Synthesis of Palladium(II) and Platinum(II) Complexes with Crown Ether Phosphane Ligands: Stille Coupling of Aryl Iodides in Water

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The crown ether phosphanes $PAr^{\star}Ph_2$ (**1**) and $PAr^{\star}{}_2R$ [$Ar^{\star}$ = 3,4-(18-crown-6)-phenyl; R = Me (**2**); R = Ph (**3**)], prepared from PCl_2R and $Ar^{\star}Li$, have been studied. The syntheses and characterization of their oxides (**4**–**6**), and their BH_3 (**7**–**9**), $PdCl_2$ (**10**–**12**), and $PtCl_2$ (**13**–**15**) complexes are reported. The molecular structure of the borane complex $PAr^{\star}{}_2Ph{\cdot}BH_3$ (**9**) has been determined by X-ray structural analysis. Spectroscopic data suggest that phosphanes **1**–**3** have similar electronic properties and steric requirements to the corresponding phenylphosphane ligands PPh_2Me and PPh_3. Crown ether methylphosphane **2** and its complexes are remarkably water soluble, but **1** and **3** are only slightly soluble. Palladium(II) complexes **14** and **15** have been tested as catalysts in the Stille coupling of phenyltrichlorostannanes and aryl iodides in water.

Introduction

The synthesis and study of metal complexes for aqueous-phase homogeneous catalysis is currently an active research area in organometallic chemistry.[1] Aryl- and alkyl-substituted tertiary phosphanes are among the most common ligands present in transition-metal catalysts, but they are hydrophobic and lack water solubility. Hydrophilicity can be introduced into a phosphane by making use of polar substituents, usually anionic or cationic functions, such as sulfonate or ammonium groups.[2,3] Water solubility has also been achieved with nonionic phosphanes, for example with hydroxyalkyl or polyether substituents but, in general, nonionic phosphanes have attracted less attention than ionic phosphanes. Since the first report by Shaw et al. in 1978,[4] several examples of hybrid crown ether phosphane ligands have appeared in the literature.[5–11] Okano and coworkers have reported the synthesis of mono[3,4-(crown)-phenyl]diphenylphosphane ligands $PAr^{*}Ph_2$ with crown heterocycles of different sizes.[6] The water solubility of these phosphanes is low but the crown cavity acts as an extractant and phase-transfer agent for biphasic catalysis.[5,6,12,13] Crown ether phosphanes contain a secondary site for coordination that can play an important role in catalytic processes.[9,10,14] Here, we report the synthesis of bis[3,4-(18-crown-6)-phenyl] analogs of methyldiphenyl- and triphenylphosphane and the preparation of their $PdCl_2$ and $PtCl_2$ complexes. The palladium complexes are tested as catalysts in Stille carbon–carbon couplings[15,16] in an aqueous medium.[17]

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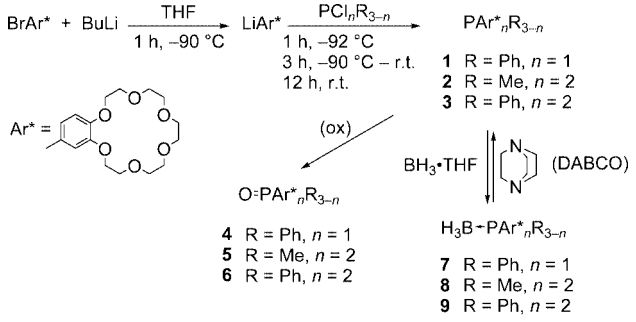
Results and Discussion

Synthesis and Characterization of Crown Ether Phosphanes and Their Complexes

The synthesis of phosphanes $PAr^{*}{}_nR_{3-n}$ [Ar* = 3,4-(18-crown-6)-phenyl, R = Me, *n* = 2 (**2**); R = Ph, *n* = 2 (**3**)] is based on the lithiation of bromo-3,4-(18-crown-6)-benzene and the subsequent reaction of the lithium crown-aryl LiAr* with the corresponding chlorophosphane PCl_nR_{3-n} (Scheme 1), according to the procedure reported previously for the synthesis of $PAr^{*}Ph_2$ (**1**).[6] The main drawback of this procedure lies in the thermal instability[4] of LiAr*, which requires keeping the temperature carefully below the decomposition point (–90 °C) until the reaction with the chlorophosphane is completed, and to use a low concentration of reactants to avoid the formation of a slush at this temperature.[9] In our hands, moderate to high yields (60–90%) were obtained only when the temperature was maintained below –90 °C for at least one hour before and one hour after the addition of the chlorophosphane. The main impurities contaminating the crude product are 1,2-(18-crown-6)-benzene and butylphosphanes derived from unreacted *n*BuLi and chlorophosphanes. In the case of **3**, these are readily removed by crystallization from ethanol/methanol (9:1). In contrast, all our efforts to purify methylphos-

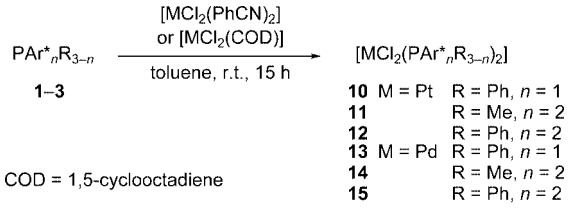
phane **2** by crystallization failed because of its high solubility in water and polar organic media (see below). Moreover, only the oxide **5** was collected from chromatography columns of silica gel or alumina even if an inert atmosphere and deoxygenated solvents were employed. Although triarylphosphanes are more stable, both **1** and **3** were transformed quantitatively into their oxides **4** or **6** when stirred under an air atmosphere for three days at room temperature.



Scheme 1.

The formation of borane adducts is a classical method for the protection of phosphanes against oxidation during purification or synthetic steps (the borane group also plays an activation role in the latter).[18] For the synthesis of the borane complexes **7**–**9**, an equimolar solution of BH_3·THF was treated with the purified phosphanes (only for **1** and **3**) or, alternatively, added directly to the crude product obtained during their preparation. In both cases pure samples of **7**–**9** were obtained in high yields as white, air-stable solids after crystallization from ethanol/methanol. The deprotected phosphanes **1**–**3** were recovered from their borane adducts **7**–**9** by decomplexation with an excess of the diamine ligand 1,4-diazabicyclo[2.2.2]octane (DABCO). A mixture of phosphane, DABCO, and DABCO·BH_3 composed the crude product, from which the phosphanes **1** and **3** were easily separated by crystallization. Again, the properties of **2** complicated the purification of this phosphane, although almost pure samples could be obtained by repeated washings with hexane and long high-vacuum treatments. In practice, we limited the purification step to a short high-vacuum treatment until complete sublimation of the DABCO. Samples thus obtained consisted of a 1.6:1 mixture of phosphane **2** and DABCO·BH_3 and were appropriate for the synthesis of the complexes described here. A clear difference was observed in the complexation/decomplexation process between triarylphosphanes **1** and **3** and methylphosphane **2**. Complexation of the former with BH_3·THF is slower (at room temperature, 24 h for **1** and **3**, and 4 h for **2**) but decomplexation seems to be easier (4 h at 40 °C and 1.2 equiv. of DABCO for **1** and **3**, 5 h at THF reflux and 3.5 equiv. of DABCO for **2**). The enhanced strength of the P–B bond in the more electron-rich phosphane **2** is presumably responsible for these observations. It has been pointed out that BH_3 decomplexation by amine exchange can be an inefficient process for electron-rich, sterically hindered phosphanes.[19]

The platinum (**10**–**12**) and palladium (**13**–**15**) complexes $[MCl_2(PAr^*_nR_{3-n})_2]_2$ were prepared by the displacement of the labile ligand in $[MCl_2(COD)]$ or $[MCl_2(PhCN)_2]$ (Scheme 2). Palladium complex **13** has already been reported[5,6] and is described here only for comparative purposes. The platinum complexes are white solids containing only the *cis* isomers, whereas the palladium ones are yellow and were obtained as *cis*-*trans* mixtures. The *cis*-*trans* ratios obtained (*cis* amount: traces for **13**, 60% for **14**, and 30% for **15**) are independent of the starting material, $[PdCl_2(COD)]$ or $[PdCl_2(PhCN)_2]$. The *cis* and *trans* isomers of **15** were separated on the basis of their different solubility in toluene. The assigned stereochemistry is in agreement with the following experimental data and observations: (*a*) the order of the $^2J(^{31}P\text{-}^{31}P)$ coupling constant, estimated from second-order analysis of the ^1H NMR methyl resonance of PAr^*_2Me complexes,[20] and the ring ^{13}C signals (see below); (*b*) the number of ν(M–X) IR absorptions, two (A_1 + B_1) for *cis*, but one (B_{1u}) for *trans*; (*c*) in square-planar $[MCl_2(PR_3)_2]$ complexes, it has been observed that lower field phosphorus chemical shifts correspond to *cis* and higher field chemical shifts to *trans* isomers in Pd^{II} complexes, whereas the reverse is true for Pt^{II}; (*d*) the estimated phosphorus chemical shift value employing the reported[21] empirical correlation between the chemical shifts of free and coordinated phosphanes; estimated/experimental values are δ = 34.7/33.0 (*cis*-**13**), 23.3/24.1 (*trans*-**13**), 18.4/19.7 (*cis*-**14**), 9.0/7.7 (*trans*-**14**), 35.1/33.4 (*cis*-**15**), and 23.7/23.8 ppm (*trans*-**15**); (*e*) for Pt complexes, yellow colors are typical of *trans* isomers whereas *cis* isomers are usually white;[22] the $^1J(^{31}P\text{-}^{195}Pt)$ value is typically in the range of 2200–2500 Hz for *trans* and 3500–3700 Hz for *cis*-$[PtCl_2(PR_3)_2]$ complexes (3641–3673 Hz for *cis* **10**–**12**).[23]



Scheme 2.

