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Synthesis of 6,6′-Bis(dimethylamino)- and 6,6′-Dibromo-Substituted 2,2′-Diphosphanylbiphenyls and Their Palladium Complexes

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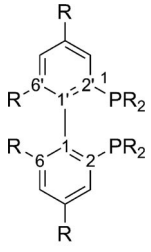
New 6,6′-dibromo- and 6,6′-bis(dimethylamino)-substituted 2,2′-diphosphanylbiphenyl ligands **11**–**14** were prepared starting from 2,2′-dibromo-4,4′-dimethyl-6,6′-dinitro-1,1′-biphenyl (**4**). Depending on the phosphane groups [diphenylphosphanyl (**11**, **13**) or diisopropylphosphanyl (**12**, **14**)] the palladium dichloride complexes show different coordination symmetry. Whereas the smaller diphenylphosphanyl groups lead to C_2-symmetric complexes, the respective bis(diisopropyl)phosphanes **12** and **14** form C_1-symmetric complexes that show fluxional behavior due to the restricted rotation of the isopropyl groups as well as the exchange of atom positions within the C_1-symmetric conformer. All complexes have been tested as precatalysts in the Suzuki–Miyaura cross coupling reaction of 2-bromotoluene and phenylboronic acid. The activity of the catalytic system increases with the size of the diphosphanes and the donating ability of the ligand. In contrast to C_2-symmetric palladium complex **15**, platinum complex **19** was found to be C_1-symmetric in the solid state despite the fact that both complexes have the small bis(diphenylphosphanyl)-substituted diphosphane ligand **11** in common. $NiBr_2$ adduct **20** with a similar diphosphane **13** exists as a mixture of distorted square-planar and tetrahedral coordination sphere geometries in equilibrium with each other.

Introduction

Diphosphanes with general structure **A** (Scheme 1) employing a 1,1′-biphenyl-2,2′-diyl bridge have attracted much interest as supporting ligands in numerous transition-metal-catalyzed transformations,[1–3] including Suzuki–Miyaura cross coupling reactions,[4] amination reactions,[5] Mizoroki–Heck reactions,[6,7] hydroaminations,[8] hydrogenations,[9] additions,[10–14] N-heterocyclizations[15] and others.[16–18]

Not only the employed phosphane substituents but also the size and electronic properties of the substituents at the 6- and 6′-position affect the catalytic activity of the derived transition metal complexes.[3,19,20] In conjunction with our recent efforts to synthesize 2,2′,6,6′-tetraphosphanylbiphenyls[21] we gained access to valuable 2,2′,6,6′-tetrasubstituted biphenyls that allow the syntheses of new members of the above-mentioned class of diphosphanes. In this account we wish to present the syntheses of 6,6′-dibromo- and 6,6′-bis(dimethylamino)-substituted 2,2′-diphosphanylbiphenyls and their palladium complexes. These diphosphanes are of interest, as the large bromo substituents in the *ortho* positions lead to high activation barriers for the rotation around the central C–C bond.[22] Additionally, the dimethylamino groups can increase the electron density of the biphenyl system,[23] act as additional hemilabile donors[24] or form proton sponge systems.[25–27]



A

Scheme 1. 1,1′-Biphenyl-2,2′-diyl-bridged diphosphanes discussed below and the numbering for relevant positions.

Results and Discussion

Ligands based on 2-phosphanyl- and 2,2′-diphosphanylbiphenyls are accessible by various methods employing electrophilic,[28] nucleophilic,[29] and radical chemistry[30] as well as transition-metal-catalyzed[31,32] reactions. A particularly effective method has been the treatment of a 2,2′-di-

