2$] (13). Starting from **9** (0.22 g, 0.54 mmol) and [PdCl$_2$(COD)] (79.0 mg, 0.27 mmol) after normal workup, the final product was obtained by washing of the crude product with *n*-pentane. The product was isolated as a yellow solid (0.19 g, 0.19 mmol, 70%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 0.24 (s, 36 H, Si*Me*$_3$), 7.32−7.83 (br m, 24 H, H-*aryl* and H-*pyridyl*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 0 °C): δ −0.65 (s, Si*Me*$_3$), 124.89 (s), 128.23 (s), 132.81 (s), 132.95 (s), 133.65 (s), 133.83 (s), 134.22 (s), 144.63 (s), 149.14 (s). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 22.61 (s, *trans*-isomer), 27.93 (s, *cis*-isomer). Anal. Calcd for $C_{46}H_{60}Cl_2N_2P_2PdSi_4$: C 55.66, H 6.09, P 6.24, Pd 10.72. Found: C 56.01, H 6.21, P 6.18, Pd 10.65.

General Procedure for Synthesis of *trans*-[PdCl(Me)(2-[bis(aryl)phosphino]pyridine)$_2$] Complexes 14−16.[28] To a solution of the appropriate ligand in CH_2Cl_2 was added 0.5 equiv of [PdCl(Me)(TMEDA)]. The resulting red solution was stirred at ambient temperature for 45 min, after which all volatiles were removed in vacuo. The resulting solid was washed twice with *n*-pentane to afford the final product.

***trans*-[PdCl(Me)(2-[diphenylphosphino]pyridine)$_2$] (14).** Starting from **2** (0.27 g, 1.03 mmol) and [PdCl(Me)(TMEDA)]

(49) Sheldrick, G. M. *SHELXS-86*, Program for crystal structure solution; Universität Göttingen: Germany, 1986.
(50) Sheldrick, G. M. *SHELXL-97*, Program for crystal structure refinement; Universität Göttingen: Germany, 1997.
(51) Spek. A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(0.14 g, 0.52 mmol) a light yellow solid was obtained as the final product (0.30 g, 0.44 mmol, 85% based on [PdCl(Me)-(TMEDA)]).

^{1}H NMR (CD_2Cl_2, 499.8 MHz): δ −0.01 (s, 3 H, Pd-*Me*), 7.34 (t, J = 5.7 Hz, 2H, H-*pyridyl*), 7.46 (m, 12 H, H-*aryl*), 7.75 (t, J = 7.5 Hz, 2 H, H-*pyridyl*), 7.85 (d, J = 5.0 Hz, 8 H, H-*aryl*), 8.06 (d, J = 6.0 Hz, 2 H, H-*pyridyl*), 8.78 (d, J = 4.0 Hz, 2 H, H-*pyridyl*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.7 MHz): δ 4.43 (br s, Pd-*Me*), 124.39 (s, C(2)), 128.57 (vt, $J_{C,P}$ = 9.8 Hz, C(8)), 130.83 (s, C(9)), 131.73 (vt, $J_{C,P}$ = 45.0 Hz, C(6)), 132.42 (vt, $J_{C,P}$ = 27.8 Hz, C(3)), 135.93 (vt, $J_{C,P}$ = 12.2 Hz, C(7)), 150.44 (vt, $J_{C,P}$ = 13.8 Hz, C(1)), 157.45 (vt, $J_{C,P}$ = 64.6 Hz, C(5)). ^{31}P-{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 30.33 (s). Anal. Calcd for $C_{35}H_{31}ClN_2P_2Pd$: C 61.51, H 4.57, P 9.06, Pd 15.57. Found: C 61.40, H 4.68, P 9.42, Pd 15.23.

***trans*-[PdCl(Me)(2-[bis{4-(bromo)phenyl}phosphino]-pyridine)$_2$] (15).** Starting from **8** (0.52 g, 1.24 mmol) and [PdCl(Me)(TMEDA)] (168.2 mg, 0.62 mmol) a yellow solid was obtained as the final product (0.50 g, 0.50 mmol, 81% based on [PdCl(Me)(TMEDA)]).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ −0.03 (s, 3 H, Pd-*Me*), 7.28 (d, $J_{H,H}$ = 7.2 Hz, 2 H, H-*pyridyl*), 7.52 (d, $J_{H,H}$ = 7.5 Hz, 8 H, H-*aryl*), 7.67 (m, 10 H, H-*aryl* + H-*pyridyl*), 7.96 (d, $J_{H,H}$ = 6.0 Hz, 2 H, H-*pyridyl*), 8.74 (s, 2 H, H-*pyridyl*). ^{31}P{^{1}H} NMR ($CDCl_3$, 81.0 MHz): δ 29.37 (br s). No good elemental analyses could be obtained for this compound.