Spectroscopic and analytical data for compounds **2**–**15** are given in the Experimental Section. For the assignment of ^1H and ^{13}C NMR signals and the determination of coupling constants, we applied a combination of selective and broadband ($\{^1H\}$ and $\{^{31}P\}$) decoupling techniques together with the simulation of second-order spectra. The ^{31}P nuclei of the crown ether aryl derivatives **2**–**15** resonate almost at the same position as their parent phenyl analogs (PPh_2Me and PPh_3). For example, the ^{31}P NMR chemical shifts for the pair PAr^*_2Me (**2**)/PPh_2Me are as follows (in $CDCl_3$): δ = –25.6/–28 ppm for the free phosphane,[24] δ = 0.9/–1.2 ppm for the *cis* platinum complex,[25] and δ = 7.7/7.8 ppm for the *trans* palladium complex.[26] Therefore, the steric requirements and electronic properties imposed by the Ar* group to the phosphane ligand are possibly very

similar to those of a Ph group. In fact, Storhoff et al.[11] have evaluated the donor/acceptor characteristics of several crown ether containing phosphanes, including **1**, from the A_1 ν(CO) bands for $[Ni(CO)_3L]$ complexes.[27] They reported that the PPh_2Ar^* complex absorbs 0.6 cm^{-1} lower than the PPh_3 analog, thus indicating that the donor ability of crown ether phosphane **1** is apparently only slightly greater than that of triphenylphosphane. The steric bulk of phosphanes is typically expressed in terms of cone angles, usually the Tolman cone angle, θ_{Tol}, originally derived from space-filling models,[28] or the Musco cone angle, θ_{Mus}, derived from phosphane X-ray diffraction data.[29] The estimation of these angles from the ^{31}P NMR spectroscopic data of *trans*-$[PdCl_2(PR_3)_2]$ complexes is possible because an empirical linear relationship has been demonstrated between the ^{31}P chemical shift and θ.[30] As remarked above, chemical shifts of crown ether complexes *trans*-$[PdCl_2(PAr^*_{3-n}R_n)_2]$ [δ = 24.1 (**13**), 7.7 (**14**), and 23.8 ppm (**15**)] match almost exactly those of the related non-crown ether *trans*-$[PdCl_2L_2]$ [δ = 24.4 (L = PPh_3),[31] 7.8 ppm (L = PPh_2Me)[26]]. Thus, it is predicted that Ar* phosphanes should have identical cone angles to Ph phosphanes. The estimated[32] values are θ_{Tol} = 131° and 147°, and θ_{Mus} = 126° and 134° for methyldiaryl and triarylphosphanes, respectively (actual values for PPh_2Me and PPh_3 are θ_{Tol} = 136° and 145°,[28] respectively).

The magnitude of the ^{13}C–^{31}P coupling constants is highly dependent on structural parameters, such as the coordination state of the P atom.[33] One-bond coupling constants between *ipso* Ph or Ar* carbon-13 and phosphorus-31 appear in a well-defined range for each type of compound: $^1J(^{13}C\text{-}^{31}P)$ = 9–11 (**2** and **3**), 105–108 (**4**–**6**), 58–63 (**7**–**9**), 68–71 (*cis*, **10**–**12**), 55–65 (*cis*, **13**–**15**), and 45–55 Hz (*trans*, **13**–**15**). The pattern of the ^{13}C NMR signals is a source of information about the magnitude of $^2J(^{31}P\text{-}^{31}P)$ coupling constants and serves to elucidate the *cis*-*trans* stereochemistry of square-planar $[MCl_2(PR_3)_2]$ complexes. The Me, Ar*, or Ph ^{13}C nuclei in **10**–**15** constitute the X part of an AA′X spin system,[34] where A and A′ are, respectively, the nearest and the most distant ^{31}P nuclei, for which five symmetrically disposed spectral lines are expected. If we assume $J(^{13}C\text{-}^{31}P_{A'})$ to be essentially zero, the actual appearance of the ^{13}C resonance lies between two limiting cases depending on the relative values of $J(^{13}C\text{-}^{31}P_A)$ and $^2J(^{31}P_A\text{-}^{31}P_{A'})$:[23] (*a*) a triplet produced by the weakening of the two outer lines (resonances marked as *pseudo triplets* in the Experimental Section), favored by larger $^2J(^{31}P_A\text{-}^{31}P_{A'})$ values; (*b*) lower $^2J(^{31}P_A\text{-}^{31}P_{A'})$ values favor an apparent doublet of doublets (or a doublet in the limiting case) due to the vanishing of the central line (*pseudo dd* or *d* in the experimental section). For *cis*-Pd complex **15**, all the carbons are split into doublets when coupled with ^{31}P, as expected for $^2J(^{31}P_A\text{-}^{31}P_{A'}) \approx 0$. For *cis*-Pt complexes, the carbons coupled to ^{31}P appear as pseudo triplets, except those with the largest $J(^{13}C\text{-}^{31}P_A)$ (*ipso* Ph, *ipso* Ar*, and Me carbons), which are observed as pseudo dd or d [a quantitative analysis of *ipso* Ph and *ipso* Ar* resonances gives an estimation for $^2J(^{31}P_A\text{-}^{31}P_{A'})$ of 10–14 Hz]. Finally, pseudo triplets for *ipso* Ph, *ipso* Ar*, or Me carbons are observed in the *trans* complexes, according to the larger P–P coupling constants. The simulated spectra of the Ar* protons match the experimental ones satisfactorily when P–P couplings of 0 (for *cis*-Pd), approx. 12 Hz (for *cis*-Pt), and >100 Hz (for *trans*-Pd) are considered in the second-order interpretation.

The solubility of catalysts in water is a relevant parameter when considering processes in this media. Triarylphosphanes **1** and **3** are only slightly soluble in water. Within this reduced solubility, the affinity for water increases with the number of crown-ether aryl groups as shown by the measured water/toluene distribution constants (7.4×10^{-3} for **1**, 1.46×10^{-3} for **3**). In contrast, the methylphosphane **2** is exceptionally water soluble. These differences are reflected in their metal complexes; for example, the palladium triarylphosphane complex **10** is poorly soluble in water (0.002 g/100 mL), whereas the palladium methyldiarylphosphane complex **11** has a remarkable solubility (>10 g/100 mL).

Crystal Structure of Borane–Phosphane 9

The molecular structure of borane complex $PAr^*_2Ph{\cdot}BH_3$ (**9**) based on X-ray structural analysis is given in Figure 1. In spite of the presence of two 18-crown-6 ether rings, the bond distances and angles around the phosphorus atom, which are listed in Table 1, are almost equal to those of $Ph_3P{\cdot}BH_3$.[35] For example, the mean P–C_{ipso} and P–B distances and C_{ipso}–P–C_{ipso} and B–P–C_{ipso} bond angles are, respectively, 1.811(4) and 1.917(5) Å, and 106.0(2)° and 112.6(2)° in **9**, compared with 1.818 and 1.917 Å, and 106.3° and 112.6° in $Ph_3P{\cdot}BH_3$. Complex **9** adopts a three-fold rotor conformation, according to the Dance and Scudder nomenclature,[36] with B–P–C_{ipso}–C_{ortho} torsion angles within the range 30.4–41.5° (mean: 36.8°). In contrast, the conformation of $Ph_3P{\cdot}BH_3$ is irregular, with two rotor rings and the other parallel to the P–B bond. The crown ether ring O(1)–O(6) is folded toward a face of the phenyl ring with an angle between crown and phenyl mean planes of 129.3(1)°, whereas the disposition of the crown ether O(7)–O(12) is almost coplanar [angle between mean planes = 172.4(1)°]. With respect to the plane defined by the *ipso* carbon atoms [C(1), C(17), and C(33)], the crown O(1)–O(6) is placed completely within the semispace opposite the P–B bond (*endo* orientation), whereas O(7)–O(12) has an *exo* orientation, with half of the crown atoms situated in each semispace. The crystallographic cone angle calculated[37] for the phosphane PAr^*_2Ph (**3**) in the solid-state structure of complex **9** is very large (175°). However, single crystallographic cone angles of ligands with significant conformational freedom are not relevant in describing steric effects in solution and are only representative of the conformation adopted in the particular structure. In this sense, the conformation adopted by the crown ether groups in the solid structure of **9** (*exo*-*endo*) is better ascribed to crystal-packing forces than to intermolecular interactions; chang-

ing the conformation to an *endo-endo* disposition reduces the cone angle to 160°. This value is only slightly larger than that of PPh_3 in $Ph_3P{\cdot}BH_3$ (155°).[38]

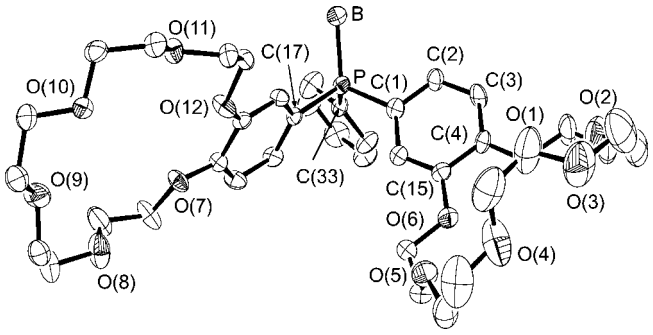


Figure 1. View of the molecular structure of **9** with the atom-numbering scheme.