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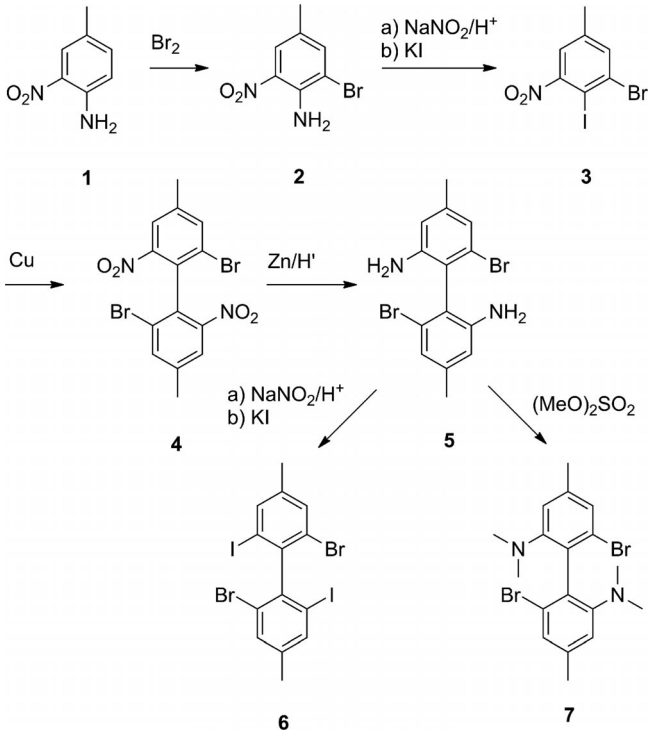
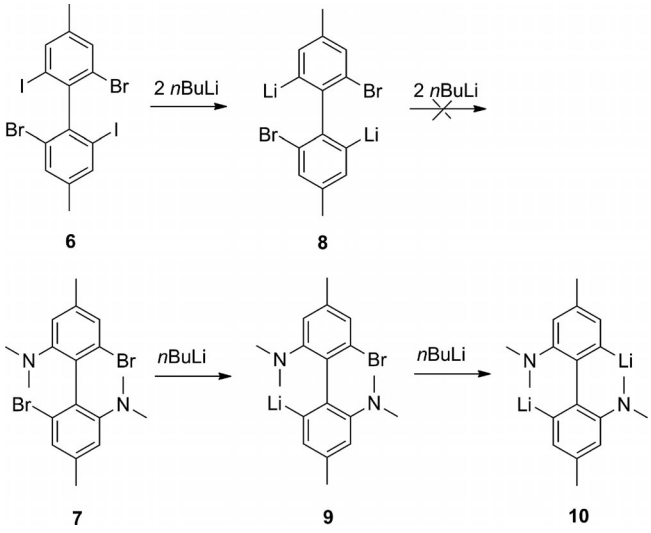
lithiated biphenyl with a chlorophosphane.[28,33,34] Dilithiated biphenyl species are easily prepared by halogen/lithium exchange from the 2,2′-diiodo-/2,2′-dibromobiphenyls. We prepared diiodobiphenyl **6** and dibromobiphenyl **7** by the route depicted in Scheme 2.[35,36] The known diamine derivative **5** can be prepared from inexpensive and commercially available 4-methyl-2-nitroaniline (**1**). The methyl group in the 4-position blocks the C-4 atom from electrophilic attack by bromine in the first step to derivative **2**; consequently, **2** is the only isolable regioisomer.[37] Moreover, the 4-methyl group improves the solubility of all compounds and simplifies workup procedures. The key step in the synthesis is an Ullmann[35,38] homo-coupling of iodo compound **3** to form the central C–C bond in **4**. This reaction is highly selective and proceeds smoothly under relatively mild conditions in good yields due to the activating nitro group in the *ortho* position.[35] Side products (e.g. 1-bromo-3-methyl-5-nitrobenzene) are effectively removed by washing crude biphenyl **4** with ethanol. Following reduction of **4** with Zn/HCl[36] yields **5** neatly. Altogether, **5** can be prepared by this route on a 20 g scale in a cost-effective manner that does not require column chromatography.



Scheme 2. Synthetic route to biphenyl species **6** and **7** used for subsequent modifications.