***trans*-[PdCl(Me)(2-[bis{4-((2-(perfluorohexyl)ethyl)-dimethylsilyl)phenyl}phosphino]pyridine)$_2$] (16).** Starting from **10** (0.30 g, 0.28 mmol) and [PdCl(Me)(TMEDA)] (38.1 mg, 0.14 mmol) a light yellow solid was obtained as the final product (0.26 g, 0.11 mmol, 81% based on [PdCl(Me)(TMEDA)]).

^{1}H NMR (CD_2Cl_2, 499.8 MHz): δ −0.01 (s, 3 H, Pd-*Me*), 0.38 (s, 24 H, Si*Me*$_2$), 1.05 (m, 8 H, SiC*H*$_2$CH$_2$), 2.09 (m, 8 H, SiCH$_2$C*H*$_2$), 7.34 (t, J = 6.0 Hz, 2 H, H-*pyridyl*), 7.59 (d, J = 7.5 Hz, 8 H, H-*aryl*), 7.75 (t, J = 7.0 Hz, 2 H, H-*pyridyl*), 7.85 (m, 8 H, H-*aryl*), 8.04 (br s, 2 H, H-*pyridyl*), 8.78 (d, J = 4.0 Hz, 2 H, H-*pyridyl*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.7 MHz): δ −3.35 (s, Si*Me*$_2$), 4.40 (br s, Pd-*Me*), 5.50 (s, Si*C*H$_2$CH$_2$), 26.41 (t, $^2J_{C,F}$ = 23.6 Hz, SiCH$_2$*C*H$_2$), 108.68−120.90 (several m, C_6F_{13}-tail), 124.51 (s, C(2)), 132.60 (m), 133.63 (vt, $J_{C,P}$ = 8.6 Hz, C(8)), 135.24 (vt, $J_{C,P}$ = 11.6 Hz, C(7)), 136.03 (br s), 141.08 (s, C(9)), 150.49 (vt, $J_{C,P}$ = 13.8 Hz, C(1)), 157.23 (vt, $J_{C,P}$ = 63.4 Hz, C(5)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 29.79 (s). Anal. Calcd for $C_{75}H_{67}ClN_2P_2PdSi_4$: C 39.16, H 2.94, P 2.69, Pd 4.63. Found: C 39.54, H 3.31, P 2.74, Pd 4.30.

General Procedure for the Synthesis of [Pd(2-[bis-(aryl)phosphino]pyridine)$_2$(*cyclo*-(−CH=CHC(O)OC(O)−))] Complexes.[32] To a solution of the appropriate phosphine in acetone was added 0.5 equiv of [Pd(*t*-BuDAB)(*cyclo*-(−CH=CHC(O)OC(O)−))]. The resulting orange solution was stirred at ambient temperature for 30 min, after which the volume of the solution was reduced to about 2 mL. Et_2O was added, and the formed precipitate was collected by decantation of the liquids and drying of the residue in vacuo.

[Pd(2-[diphenylphosphino]pyridine)$_2$(*cyclo*-(−CH=CH-C(O)OC(O)−))] (17). Starting from **2** (0.26 g, 0.99 mmol) and [Pd(*t*-BuDAB)(*cyclo*-(−CH=CHC(O)OC(O)−))] (0.14 g, 0.37 mmol) the desired product was isolated as a yellow solid (0.21 g, 0.29 mmol, 76% based on [Pd(*t*-BuDAB)(*cyclo*-(−CH=CHC-(O)OC(O)−))]) after workup as above and washing with *n*-pentane.

^{1}H NMR (CD_2Cl_2, 499.8 MHz, −30 °C): δ 4.14 (d, $^3J_{H,P}$ = 5.5 Hz, 2 H, C*H*=C*H*), 6.92 (d, $^3J_{H,H}$ = 6.5 Hz, 2 H, H(3)), 7.13 (t, $^3J_{H,H}$ = 6.0 Hz, 2 H, H(2)), 7.30 (t, $^3J_{H,H}$ = 6.0 Hz, 8 H, H(8)), 7.37 (m, 12 H, H(7 + 9), 7.47 (t, $^3J_{H,H}$ = 7.8 Hz, H(4)), 8.49 (d, $^3J_{H,H}$ = 4.5 Hz, 2 H, H(1)). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.7 MHz, −40 °C): δ 55.05 (m, $^2J_{C,P}$ = 21.9 Hz, $^2J_{C,P}$ = 21.4 Hz, *C*H=*C*H), 123.22 (s, C(2)), 127.63 (vt, $J_{C,P}$ = 20.2 Hz, C(3)), 128.35 (m, C(8)), 130.06 (s, C(9)), 130.27 (s, C(9)), 131.75 (m, $J_{C,P}$ = 72.2 Hz, C(6)), 132.85 (m, $J_{C,P}$ = 72.6 Hz, C(6)), 133.83 (vt, $J_{C,P}$ = 14.0 Hz, C(7)), 134.60 (vt, $J_{C,P}$ = 14.0 Hz, C(7)), 135.61 (s, C(4)), 150.04 (vt, $J_{C,P}$ = 15.0 Hz, C(1)), 158.56 (m, $J_{C,P}$ = 60.7 Hz, C(5)), 170.43 (s, *C*=O *cyclo*-(−CH=CHC(O)OC(O)−)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 30.06 (s). Anal. Calcd for $C_{37}H_{30}N_2O_3P_2Pd$: C 62.42, H 4.14, N 3.83, P 8.47, Pd 14.55. Found: C 62.30, H 4.19, N 3.75, P 8.36, Pd 14.38.