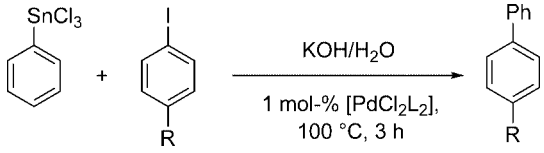
Table 1. Selected bond distances [Å] and angles [°] for **9**.

P–B	1.917(5)
P–C(1)	1.805(4)
P–C(17)	1.812(4)
P–C(33)	1.817(4)
C(1)–P–B	113.0(2)
C(17)-P–B	112.7(2)
C(33)-P–B	112.3(2)
C(1)–P–C(17)	105.6(2)
C(17)–P–C(33)	106.5(2)
C(33)–P–C(1)	106.2(2)

Palladium-Catalyzed Stille Couplings of Phenyltrichlorostannanes and Aryl Halides in Aqueous Solution

In 1993, Zhang and Daves[39] reported the achievement of Stille coupling reactions in aqueous media that they had been unable to accomplish in nonaqueous solvents. However, reactions carried out in water alone gave very low yields owing to the limited solubility of the reactants. Beletskaya[40] and Collum[41] independently reported successful couplings in water alone, thanks to the application of alkyltrichlorostannanes instead of tetraorganotin compounds; the former are less toxic and expensive, and produce water-soluble anionic alkylhydroxostannates in situ in aqueous alkaline solution. The catalyst employed was $PdCl_2$ with or without the addition of sulfonated water-soluble phosphane ligands such as P(*m*-$C_6H_4SO_3Na)Ph_2$[40] or P(*m*-$C_6H_4SO_3Na)_2Ph$,[41] or, in a recent paper by Wolf, $P(OH)(tBu)_2$.[42]

We chose the coupling of $PhSnCl_3$ and *p*-iodotoluene or *p*-iodoaniline, under the Belestkaya–Collum conditions (Scheme 3), to test the efficiency of the palladium complexes **14** and **15** as aqueous-phase catalysts. [$PdCl_2$(COD)] and [$PdCl_2(PPh_3)_2$] were also tested as a reference. Table 2 summarizes our results. Yields were especially high (>86%) for both crown catalysts **14** or **15**, but the less-soluble catalyst **15** gave quantitative yields whereas those of the highly soluble **14** were a bit lower (may be because of the lower stability of methyldiarylphosphane towards oxidation). Surprisingly, Beletskaya and co-workers[40] reported yields of about 85% when employing 1:2 mixtures of $PdCl_2$ and the monosulfonated phosphane P(*m*-$C_6H_4SO_3Na)Ph_2$. Reactions with [$PdCl_2$(COD)] and [$PdCl_2(PPh_3)_2$] proceed in 62 to 75% yields, normally with decomposition of the catalysts and formation of Pd^0.[43]



Scheme 3.

Table 2. Yields in reactions of ArI with $PhSnCl_3$ in the presence of palladium complexes **14** and **15** in aqueous alkaline medium.

Aryl iodide	Product	Catalyst[a]	Yield[b]
p-$NH_2C_6H_4I$	*p*-$NH_2C_6H_4$-C_6H_5	[$PdCl_2$(COD)]	62%
p-$NH_2C_6H_4I$	*p*-$NH_2C_6H_4$-C_6H_5	[$PdCl_2(PPh_3)_2$]	75%
p-$NH_2C_6H_4I$	*p*-$NH_2C_6H_4$-C_6H_5	[$PdCl_2(PAr^*_2Me)_2$] (**14**)	95%
p-$NH_2C_6H_4I$	*p*-$NH_2C_6H_4$-C_6H_5	[$PdCl_2(PAr^*_2Ph)_2$] (**15**)	98% [c]
p-$CH_3C_6H_4I$	*p*-$CH_3C_6H_4$-C_6H_5	[$PdCl_2(PPh_3)_2$]	69%
p-$CH_3C_6H_4I$	*p*-$CH_3C_6H_4$-C_6H_5	[$PdCl_2(PAr^*_2Me)_2$] (**14**)	86%
p-$CH_3C_6H_4I$	*p*-$CH_3C_6H_4$-C_6H_5	[$PdCl_2(PAr^*_2Ph)_2$] (**15**)	98% [c]

[a] 1.0 mol-% with respect to the aryl iodide. See Experimental Section for details. [b] Yield of isolated product based on starting ArI. Differences up to 100% were mainly due to unchanged ArI. [c] The reaction proceeded quantitatively and neither starting aryl iodide nor by-products were detected by ^1H NMR spectroscopy or TLC.

Conclusions

We have synthesized the new hybrid phosphane crown ether molecules PAr^*_2Me (**2**) and PAr^*_2Ph (**3**), where Ar* = 3,4-(18-crown-6)-phenyl, and their BH_3, $PtCl_2$, and $PdCl_2$ complexes. Because of the conformational flexibility of the crown ether substituents, the available data suggest that compounds **1–3** are isosteric to the corresponding phenylphosphane ligands (PPh_2Me or PPh_3). If we consider, in addition, the electronic similarity between crown and non-crown ligands, we can conclude that **1–3** are good alternatives to PPh_2Me and PPh_3 when working in aqueous medium. Moreover, the methylphosphane PAr^*_2Me (**2**) furnishes to their complexes a water solubility comparable to those of sulfonated phosphanes. However, solubility is not the only parameter to be considered, as shown by the fact that the only slightly water-soluble phenylphosphane PAr^*_2Ph (**3**) gives the best yields in the Stille coupling reactions in water here studied. Taking into account these preliminary but promising results in catalysis, the work here undertaken is being pursued with the synthesis of new crown ether phosphanes and a more detailed study of Stille and other C–C coupling reactions in water.

Experimental Section

Reagents and General Techniques: All operations were performed under an argon atmosphere by using Schlenk or dry-box tech-

niques. Solvents were dried and distilled under argon and degassed prior to use, as described elsewhere.[44] Unless otherwise stated, reagents were obtained from commercial sources and used as received. PAr^*Ph_2 (**1**),[6,9] $[PtCl_2(COD)]$, and $[PdCl_2(COD)]$[45] were prepared according to reported procedures. ^1H, ^{13}C, ^{31}P, and ^{11}B NMR spectra were recorded on Varian Unity 300 or 500 Plus spectrometers. Chemical shifts (δ, ppm) are relative to $SiMe_4$ (^1H, ^{13}C), 85% H_3PO_4 (^{31}P), or $F_3B{\cdot}OEt_2$ (^{11}B), and were measured by internal referencing to the deuterated solvent (^{13}C and residual ^1H resonances), or by the substitution method (^{31}P and ^{11}B references). Coupling constants (J) are given in hertz. The ring-numbering system employed in the description of NMR spectroscopic data is given in Figure 2. In ^{13}C NMR, $J_{P\ virtual}$ of *pseudo triplets* (see Results and Discussion) corresponds to $J(^{13}C–^{31}P_A) + J(^{13}C–^{31}P_{A'})$. IR spectra were recorded on a Perkin–Elmer Spectrum 2000 FT-IR spectrometer and data are given in cm^{-1}. The Analytical Services of the Universidad de Alcalá performed the C, H, and N analyses in a Heraeus CHN-O-Rapid microanalyzer, and the MS-ESI+ mass spectra in an Automass Multi, ThermoQuest. MALDI-TOF mass spectra were recorded by the Analytical Services of the Universidad Autónoma de Madrid.

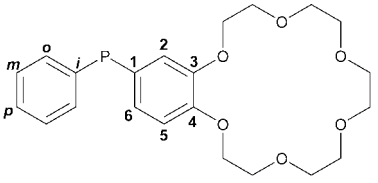


Figure 2. Selected $^{13}C\{^1H\}$ chemical shifts (in ppm) and coupling constants (in Hz) for compounds **2**–**15**, with the ring-labeling scheme employed in the Experimental Section.

PAr^*_2Me (2): The procedure described below for **3** was used for the synthesis of phosphane **2** (0.28 g, 65%) as a colorless oil starting from 4-bromobenzo-3,4-(18-crown-6) (0.500 g, 1.28 mmol), a 1.6 M hexane solution of *n*-butyllithium (0.88 mL, 1.41 mmol), and a 1.0 M solution of dichloromethylphosphane in hexane (0.70 mL, 0.70 mmol). However, this phosphane could not be purified by crystallization as described for **3**, because of its high solubility in water and polar organic media such as methanol or THF. ^1H NMR ($CDCl_3$, 500 MHz): δ = 6.93 [td, J_P = 7.0, J_{H5} = 7.8, J_{H2} = 1.7, 2 H, Ar*(H^6)], 6.87 [dd, J_P = 7.5, 2 H, Ar*(H^2)], 6.82 [dd, J_P = 1.3, 2 H, Ar*(H^5)], 4.12 (m, 4 H, CH_2 crown), 4.07 (m, 4 H, crown), 3.90 (m, 4 H, crown), 3.87 (m, 4 H, crown), 3.74 (m, 8 H, crown), 3.70 (m, 8 H, crown), 3.66 (s, 8 H, crown), 1.51 (d, J_P = 3.3, 3 H, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 149.53 [s, Ar*(C^4)], 148.38 [d, J_P = 8.1, Ar*(C^3)], 132.23 [d, J_P = 10.3, Ar*(C^1)], 125.46 [d, J_P = 19.9, Ar*(C^2)], 118.02 [d, J_P = 21.4, Ar*(C^6)], 114.00 [d, J_P = 8.1, Ar*(C^5)], 70.85, 70.78, 70.75, 69.65, 69.61, 69.30, 69.03 (s, CH$_2$ crown), 13.24 (d, $J_{C,P}$ = 8.1, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = –25.6 ppm.