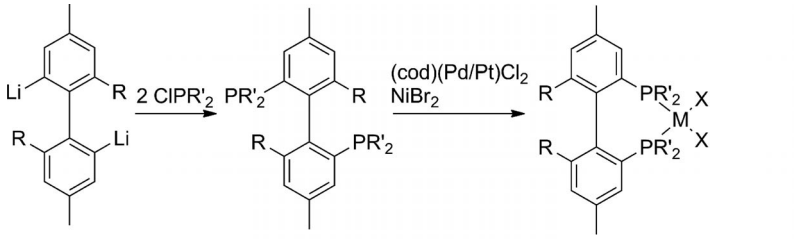
Starting from diamine **5**, diiodo derivative **6**[36] as well as bis(dimethylamino) derivative **7**[26,27] were obtained by Sandmeyer (**6**) or *N*-methylation (**7**) reactions, respectively (Scheme 2). The iodide/lithium exchange with **6** to form dilithiated species proceeds quickly in diethyl ether solution at low temperatures (–80 °C) with *n*- or *t*BuLi (Scheme 3). Even when using excess *n*- or *t*BuLi, only dilithiated species **8** was generated. Due to the electron-rich aromatic system in **7** the bromine/lithium exchange is considerably slower. Therefore, to find optimal conditions for complete formation of **10** (but at the same time avoiding degradation of the solvent and of dilithiated species **10**) this reaction was monitored by sampling small quantities from a reaction mixture of **7** and 3 equiv. of *n*BuLi in diethyl ether solution stirred at 0 °C. Reaction samples were analyzed by ^{1}H and $^{13}C\{^{1}H\}$-DEPT90 NMR spectra following a small-scale water quench. Samples taken after 5 and 15 min reaction times revealed incomplete reaction. All NMR signals for **7** as well as quenched **9** and **10** were assigned by 2D NMR methods. Comparisons between different spectra, especially $^{13}C\{^{1}H\}$-DEPT90 data sets, allowed rough quantitation of compound ratios in the reaction mixtures. Another sample taken after 45 min revealed almost complete reaction, and only small amounts of quenched **9** were found after 2 h. At this point the remaining reaction mixture was quenched using D_2O. The absence of vicinal coupling in **10**, which was quenched with D_2O, points to the low reactivity of **10** towards the organic solvent in the sense of proton abstraction (Figure S1).



Scheme 3. Syntheses of dilithiated reagents **8** and **10**.

Treatment of lithiated species **8** or **10** with a slight excess of chlorodiphenyl- or chloro(diisopropyl)phosphane led to the formation of diphosphanes **11**–**14** (Scheme 4). Attempts to make **8** or **10** react with di-*tert*-butyl(chloro)phosphane failed; even under reflux conditions only quenched **10** [2,2′-bis(dimethylamino)-4,4′-dimethylbiphenyl] was identified following workup. It is worth noting that, for the synthesis of the PPh_2-substituted diphosphane **11**, a "one shot" or inverse addition is recommended to avoid formation of a monolithiated monophosphane species that likely decomposes by P–C bond cleavage to a phosphafluorene derivative.[32,39]

It appears that dibromo-substituted diphosphanes **13** and **14** can be handled in air without significant oxidation. In contrast, both dimethylamino-substituted phosphanes **11** and **12** are significantly more sensitive to oxidation.[40] The dibromo-substituted diphosphane **14** crystallized as well-shaped crystals and was therefore further investigated by X-



8 R = Br
10 R = NMe_2

11 R = NMe_2, R' = Ph
12 R = NMe_2, R' = *i*Pr
13 R = Br, R' = Ph
14 R = Br, R' = *i*Pr

15 R = NMe_2, R' = Ph, M = Pd, X = Cl
16 R = NMe_2, R' = *i*Pr, M = Pd, X = Cl
17 R = Br, R' = Ph, M = Pd, X = Cl
18 R = Br, R' = *i*Pr, M = Pd, X = Cl
19 R = NMe_2, R' = Ph, M = Pt, X = Cl
20 R = Br, R' = Ph, M = Ni, X = Br

Scheme 4. Syntheses of diphosphanes **11**–**14** and complexes **15**–**20**.

ray structure analysis (Tables S2 and S3). In the asymmetric unit one molecule of **14** is found with C_1 symmetry. However, the deviation from the expected C_2 symmetry is small and can be fully explained by packing effects. Figure S14 (left side) depicts the molecular structure of **14**. The two aromatic rings of the biphenyl core are twisted by about 80 °, the electron lone pairs of the phosphane substituents are directed towards the indirectly bound aromatic ring of the biphenyl moiety, and the intramolecular distance between the two phosphorus atoms is 3.7280(10) Å.