Attempted Synthesis of [Pd(2-[bis{4-((2-(perfluorohexyl)ethyl)dimethylsilyl)phenyl}phosphino]pyridine)$_2$-(*cyclo*-(−CH=CHC(O)OC(O)−))] (18). Starting from **10** (0.52 g, 0.49 mmol) and [Pd(*t*-BuDAB)(*cyclo*-(−CH=CHC(O)OC(O)−))] (72.3 mg, 0.19 mmol) a yellow oil was obtained after workup as described above. After several washings with *n*-pentane at −50 °C a light yellow oil was obtained (0.49 g), which contained the desired product together with about 25% of free *t*-BuDAB.

^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ 0.34 (s, 24 H, Si*Me*$_2$), 1.01 (m, 8 H, SiC*H*$_2$CH$_2$), 1.25 (s, C*Me*$_3$ of *t*-BuDAB), 2.08 (m, 8 H, SiCH$_2$C*H*$_2$), 4.15 (br s, 2 H, C*H* of *cyclo*-(−CH=CHC(O)OC-(O)−)), 7.11 (br m, 4 H, H-*pyridyl*), 7.42 (m, 18 H, H-*aryl* and H-*pyridyl*), 8.51 (br s, 2 H, H-*pyridyl*). ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ 29.72 (br s).

Catalytic Methoxycarbonylation of Phenylacetylene. For catalysis employing the in situ prepared catalysts the following procedure was used.[10] [Pd(OAc)$_2$] was weighed under N_2 in a Schlenk vessel. In a second Schlenk vessel were subsequently added the appropriate amounts of ligand, methane sulfonic acid, *n*-decane (GC internal standard), phenylacetylene, and solvents (pure methanol or methanol and α,α′,α″-trifluoro toluene, 1:1 (v/v)). After mixing, this solution was transferred to the first Schlenk vessel via syringe. The resulting solution was charged to the autoclaves under N_2 flow. After sealing the autoclaves three vacuum-nitrogen cycles were performed, followed by three times flushing with CO (15 bar). The autoclaves were heated to the desired temperature and pressurized with CO. After the desired reaction time the autoclaves were cooled and carefully vented. A sample of the autoclave content was analyzed by GC after filtration over basic alumina and dilution with diethyl ether.

For catalysis experiments employing the zerovalent palladium complex **17** the same procedure as above was followed, except that now the palladium complex instead of [Pd(OAc)$_2$] was weighed in the first Schlenk vessel.

For experiments in $scCO_2$ the 50 mL home-built autoclave was utilized. After charging the autoclave with the reaction mixture, three vacuum-nitrogen cycles were performed, followed by flushing three times with CO (15 bar). The autoclave was heated to the desired temperature (50 °C) and subsequently pressurized with CO (40 bar). Then, CO_2 was pumped into the autoclave using an ISCO DM-100 high-pressure pump to achieve a total pressure of 150 bar, after which stirring was initiated by a magnetic stirring bar. During the reaction the pressure dropped from 150 to 145 bar. After the reaction the autoclave was cooled to −20 °C and the excess CO and CO_2 were carefully vented via a cold trap cooled to −60 °C. *Note: when working with supercritical fluids, the user should never be directly exposed to the autoclave. The use of suitable polycarbonate shielding between the autoclave and the user is therefore strongly recommended.*

For the catalytic experiments which were sampled during the reaction a 100 mL in-house built autoclave was used, using the same procedures as described earlier for the in situ prepared catalysts. This autoclave was equipped with a motor-driven top-stirrer, thermocouples inside the autoclave and heating mantle, water-cooling of the interior of the autoclave, a rupture-disk assembly (set at 80 bar), a pressure transducer, and appropriate control devices for the temperature. Sampling at regular intervals was achieved via a piece of 1/16 in. stainless steel tubing inside the autoclave, equipped with a valve at the end.

After every catalytic run the autoclaves were cleaned by rinsing with aqua regia, water, and acetone, respectively, followed by drying in vacuo.

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Supporting Information Available: CIF file of crystal data collection and refinement parameters, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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