PAr^*_2Ph (3): In a 100-mL round-bottomed flask equipped with a low-temperature thermometer, a magnetic stirrer, and a dropping funnel, 4-bromobenzo-3,4-(18-crown-6) (0.500 g, 1.28 mmol) was dissolved in freshly distilled THF (60 mL) and cooled in a methanol/liquid nitrogen slush. The temperature was lowered to –95 °C and then a 1.6 M hexane solution of *n*-butyllithium (0.88 mL, 1.41 mmol) was added dropwise to the cooled and stirred solution, keeping the temperature below –92 °C. The stirring was continued for 90 min while the temperature was carefully maintained in the stated range. Then, dichlorophenylphosphane (0.10 mL, 0.73 mmol) dissolved in THF (1 mL) was added gradually to the stirred mixture over a period of 10 min. The temperature was kept below –90 °C over a period of 60 min and then the reaction mixture was allowed to warm up to room temperature in the course of 3 h. Stirring was continued overnight. The solvent was removed in vacuo and the resulting residue was extracted with dichloromethane (3 × 30 mL). The dichloromethane was removed under reduced pressure to provide a colorless oil. Pure **3** (0.390 g, 83%) was obtained by crystallization of the crude from a mixture of absolute ethanol and methanol (9:1). $C_{38}H_{51}O_{12}P$ (730.79): calcd. C 62.46, H 7.03; found C 62.21, H 6.89. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.28 (m, 3 H, Ph), 7.22 (m, 2 H, Ph), 6.81 (m, 6 H, Ar*), 4.13 (m, 4 H, CH_2 crown), 4.01 (m, 4 H, crown), 3.91 (m, 4 H, crown), 3.83 (m, 4 H, crown), 3.75 (m, 4 H, crown), 3.74–3.68 (m, 12 H, crown), 3.67 (s, 8 H, crown) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 149.68 [s, Ar*(C^4)], 148.84 [d, J_P = 9.0, Ar*(C^3)], 138.13 [d, J_P = 10.6, Ar*(C_{ipso})], 133.18 [d, J_P = 18.9, Ph(C_{ortho})], 128.98 [d, J_P = 8.7, Ph(C^1)], 128.38 [s, Ph(C_{para})], 128.33 [d, J_P = 6.7, Ph(C_{meta})], 127.31 [d, J_P = 20.0, Ar*(C^6)], 119.10 [d, J_P = 22.5, Ar*(C^2)], 113.73 [d, J_P = 8.3, Ar*(C^5)], 70.90, 70.79, 70.75, 69.68, 69.57, 69.05, 68.91 (s, CH$_2$ crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = –4.4 ppm.

$P(O)Ar^*Ph_2$ (4): Phosphane PAr^*Ph_2 (**1**) (0.15 g, 0.30 mmol) was dissolved in $CHCl_3$ (10 mL). The solution was stirred at room temperature for 3 d under an air atmosphere. Subsequently, the solvent was evaporated to dryness and the residue crystallized from ethanol at –25 °C to give pure oxide **4** as a white solid (0.13 g, 84%). $C_{28}H_{33}O_7P$ (512.54): calcd. C 65.62, H 6.49; found C 65.71, H 6.42. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.62 [m, J_P = 11.9, 4 H, Ph(H_{ortho})], 7.50 [m, 2 H, Ph(H_{para})], 7.42 [m, 4 H, Ph(H_{meta})], 7.22 [dd, J_P = 12.1, J_{H6} = 1.8, 1 H, Ar*(H^2)], 7.03 [ddd, J_P = 12.1, J_{H5} = 8.1, 1 H, Ar*(H^6)], 6.86 [dd, J_P = 3.1, 1 H, Ar*(H^5)], 4.16 (m, 2 H, CH_2 crown), 4.08 (m, 2 H, crown), 3.91 (m, 2 H, crown), 3.84 (m, 2 H, crown), 3.77–3.66 (m, 12 H, crown) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 152.09 [s, Ar*(C^4)], 148.90 [d, J_P = 14.7, Ar*(C^3)], 132.89 [d, J_P = 104.7, Ph(C_{ipso})], 131.89 [d, J_P = 14.0, Ph(C_{ortho})], 128.41 [d, J_P = 11.8, Ph(C_{meta})], 131.79 [d, J_P = 2.9, Ph(C_{para})], 126.27 [d, J_P = 11.6, Ar*(C^6)], 124.12 [d, J_P = 108.4, Ar*(C^1)], 116.87 [d, J_P = 11.1, Ar*(C^2)], 112.81 [d, J_P = 14.7, Ar*(C^5)], 70.98, 70.94, 70.83, 70.75, 70.68, 69.49, 69.41, 69.23, 68.94 (s, CH$_2$ crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 30.5 ppm.

$P(O)Ar^*_2Me$ (5) and $P(O)Ar^*_2Ph$ (6): The procedure described above for **4** was used for the synthesis of phosphane oxides **5** (0.084 g, 55%) from **2** (0.150 g, 0.224 mmol), and **6** (0.138 g, 90%) from **3** (0.150 g, 0.205 mmol). The latter was obtained as an oil which was purified by chromatography on a silica gel column using a 1:1 mixture of toluene and ethanol as the mobile phase.

5: $C_{33}H_{49}O_{13}P$ (684.72): calcd. C 57.89, H 7.21; found C 57.95, H 7.08. MS (ESI+): m/z = 707.3 (calcd. for MNa^+: 707.0). ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.19 [dd, J_P = 12.3, J_{H6} = 1.9, 2 H, Ar*(H^2)], 7.13 [ddd, J_P = 12.0, J_{H5} = 8.0, 2 H, Ar*(H^6)], 6.87 [dd, J_P = 2.9, 2 H, Ar*(H^5)], 4.15 (m, 4 H, CH_2 crown), 4.13 (m, 4 H, crown), 3.91 (m, 4 H, crown), 3.89 (m, 4 H, crown), 3.78 (m, 8 H, crown), 3.73 (m, 8 H, crown), 3.65 (s, 8 H, crown), 1.91 (d, J_P = 13.2, 3 H, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 151.81 [s, Ar*(C^4)], 148.85 [d, J_P = 14.5, Ar*(C^3)], 125.95 [d, J_P = 106.2, Ar*(C^1)], 124.30 [d, J_P = 10.6, Ar*(C^2)], 115.49 [d, J_P = 11.7, Ar*(C^6)], 112.87 [d, J_P = 15.0, Ar*(C^5)], 70.87, 70.81, 70.75, 70.67, 70.66, 70.60, 69.42, 69.32, 69.15, 68.82 (s, CH$_2$ crown), 16.99 (d, J_P = 75.5, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 31.5 ppm.

6: $C_{38}H_{51}O_{13}P$ (746.79): calcd. C 61.12, H 6.88; found C 60.97, H 6.82. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.60 [m, J_P = 12.1, 2 H,

Ph(H_{ortho})], 7.50 [m, 1 H, Ph(H_{para})], 7.43 [m, 2 H, Ph(H_{meta})], 7.21 [dd, J_P = 12.5, J_{H6} = 1.7, 2 H, Ar*(H^2)], 7.00 [ddd, J_P = 12.1, J_{H5} = 8.2, 2 H, Ar*(H^6)], 6.86 [dd, J_P = 2.9, 2 H, Ar*(H^5)], 4.13 (m, 4 H, CH_2 crown), 4.01 (m, 4 H, crown), 3.91 (m, 4 H, crown), 3.83 (m, 4 H, crown), 3.75 (m, 4 H, crown), 3.74–3.67 (m, 12 H, crown), 3.66 (s, 8 H, crown) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 151.82 [s, Ar*(C^4)], 148.87 [d, J_P = 14.5, Ar*(C^3)], 132.92 [d, J_P = 12.4, Ph(C_{ortho})], 131.52 [d, J_P = 2.6, Ph(C_{para})], 130.01 [d, J_P = 105.6, Ph(C_{ipso})], 128.55 [d, J_P = 11.5, Ph(C_{meta})], 126.68 [d, J_P = 12.0, Ar*(C^6)], 124.02 [d, J_P = 106.9, Ar*(C^1)], 117.52 [d, J_P = 12.1, Ar*(C^2)], 113.03 [d, J_P = 14.3, Ar*(C^5)], 70.93, 70.83, 70.80, 70.67, 70.65, 70.42, 69.45, 69.18, 68.89 (s, CH$_2$ crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 31.3 ppm.