All phosphanes **11**–**14** were treated with [Pd(cod)Cl_2] (cod = 1,5-cyclooctadiene) to generate corresponding palladium complexes **15**–**18**. Phosphane **11** was additionally treated with [Pt(cod)Cl_2] to yield complex **19**, and phosphane **13** was treated with $NiBr_2$ to yield nickel complex **20**. The $^{31}P\{^1H\}$ NMR spectra of the PPh_2 complexes **15**, **17** and **19** show a single sharp signal. In contrast, spectra of the P(*i*Pr_2)-substituted complexes **16** and **18** revealed one very broad singlet. Similar broadening was also found in the ^1H NMR spectra, but to a smaller extent. Obviously, complexes **16** and **18** show fluxional behavior. Indeed, when **16** was dissolved in [D_7]dmf (dmf = *N*,*N*-dimethylformamide) and $^{31}P\{^1H\}$ NMR spectra were recorded at 100 °C (Figure S2), a single sharp singlet was formed revealing the equivalence of the two phosphorus atoms in averaged spectra at high temperature that corroborate the expected structure. For further investigation of the dynamics in this system, VT-NMR experiments were performed. Lowering the temperature of a solution of **18** in CD_2Cl_2 led to the appearance of two broad singlets with equal intensity but different broadening, clearly visible at –35 °C. These two singlets each split into two broad singlets with different intensities (45:55 for **18** at –90 °C in CD_2Cl_2), the ratio between the intensities of these two pairs of signals is the same (Figure 1). This behavior is consistent with a lowering of the symmetry in complex **18** from C_2 symmetry to C_1 symmetry that would lead to the appearance of two singlets with equal intensity; P_A mutually exchanges slowly with P_B, in the sense that they exchange the chemical environment but keeping all bonds intact. Such behavior was also observed in similar systems.[4] Additional splitting can be explained by a slow fluctuation between two different C_1-symmetric conformers with different stability, most likely caused by hindered rotation of one or more isopropyl groups; P_{A1} exchanges with P_{A2} as well as P_{B1} exchanges with P_{B2}; the index A and B defines the position of the phosphorus atom in the molecule, and the number defines the conformer (Figure 1).

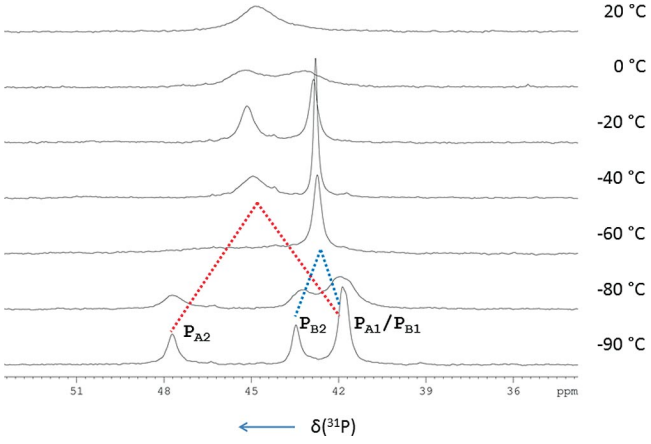


Figure 1. $^{31}P\{^1H\}$ VT-NMR spectra (in CD_2Cl_2 from 20 °C to –90 °C) of complex **18**. Signals P_A and P_B undergo mutual exchange only at higher temperatures (above 0 °C). Splitting of the signals P_A and P_B is due to the presence of two different conformers that have some minor differences regarding the coordination geometry and that slowly interconvert.