Ar*Ph$_2$P·BH$_3$ (7): PAr*Ph$_2$ (**1**; 0.11 g, 0.22 mmol) was dissolved in THF (20 mL) and a 1.0 M solution of BH_3·THF in THF (0.22 mL, 0.22 mmol) was added with a syringe. The mixture was stirred at room temperature for 24 h. The solvent was subsequently removed under vacuum to give a white solid. Pure borane complex **7** (0.097 g, 85%) was obtained after crystallization of the crude product from a mixture of absolute ethanol and methanol (18:1) at –25 °C. $C_{28}H_{36}BO_6P$ (510.38): calcd. C 65.89, H 7.11; found C 66.01, H 7.08. MS (ESI+): m/z = 534.0 (calcd. for MNa^+: 533.2), 520.0 (calcd. for MNa^+ – BH_3: 519.2). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.52 [m, J_P = 10.8, 4 H, Ph(H_{ortho})], 7.47 [m, 2 H, Ph(H_{para})], 7.43 [m, 4 H, Ph(H_{meta})], 7.10 [dd, J_P = 11.4, J_{H6} = 1.8, 1 H, Ar*(H^2)], 7.05 [ddd, J_P = 10.4, J_{H5} = 8.2, 1 H, Ar*(H^6)], 6.87 [dd, J_P = 2.4, 1 H, Ar*(H^5)], 4.15 (m, 2 H, CH_2 crown), 4.05 (m, 2 H, crown), 3.91 (m, 2 H, crown), 3.84 (m, 2 H, crown), 3.74 (m, 2 H, crown), 3.71 (m, 2 H, crown), 3.70 (m, 2 H, crown), 3.68 (m, 2 H, crown), 3.65 (s, 4 H, crown), 1.5–0.6 (very broad, BH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 151.64 [d, J_P = 2.2, Ar*(C^4)], 148.98 [d, J_P = 12.8, Ar*(C^3)], 133.03 [d, J_P = 9.5, Ph(C_{ortho})], 132.04 [d, J_P = 2.2, Ph(C_{para})], 129.65 [d, J_P = 57.8, Ph(C_{ipso})], 128.67 [d, J_P = 10.0, Ph(C_{meta})], 127.38 [d, J_P = 9.5, Ar*(C^6)], 120.07 [d, J_P = 62.3, Ar*(C^1)], 118.21 [d, J_P = 12.8, Ar*(C^2)], 113.28 [d, J_P = 12.23, Ar*(C^5)], 70.94, 70.89, 70.80, 70.71, 70.67, 69.45, 69.37, 69.17, 68.88 (s, CH$_2$ crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 21.5 ppm.

Ar*$_2$MeP·BH$_3$ (8): The procedure described above for **7** was used for the synthesis of borane complex **8** starting from the crude product **2** (0.35 g, 0.52 mmol) and a 1.0 M solution of BH_3·THF in THF (0.52 mL, 0.52 mmol). In this case, the reaction time was reduced to 4 h, and the crude product was recrystallized three times from a mixture of absolute ethanol and methanol (18:1) at –25 °C to provide 0.21 g (60%) of an analytically pure solid which was identified as **8**. $C_{33}H_{52}BO_{12}P$ (682.55): calcd. C 58.07, H 7.68; found C 58.30, H 7.63. MS (ESI+): m/z = 706.0 (calcd. for MNa^+: 705.3). IR (KBr pellets): ν(BH) = 2371 s. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.19 [dd, J_P = 12.3, J_{H6} = 1.9, 2 H, Ar*(H^2)], 7.13 [ddd, J_P = 12.0, J_{H5} = 8.0, 2 H, Ar*(H^6)], 6.87 [dd, J_P = 2.9, 2 H, Ar*(H^5)], 4.15 (m, 4 H, CH_2 crown), 4.13 (m, 4 H, crown), 3.91 (m, 4 H, crown), 3.89 (m, 4 H, crown), 3.78 (m, 8 H, crown), 3.73 (m, 8 H, crown), 3.65 (s, 8 H, crown), 1.74 (d, J_P = 10.3, 3 H, Me), 1.3–0.5 (very broad, BH_3) ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$, 160 MHz): δ = –39 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 151.52 [s, Ar*(C^4)], 148.97 [d, J_P = 13.3, Ar*(C^3)], 125.52 [d, J_P = 8.9, Ar*(C^6)], 122.20 [d, J_P = 60.5, Ar*(C^1)], 117.25 [d, J_P = 11.8, Ar*(C^2)], 113.55 [d, J_P = 13.3, Ar*(C^5)], 70.91, 70.85, 70.77, 70.68, 69.50, 69.39, 68.94 (s, CH$_2$ crown), 12.5 (d, J_P = 41.3, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 10.2 ppm.

Ar*$_2$PhP·BH$_3$ (9): The procedure described above for **7** was used for the synthesis of borane complex **9** (0.308 g, 90%) from **3** (0.250 g, 0.342 mmol). The presence of 1 equiv. of MeOH in the crystalline white solid is suggested by the elemental analyses and confirmed by NMR spectra (resonances of the methanol are omitted in the spectroscopic data below). $C_{38.5}H_{56}BO_{12.5}P$ (760.65, includes 1/2 a molecule of methanol): calcd. C 60.79, H 7.42; found C 60.74, H 7.36. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.49 [m, J_P = 10.8, 2 H, Ph(H_{ortho})], 7.47 [m, 1 H, Ph(H_{para})], 7.38 [m, 2 H, Ph(H_{meta})], 7.08 [dd, J_P = 11.4, J_{H6} = 1.8, 2 H, Ar*(H^2)], 7.00 [ddd, J_P = 8.6, J_{H5} = 8.4, 2 H, Ar*(H^6)], 6.85 [dd, J_P = 2.6, 2 H, Ar*(H^5)], 4.15 (m, 4 H, CH_2 crown), 4.05 (m, 4 H, crown), 3.91 (m, 4 H, crown), 3.84 (m, 4 H, crown), 3.75 (m, 4 H, crown), 3.74–3.67 (m, 12 H, crown), 3.66 (s, 8 H, crown), 1.5–0.6 (very broad, BH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.50 [s, Ar*(C^4)], 148.98 [d, J_P = 13.3, Ar*(C^3)], 132.89 [d, J_P = 9.6, Ph(C_{ortho})], 130.95 [d, J_P = 3.0, Ph(C_{para})], 130.11 [d, J_P = 58.2, Ph(C_{ipso})], 128.60 [d, J_P = 10.3, Ph(C_{meta})], 127.17 [d, J_P = 8.9, Ar*(C^6)], 120.57 [d, J_P = 62.7, Ar*(C^1)], 117.97 [d, J_P = 12.5, Ar*(C^2)], 113.17 [d, J_P = 12.5, Ar*(C^5)], 70.90, 70.82, 70.78, 70.69, 70.63, 70.41, 69.36, 69.12, 68.84 (s, CH$_2$ crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 21.0 ppm.

Decomplexation of Phosphane–Borane Complex 7: This was carried out as described below for complex **9**.

Decomplexation of Phosphane–Borane Complex 8: Complex **8** (0.044 g, 0.065 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.0174, 0.16 mmol) were dissolved in THF (5 mL). The mixture was refluxed at 85 °C for 5 h and then allowed to cool to room temperature. The solvent was removed under reduced pressure and complete decomplexation was evidenced by ^1H NMR spectroscopy. The excess of DABCO was completely eliminated under high vacuum at room temperature and the DABCO·BH_3 formed in the reaction was partially removed in this treatment. The final product was found to be a mixture of phosphane **2** and DABCO·BH_3 (1.6:1, ^1H NMR).

Decomplexation of Phosphane–Borane Complex 9: Complex **9** (0.22 g, 0.30 mmol) and the DABCO ligand (0.040, 0.36 mmol) were dissolved in toluene (20 mL). The mixture was stirred at 40 °C for 4 h. The solvent was removed under reduced pressure and the crude product was identified as a 1:1 mixture of phosphane **3** and complex BH_3·DABCO (^1H NMR), showing that decomplexation was complete. Phosphane **3** (0.20 g, 90%) could be purified by crystallization of the crude mixture with ethanol at –25 °C.

[PtCl$_2$(PAr*Ph$_2$)$_2$] (10): The procedure described below for **12** was used for the synthesis of platinum complex **10** starting from phosphane **1** (0.067 g, 0.13 mmol) and [$PtCl_2$(PhCN)$_2$] (0.028 g, 0.059 mmol). Complex **10** was obtained as a pure white solid containing only the *cis* isomer (0.062 g, 83%). $C_{56}H_{66}Cl_2O_{12}P_2Pt$ (1259.07): calcd. C 53.42, H 5.28; found C 53.11, H 5.31. MS (ESI+): m/z = 1281.0 (calcd. for MNa^+: 1280.3). IR (Nujol): ν(Pt–Cl) = 318, 292. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.44 [m, 8 H, Ph(H_{ortho})], 7.28 [m, 4 H, Ph(H_{para})], 7.14 [m, 8 H, Ph(H_{meta})], 7.09 [m, J_P = 10.5, J_{H6} = 2.0, 2 H, Ar*(H^2)], 6.93 [m, $J_P \approx$ 8, 2 H, Ar*(H^6)], 6.59 [dd, J_P = 2.2, J_{H5} = 8.3, 2 H, Ar*(H^5)], 4.10 (m, 4 H, CH_2 crown), 3.90 (m, 4 H, crown), 3.76 (m, 8 H, crown), 3.74 (m, 8 H, crown), 3.69 (m, 8 H, crown), 3.66 (s, 8 H, crown) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.07 [d, J_P = 2.2, Ar*(C^4)], 147.67 [pseudo t, $J_{P\,virtual}$ = 14.4, Ar*(C^3)], 134.44 [pseudo t, $J_{P\,virtual}$ = 9.6, Ph(C_{ortho})], 130.47 [s, Ph(C_{para})], 130.01 [pseudo dd, $J_{apparent}$ = 68.0 and 2.4, Ph(C_{ipso})], 129.01 [pseudo t, $J_{P\,virtual}$ = 9.6, Ar*(C^6)], 127.66 [pseudo t, $J_{P\,virtual}$ = 11.6, Ph(C_{meta})], 120.09 [pseudo dd, $J_{apparent}$ = 68.0 and 1.6, Ar*(C^1)], 120.39 [pseudo t, J_P = 12.6, Ar*(C^2)], 112.03 [pseudo t, J_P = 12.8, Ar*(C^5)], 70.93, 70.90, 70.79, 70.69, 70.58, 69.32, 68.92, 68.79 (s, CH$_2$ crown) ppm.

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 15.1 (s with ^{195}Pt satellites, J_{Pt} = 3669 Hz).

[$PtCl_2$(PAr*$_2$Me)$_2$] (11): Phosphane–borane complex **8** (0.044 g, 0.065 mmol) and DABCO (0.0174 g, 0.15 mmol) were refluxed in THF for 5 h. The solvent was removed and the residue was treated with 1 equiv. of [$PtCl_2$(PhCN)$_2$] (0.015 g, 0.032 mmol) in toluene (5 mL). The mixture was stirred at room temperature for 15 h. Subsequently, the solvent was removed in vacuo and the residue washed with hexane. The crude product thus obtained, a mixture of *cis*-**11** and BH_3·DABCO, was chromatographed on a neutral alumina column using a 9:1 mixture of toluene and ethanol as mobile phase. Complex **11** was obtained as a solid and the *cis* isomer (0.032 g, 63%). $C_{66}H_{98}Cl_2O_{24}P_2Pt$ (1603.42): calcd. C 49.44, H 6.16; found C 49.20, H 6.08. MS (MALDI-TOF): *m*/*z* = 1624.4 (calcd. for MNa^+: 1624.48). IR (Nujol): ν(Pt–Cl) = 312, 285. ^1H NMR ($CDCl_3$, 500 MHz,): δ = 7.08 [m, J_P = 12.1, 4 H, Ar*(*H*^{2})], 6.99 [m, $J_P \approx$ 8, 4 H, Ar*(*H*^{6})], 6.71 [dd, J_{H5} = 8.3, J_P = 2.0, 4 H, Ar*(*H*^{5})], 4.12 (m, 8 H, CH_2 crown), 4.00–3.83 (m, 16 H, CH_2 crown), 3.74–3.67 (m, 32 H, CH_2 crown), 3.65 (s, 16 H, CH_2 crown), 1.79 (d, J_P = 10.3, 6 H, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 151.35 [s, Ar*(*C*^{4})], 148.46 [pseudo t, $J_{P\ virtual}$ = 13.4, Ar*(*C*^{3})], 126.65 [pseudo t, $J_{P\ virtual}$ = 11.2, Ar*(*C*^{6})], 122.23 [d, J_P = 68.4, Ar*(*C*^{1})], 118.26 [pseudo t, $J_{P\ virtual}$ = 14.4, Ar*(*C*^{2})], 112.81 [pseudo t, $J_{P\ virtual}$ = 14.4, Ar*(*C*^{5})], 70.91, 70.84, 70.79, 70.74, 70.67, 70.62, 69.41, 69.38, 68.90 (s, *C*H_2 crown), 17.71 (d, J_P = 47.8, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 0.9 (s with ^{195}Pt satellites, J_{Pt} = 3641 Hz).

[$PtCl_2$(PAr*$_2$Ph)$_2$] (12): Phosphane **3** (0.185 g, 0.25 mmol) and [$PtCl_2$(PhCN)$_2$] (0.060 g, 0.125 mmol) were dissolved in toluene (5 mL). The mixture was stirred at room temperature for 15 h. Then, the solvent was removed in vacuo, the residue washed several times with hexane, and crystallized by addition of absolute methanol to afford **12** as a white solid (0.198 g, 90%). Alternatively, the reaction time was reduced to 1 h when [$PtCl_2$(COD)] (COD = 1,5-cyclooctadiene) was used instead of [$PtCl_2$(PhCN)$_2$]. In both cases, only the *cis* isomer was detected. $C_{76}H_{102}Cl_2O_{24}P_2Pt$ (1727.56): calcd. C 52.84, H 5.95; found C 52.78, H 5.98. IR (Nujol): ν(Pt–Cl) = 317, 290. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.42 [m, J_P = 9.0, 4 H, Ph(*H*$_{ortho}$)], 7.27 [m, 2 H, Ph(*H*$_{para}$)], 7.15 [m, 4 H, Ph(*H*$_{meta}$)], 7.09 [m, J_P = 12.0, J_{H6} = 1.8, 4 H, Ar*(*H*^{2})], 6.86 [m, J_P = 10.2, 4 H, Ar*(*H*^{6})], 6.57 [dd, J_{H5} = 8.5, J_P = 2.3, 4 H, Ar*(*H*^{5})], 4.11 (m, 8 H, CH_2 crown), 3.90 (m, 8 H, crown), 3.75 (m, 16 H, crown), 3.70 (m, 16 H, crown), 3.67 (m, 16 H, crown), 3.65 (s, 16 H, crown) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.02 [s, Ar*(*C*^{4})], 147.75 [pseudo t, $J_{P\ virtual}$ = 15.2, Ar*(*C*^{3})], 134.25 [pseudo t, $J_{P\ virtual}$ = 9.4, Ph(*C*$_{ortho}$)], 131.00 [pseudo dd, $J_{apparent}$ = 62.4 and 2.3, Ph(*C*$_{ipso}$)], 130.38 [s, Ph(*C*$_{para}$)], 128.88 [pseudo t, $J_{P\ virtual}$ = 10.6, Ar*(*C*^{6})], 127.62 [pseudo t, J_P = 11.4, Ph(*C*$_{meta}$)], 120.85 [pseudo dd, $J_{apparent}$ = 70.6 and 1.5, Ar*(*C*^{1})], 120.40 [pseudo t, J_P = 13.2, Ar*(*C*^{2})], 112.04 [d, J_P = 13.2, Ar*(*C*^{5})], 70.91, 70.85, 70.79, 70.72, 70.69, 70.56, 69.38, 69.31, 68.97, 68.79 (s, *C*H_2 crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 14.8 (s with ^{195}Pt satellites, J_{Pt} = 3673 Hz).

[$PdCl_2$(PAr*Ph_2)$_2$] (13): This complex has been previously reported by Okano et al.[6] We employed the same procedure as described above for **12**. The crude product contains traces of the *cis* isomer (δ_P = 33.0 ppm), but after crystallization complex **13** was obtained as a pure yellow solid containing only the *trans* isomer (90%). $C_{56}H_{66}Cl_2O_{12}P_2Pd$ (1170.41): calcd. C 57.47, H 5.68; found C 57.80, H 5.63. MS (ESI+): *m*/*z* = 1193.6 (calcd. for MNa^+: 1192.2). IR (Nujol): ν(Pd–Cl) = 359. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.62 [m, 8 H, Ph(*H*$_{ortho}$)], 7.45 [td, $J_{P\ virtual}$ = 12.0, J_{H6} = 1.9, 2 H, Ar*(*H*^{2})], 7.40–7.30 [m, 12 H, Ph(*H*$_{meta}$) and Ph(*H*$_{para}$) overlapping], 7.14 [m, $J_{P\ virtual}$ = 10.4, J_{H5} = 8.4, 2 H, Ar*(*H*^{6})], 6.82 [br. d, $J_{P\ virtual} \approx$ 2.0, 2 H, Ar*(*H*^{5})], 4.14 (m, 4 H, CH_2 crown), 4.00 (m, 4 H, crown), 3.91 (m, 4 H, crown), 3.79 (m, 4 H, crown), 3.74 (m, 4 H, crown), 3.70–3.68 (m, 12 H, crown), 3.65 (s, 8 H, crown) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.03 [s, Ar*(*C*^{4})], 148.16 [pseudo t, $J_{P\ virtual}$ = 14.8, Ar*(*C*^{3})], 134.79 [pseudo t, $J_{P\ virtual}$ = 11.8, Ph(*C*$_{ortho}$)], 130.33 [s, Ph(*C*$_{para}$)], 130.21 [pseudo t, J_P = 50.1, Ph(*C*$_{ipso}$)], 128.94 [pseudo t, $J_{P\ virtual}$ = 11.8, Ar*(*C*^{6})], 127.90 [pseudo t, $J_{P\ virtual}$ = 8.8, Ph(*C*$_{meta}$)], 121.08 [pseudo t, $J_{P\ virtual}$ = 14.8, Ar*(*C*^{2})], 120.80 [pseudo t, $J_{P\ virtual}$ = 53.2, Ar*(*C*^{1})], 112.76 [pseudo t, $J_{P\ virtual}$ = 5.6, Ar*(*C*^{5})], 70.97, 70.83, 70.79, 70.75, 70.66, 69.46, 69.05, 68.84 (s, *C*H_2 crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 24.1 ppm.