The variable-temperature $^{31}P\{^1H\}$ NMR spectroscopic data obtained for **18** were used in a line-shape analysis (Figure S6) by exploiting the calculated spectra, and assuming the above discussed exchange scheme the agreement with the experimental spectra is reasonably good. The calculated rate constants (Table S1) were further used in an Arrhenius plot (Figure S7). Interestingly, the activation energy E_a for mutual exchange [E_a = 30.5(1.1) kJ/mol and A = 149(+121/–67) GHz] is almost identical to that obtained for the interconversion between the two conformers [E_a = 30.0(2.5) kJ/mol and A = 0.8(+1.8/–0.55) GHz]. The differences in reaction rate seem to solely result from the frequency factor, which differs by two orders of magnitude.

Complex **16** also showed fluxional behavior, in this case the $^{31}P\{^1H\}$ NMR spectrum at –90 °C (CD_2Cl_2) shows five broad singlets in a ratio of 0.23:0.44:0.44:1.23:1 (Figure S3). Similar to the related complex **18**, complex **16** was found to

exist in different conformers at low temperatures (Figures S2 and S3). To gain more insight into the signal assignment, ^{31}P EXSY spectra were recorded (Figure S4). These spectra allowed the grouping of the signals into two groups (P_A and P_B); exchange within these two groups was observed at –90 °C (max. 0.5 s mixing time), and the intensities summed together equally. Assuming that the strongest signal at δ = 47.66 ppm is coincidently an overlay of two signals, each of the two groups include three signals with a ratio of 0.23:0.44:1. In summary, we can conclude that, in the case of complex **18**, the most stable conformer is also C_1-symmetric. This isomer undergoes a dynamic exchange with two other C_1-symmetric conformers (Figure S4). The positions of P_A and P_B in **18** do not exchange at low temperatures, and the mutual exchange between P_A and P_B is significantly less likely. Due to the complicated exchange between six positions and four different time constants, determination of the dynamic parameters was not possible. All palladium complexes bearing PPh_2 groups failed to exhibit any broadening of NMR signals at low temperatures. The $^{31}P\{^1H\}$ NMR spectra of complex **19** showed the expected singlet with ^{195}Pt satellites, and again no broadening at low temperatures was observed. However, one of the two phenyl groups seems to be rotationally hindered as indicated by splitting of the ^1H NMR signal below –40 °C (Figure S5). Attempts to record $^{31}P\{^1H\}$ NMR spectra of the nickel complex **20** failed, this might be due to the low solubility as well as the presence of an equilibrium between the respective square-planar (S = 0) and tetrahedral (S = 1) isomers.[41] This is further supported by some broadening and unusually large shifts of the proton resonances, which is a typical behavior of resonances in the ^1H NMR spectra for such compounds (Figure S8); signals broaden and shift to unusually high or low field with increasing temperature.[42–45]

The platinum as well as the palladium complexes crystallize well from CH_2Cl_2/diethyl ether solutions mostly as CH_2Cl_2 solvates. Consequently, all complexes, except **20**, were investigated by single-crystal X-ray structure analysis. All investigated complexes crystallize as a racemic mixture of both enantiomers. Only complex **17** crystallizes as a C_2-symmetric molecule with a crystallographic C_2 axis perpendicular to the central C–C bond of the biphenyl backbone (Figure S13). Nevertheless, all palladium complexes with PPh_2 substituents show molecular structures close to the expected C_2 symmetry; only small deviations due to packing effects are apparent. On the other hand complexes with P(*i*Pr)$_2$ substituents were considerably distorted from the C_2 symmetry (Figures 2 and S14) which reflects the observation in the low-temperature NMR spectra. Substituents in the 6- and 6′-positions of the biphenyl backbone exert only minor effects on the coordination environment of the palladium complexes. Not surprisingly, structures found in the solid state of complexes **15/17** and **16/18**, respectively, are nearly superimposable. The molecular structure of platinum complex **19** is remarkably different from that of palladium analogue **15** (Figures S10 and 2).