[$PdCl_2$(PAr*$_2$Me)$_2$] (14): The procedure described above for **11** was used for the synthesis of palladium complex **14** starting from **8** (0.064 g, 0.094 mmol), DABCO (0.041 g, 0.37 mmol), and [$PdCl_2$(COD)] (0.012 g, 0.042 mmol). Although complex **14** was formed in greater than 95% yield (^1H NMR evidence) as a pair of *cis*/*trans* isomers (1:0.75), the resultant oil could not be purified by crystallization or chromatography and was used in this form in further catalytic studies. In the NMR spectroscopic data of the unpurified *cis*/*trans* mixture that follows, resonances corresponding to the BH_3·DABCO impurity are omitted, and the *cis*/*trans* ratio has been taken into account in integral values. IR (Nujol): ν(Pd–Cl) = 356 (*trans*), 287, 276 (*cis*). ^1H NMR ($CDCl_3$, 500 MHz,): δ = 7.223 and 7.216 [overlapping m, $J_P \approx$ 10–14, 8 H, Ar*(*H*^{6}) and Ar*(*H*^{2}) *trans* isomer], 7.07 [dd, J_P = 12.4, J_{H6} = 1.9, 4 H, Ar*(*H*^{2}) *cis* isomer], 6.97 [ddd, J_P = 11.8, J_{H5} = 8.3, 4 H, Ar*(*H*^{6}) *cis* isomer], 6.86 [br. d, J_{H6} = 8.4, J_P not observed, 4 H, Ar*(*H*^{5}) *trans* isomer], 6.72 [dd, J_P = 2.6, 4 H, Ar*(*H*^{5}) *cis* isomer], 4.15–3.66 (overlapped m, 80 H, CH_2 crown, *cis* and *trans* isomers), 1.96 (pseudo t, $J_{P\ virtual}$ = 7.1, 6 H, Me *trans* isomer), 1.91 (d, J_P = 11.1, 3 H, Me *cis* isomer) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz): δ = 151.49, 150.93 [s, Ar*(*C*^{4})], 148.65 [d, J_P = 14.3, Ar*(*C*^{3}) *cis* isomer], 148.36 [pseudo t, $J_{P\ virtual}$ = 14.1, Ar*(*C*^{3}) *trans* isomer], 126.8 [m, Ar*(*C*^{6}) *cis* and *trans* overlapping], 123.61 [pseudo t, $J_{P\ virtual}$ = 52.0, Ar*(*C*^{1}) *trans* isomer], 122.78 [d, J_P = 57.5, Ar*(*C*^{1}) *cis* isomer], 118.78 [pseudo t, $J_{P\ virtual}$ = 14.4, Ar*(*C*^{2}) *trans* isomer], 118.22 [d, J_P = 13.8, Ar*(*C*^{2}) *cis* isomer], 113.00 [m, Ar*(*C*^{5}) *cis* and *trans* overlapping], 70.97, 70.95, 70.85, 70.82, 70.76, 70.69, 70.64, 69.48, 69.41, 69.24, 68.91, 68.85 (s, *C*H_2 crown), 18.6 (overlapping d and m, Me) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 19.7 (*cis*), 7.7 (*trans*).

[$PdCl_2$(PAr*$_2$Ph)$_2$] (15): The procedure described above for **12** was used for the synthesis of palladium complex **15** starting from phosphane **3** (0.168 g, 0.25 mmol) and [$PdCl_2$(PhCN)$_2$] (0.048 g, 0.125 mmol). A yellow solid was obtained (0.20 g, 98%) that was identified by NMR spectroscopy as a 3:7 mixture of *cis*/*trans* isomers of complex **15**. Both isomers were easily separated because of their different solubility in toluene. The soluble *cis* isomer was extracted in this solvent and subsequently crystallized from methanol whereas the insoluble residue containing the *trans* isomer was crystallized from CH_2Cl_2/toluene. Both were obtained as deep-yellow solids.

***trans*-15:** $C_{76}H_{102}Cl_2O_{24}P_2Pd$ (1638.90): calcd. C 55.70, H 6.27; found C 55.54, H 6.20. IR (Nujol): ν(Pd–Cl) = 356. ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.57 [m, J_P = 12.4, 4 H, Ph(*H*$_{ortho}$)], 7.40–7.30 [m, 10 H, Ph(*H*$_{para}$), Ph(*H*$_{meta}$), and Ar*(*H*^{2}) overlapping], 7.08 [m, J_P = 10.3, J_{H5} = 8.5, J_{H2} = 2.0, 4 H, Ar*(*H*^{6})], 6.80 [br. d, 4 H, Ar*(*H*^{5})], 4.13 (m, 8 H, CH_2 crown), 3.96 (m, 8 H, crown), 3.90 (m, 8 H, crown), 3.79 (m, 8 H, crown), 3.49 (m, 8 H, crown), 3.71–

3.68 (m, 24 H, crown), 3.67 (s, 16 H, crown) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 150.93 [s, Ar*(C^4)], 148.98 [pseudo t, $J_{P\ virtual}$ = 14.8, Ar*(C^3)], 134.59 [pseudo t, $J_{P\ virtual}$ = 11.8, Ph(C_{ortho})], 130.81 [pseudo t, $J_{P\ virtual}$ = 45.4, Ph(C_{ipso})], 130.19 [s, Ph(C_{para})], 128.78 [pseudo t, $J_{P\ virtual}$ = 11.8, Ar*(C^6)], 127.82 [pseudo t, J_P = 10.4, Ph(C_{meta})], 121.25 [pseudo t, $J_{P\ virtual}$ = 53.0, Ar*(C^1)], 120.86 [m, Ar*(C^2), overlapping with Ar*(C^1)], 113.17 [d, J_P = 12.5, Ar*(C^5)], 70.98, 70.94, 70.85, 70.78, 70.65, 69.49, 69.13, 68.85 (s, CH_2 crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 23.8 ppm.

***cis*-15:** $C_{76}H_{102}Cl_2O_{24}P_2Pd$ (1638.90): calcd. C 55.70, H 6.27; found C 55.78, H 6.19. IR (Nujol): ν(Pd–Cl) = 287, 276. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.63 [m, J_P = 12.6, 4 H, Ph(H_{ortho})], 7.45 [m, 2 H, Ph(H_{para})], 7.38 [m, 4 H, Ph(H_{meta})], 7.29 [dd, J_P = 13.2, J_{H6} = 1.8, 4 H, Ar*(H^2)], 7.05 [ddd, J_P = 12.1, J_{H5} = 8.4, 4 H, Ar*(H^6)], 6.80 [dd, J_P = 2.5, 4 H, Ar*(H^5)], 4.15 (m, 8 H, CH_2 crown), 4.07 (m, 8 H, crown), 3.92 (m, 8 H, crown), 3.80 (m, 8 H, crown), 3.75 (m, 8 H, crown), 3.71–3.68 (m, 24 H, crown), 3.67 (s, 16 H, crown) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 151.89 [d, $J_P \approx$ 1.0, Ar*(C^4)], 148.30 [d, J_P = 15.5, Ar*(C^3)], 134.40 [d, J_P = 11.6, Ph(C_{ortho})], 131.51 [s, Ph(C_{para})], 128.76 [d, J_P = 3.9, Ar*(C^6)], 128.31 [d, J_P = 12.2, Ph(C_{meta})], 128.28 [d, J_P = 54.7, Ph(C_{ipso})], 120.09 [d, J_P = 14.9, Ar*(C^2)], 118.31 [d, J_P = 64.7, Ar*(C^1)], 112.45 [d, J_P = 15.5, Ar*(C^5)], 71.01, 70.95, 70.86, 70.73, 70.71, 70.58, 69.39, 69.34, 69.26, 68.83 (s, CH_2 crown) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ = 33.4 ppm.

Water Solubility of Complexes 10 and 11: The extent of water solubility was assessed by placing a small, accurately weighted quantity of the compound in a vial, followed by slow addition of water, with stirring, from a 50 μL syringe. Solubility measurements were repeated several times to give an average value. Measured solubility in water at 25 °C: 0.002 g/100 mL (**10**) and 10 g/100 mL (**11**).

Distribution Coefficients Between Toluene and Water for Phosphanes 1 and 3: Previously, the UV spectra of phosphanes **1** and **3** were registered in ethanol at several concentrations (from ca. 1×10^{-5} to 1×10^{-4} M). Two absorption bands were observed at λ_{max} = 203 and 261 nm for **1**, and 208 and 283 nm for **3**. Fits of *c* versus *A* plots showed a linear correlation in the entire range of concentrations considered only in the case of the second maximum absorption ($R^2 > 0.999$). Thus, the absorptions at 261 nm (ε = 12100) for **1**, and 283 nm (ε = 13300) for **3** were used as follows in the determination of distribution coefficients. A small, accurately weighted quantity of phosphane (approx. 0.02 mmol) was added to a 1:1 mixture of toluene and water (5 + 5 mL) that was stirred for 20 min at 25 °C. An aliquot of the aqueous solution (2 mL) was removed with a pipette, evaporated to dryness, and dissolved in ethanol (3 mL). The original water-phase concentration was determined by measuring the concentration of phosphane in the ethanol solution by UV spectroscopy, using the *c* versus *A* plots previously obtained. At 25 °C, distribution constants, defined as $[phosphane]_{aq}/[phosphane]_{toluene}$, are 7.4×10^{-3} for **1**, and 1.46×10^{-2} for **3**.

Palladium-Catalyzed Stille Couplings: We used similar conditions to those previously described.[40,41] In a typical experiment, $PhSnCl_3$ (0.31 mL, 1.824 mmol) was dissolved in 2 mL of degassed water. The solution was treated with 5.5 mL of aqueous KOH (1 M) and stirred for several minutes. The *p*-iodoaniline (0.339 g, 1.52 mmol) and the Pd catalyst **14** (0.023 g, 0.0152 mmol) were then added and the mixture was stirred for 3 h at 100 °C under argon. The product was extracted with diethyl ether and dried with sodium sulfate. The solution was filtered off and the solvent removed in vacuo to give a solid. The crude product was analyzed by HPLC-MS and ^1H NMR spectroscopy (95% 4-aminobiphenyl, 5% *p*-iodoaniline) and purified by flash chromatography on silica gel with toluene/ethanol (9:1) to give pure 4-aminobiphenyl (0.244 g, 95%).

X-ray Structure Determinations: White, needle-shaped crystals of **9** were obtained from methanol/ethanol at –25 °C. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Table 3. The crystal was glued to a glass fiber and mounted on a Kappa-CCD Bruker–Nonius diffractometer with area detector, and data were collected using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 200 K, with an exposure time of 24 s per frame (3 sets; 247 frames). Raw data were corrected for Lorenz and polarization effects. The structure was solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares on F^2 (SHELXL-97).[46] Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. Most of the hydrogen atoms were found in the final Fourier map and were refined with isotropic thermal displacement parameters, others were introduced in the last cycle of refinement from geometrical calculations and refined using a riding model. A molecule of methanol with important disorder was located; the hydrogen atoms of the methyl group are not included. All the calculations were made using the WINGX system.[47]

CCDC-253624 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystallographic details for **9**.

Empirical formula	$C_{38}H_{54}BO_{12}P{\cdot}CH_4O$
Habit	needles
Formula mass	776.67
a [Å]	18.7794(19)
b [Å]	8.5756(9)
c [Å]	26.566(4)
β [°]	106.11(1)
λ (Mo-$K\alpha$) [Å]	0.71073
Temp. [K]	200(2)
Space group	monoclinic, $P2_1/n$
Crystal size [mm]	$0.5 \times 0.1 \times 0.1$
V [Å^3]	4110.3(9)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.226
μ [cm^{-1}]	1.26
θ limits [°]	5.00 to 27.51
Limiting indices	$-24 \le h \le 24$
	$-11 \le k \le 11$
	$-34 \le l \le 23$
Reflections collected	25581
Unique reflections	9222 [R(int) = 0.1577]
Reflections observed with $I > 2\sigma(I)$	4238
Data/restraints/parameters	9222/0/677
R [$I > 2\sigma(I)$]; wR^2 [a]	0.0984; 0.2027
Goodness-of-fit indicator	1.013
Max. peak in final diff. map [e Å^{-3}]	0.578
Min. peak in final diff. map [e Å^{-3}]	–0.390

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR^2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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[1] *Aqueous-Phase Organometallic Catalysis: Concepts and Applications* (Eds.: B. Cornils, W. A. Herrmann), VCH, 2nd ed., **2004**.
[2] N. Pinault, D. W. Bruce, *Coord. Chem. Rev.* **2003**, *241*, 1–25.
[3] O. Stelzer, S. Rossenbach, D. Hoff, ref.[1], pp. 100–120.
[4] E. M. Hyde, B. L. Shaw, I. Shepherd, *J. Chem. Soc., Dalton Trans.* **1978**, 1696–1705.
[5] T. Okano, M. Iwahara, T. Suzuki, H. Konishi, J. Kiji, *Chem. Lett.* **1996**, 1467–1470.
[6] T. Okano, M. Iwahara, H. Konishi, J. Kiji, *J. Organomet. Chem.* **1988**, *346*, 267–275.
[7] V. I. Kal'chenko, D. M. Rudkevich, O. A. Aleksyuk, L. N. Markovskii, *Zh. Obshch. Khim.* **1991**, *61*, 2155–2158.
[8] B. S. Muehl, B.-J. Sheu, S. A. Burns, J. E. Fritz, D. A. Tribbett, J. A. Weitgenant, B. N. Storhoff, J. C. Huffman, *J. Coord. Chem.* **1995**, *35*, 359–370.
[9] C. Nataro, H. Baseski, C. M. Thomas, B. J. Wiza, K. M. Rourke, *Polyhedron* **2001**, *20*, 1023–1028.
[10] M. Sawamura, Y. Nakayama, W.-M. Tang, Y. Ito, *J. Org. Chem.* **1996**, *61*, 9090–9096.
[11] L. A. Barg, R. W. Byrn, M. D. Carr, D. H. Nolan, B. N. Storhoff, J. C. Huffman, *Organometallics* **1998**, *17*, 1340–1346.
[12] J. Kiji, T. Okano, *Rev. Heteroatom Chem.* **1994**, *11*, 191–206.
[13] T. Okano, M. Iwahara, J. Kiji, *Synlett* **1998**, 243–244.
[14] V. Berdini, M. Bassetti, G. Mancini, L. Mandolini, D. Monti, *J. Organomet. Chem.* **1998**, *551*, 331–338.
[15] J. K. Stille, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524.
[16] P. Espinet, A. M. Echavarren, *Angew. Chem. Int. Ed.* **2004**, *43*, 4704–4734 and references cited therein.
[17] For a review on palladium-catalyzed reactions in aqueous media, see: J. P. Genet, M. Savignac, *J. Organomet. Chem.* **1999**, *576*, 305–317.
[18] B. Mohr, D. M. Lynn, R. H. Grubbs, *Organometallics* **1996**, *15*, 4317–4325 and references cited therein.
[19] H. Brisset, Y. Goudel, P. Pellon, M. L. Corre, *Tetrahedron Lett.* **1993**, *34*, 4523–4526.
[20] J. G. Verkade, *Coord. Chem. Rev.* **1972**, *9*, 1–106.
[21] $\delta_{\text{Coord P}} = \delta_{\text{Free P}} + A\delta_{\text{Free P}} + B$, where for the *trans* and *cis* isomers $A = -0.212$ and $B = 38.6$, and $A = -0.304$ and $B = 26.8$, respectively. A. W. Verstuyft, J. H. Nelson, L. W. Gary, *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 53–58. Parameters for other metal complexes can be found in ref.[26]
[22] F. R. Hartley, *Organomet. Chem. Rev. A* **1970**, *6*, 119–137.
[23] P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphane Complexes*, Springer-Verlag, Heidelberg, **1979**.
[24] L. Bemi, H. C. Clark, J. A. Davies, C. A. Fyfe, R. E. Wasylishen, *J. Am. Chem. Soc.* **1982**, 438–445.
[25] G. K. Anderson, H. C. Clark, J. A. Davies, *Inorg. Chem.* **1981**, *20*, 3607–3611.
[26] B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, R. E. Satinbank, *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 881–885.
[27] W. Strohmeir, F. J. Müller, *Chem. Ber.* **1967**, *100*, 2812–2821.
[28] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
[29] A. Immirzi, A. Musco, *Inorg. Chim. Acta* **1977**, *25*, L41–L42.
[30] T. Bartik, T. Himmler, *J. Organomet. Chem.* **1985**, *293*, 343–351.
[31] This value (δ =24.4 ppm) has been measured by us and differs from that given in ref.[30] (δ =13.3 ppm). In fact, the value of δ = 24.4 ppm correlates far better with the Tolman angle of 145°.
[32] T. Bartik, B. Bartik, B. E. Hanson, I. Guo, I. Tóth, *Organometallics* **1993**, *12*, 164–170.
[33] L. D. Quin, in *Phosphorous-31 NMR Spectroscopy in Stereochemical Analysis* (Eds.: J. G. Verkade, L. D. Quin), VCH, Deerfield Beach, **1987**, chapter 12.
[34] More rigorously speaking, they form an ABX spin system with $\delta_A \approx \delta_B$, because the ^{13}C nucleus breaks the chemical equivalence of both ^{31}P nuclei.
[35] J. C. Huffman, W. A. Skupinski, K. G. Caulton, *Cryst. Struct. Commun.* **1982**, *11*, 1435–1440.
[36] I. Dance, M. Scudder, *J. Chem. Soc., Dalton Trans.* **2000**, 1579–1585.
[37] E. C. Alyea, S. A. Dias, G. Ferguson, R. J. Restivo, *Inorg. Chem.* **1977**, *16*, 2329–2334.
[38] In a study based on 2388 phosphane complexes, the mean value obtained was 148(5)°, with a range of 129–168°: T. E. Müller, D. M. P. Mingos, *Transition Met. Chem.* **1995**, *20*, 533–539.
[39] H.-C. Zhang, G. D. Daves, Jr., *Organometallics* **1993**, *12*, 1499–1500.
[40] A. I. Roshchin, N. A. Bumagin, I. P. Beletskaya, *Tetrahedron Lett.* **1995**, *36*, 125–128.
[41] R. Rai, K. B. Aubrecht, D. B. Collum, *Tetrahedron Lett.* **1995**, *36*, 3111–3114.
[42] C. Wolf, R. Lerebours, *J. Org. Chem.* **2003**, *68*, 7551–7554.
[43] The formation of Pd^0 complexes and Pd metal precipitation when treating $[PdCl_2(PPh_3)_2]$ complexes with NaOH or KOH has been reported: V. V. Grushin, H. Alper, *Organometallics* **1993**, *12*, 1890–1901.
[44] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Butterworth-Heinemann Ltd., Oxford, **1988**.
[45] D. Drew, J. R. Doyle, *Inorg. Synth.* **1972**, *13*, 47–55.
[46] G. M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, **1997**.
[47] WinGX System: L. J. Farrugia, *J. Appl. Cryst.* **1999**, *32*, 837–838.

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