In contrast to **15**, Pt complex **19** is highly distorted from C_2 symmetry, analogous to the P(*i*Pr)$_2$-substituted palladium complexes **18/16** (Figure S12). Complexes **16**, **18** and **19** all have a more perfect planar coordination environment in common. Conversely, in the PPh_2-substituted Pd complex **17** the two chlorido ligands are skewed along the C_2 axis out of the plane. This can be explained by close contacts of the phenyl substituents (PPh_2) with the Cl atoms bonded to the metal center (Figure S10). The larger ligand field splitting in the Pt complex **19** and the higher rigidity of the coordination sphere in the case of platinum does not allow such a distortion. As a result the ligand is distorted to a C_1 symmetry allowing the Pt atom to have an almost perfect square-planar coordination sphere (Figure S10). Replacement of the phenyl groups by isopropyl groups increases the strain between the chlorido ligands and the phosphane moieties. Consequently, Pd complexes **16** and **18** appear to benefit from similar stabilizing forces, which invoke a distorted backbone. A close contact between the iso-

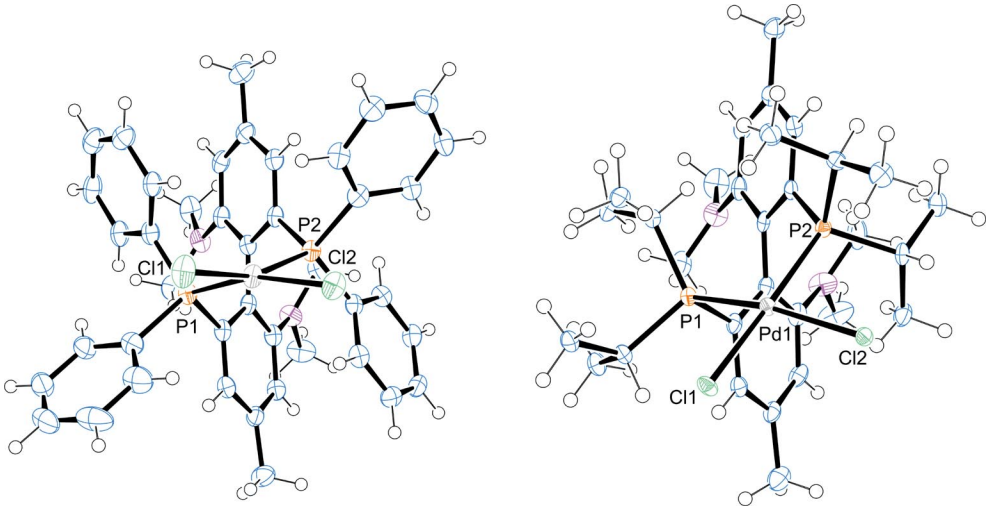


Figure 2. ORTEP[46] plot of the C_2-symmetric complex **15** (left, viewed along the crystallographic C_2 axis) and the C_1-symmetric complex **16** (right).

propyl group and one chlorido ligand is a common feature of complexes **16** and **18** and results in remarkable bending of one of the two Pd–Cl bonds out of the planar coordination sphere (by about 0.5 Å). Although no crystals suitable for X-ray analysis were obtained for the Ni complex **20**, a larger distortion of the square-planar coordination sphere for the nickel atom that retains C_2 symmetry would lead to a tetrahedral coordination sphere. This is, at least, partly the case for **20** as deduced from NMR data (vide supra, Figure S8). Due to metal–phosphane coordination, the N(1)···N(2) distances in **15**, **16** and **19** (3.23 Å, 3.02 Å, 3.10 Å) are close to or slightly smaller than the sum of the van der Waals radii (1.55 Å)[22] indicating a small interaction of the lone pairs at the nitrogen atoms. Protonation of complex **16** with 1 equiv. of weakly coordinating acid $[H(OEt_2)][B(C_6F_5)_4]$[47] leads to broadening of the proton resonances and the appearance of a new signal at δ = 12 ppm. This resonance can be assigned to a protonated dimethylamino group involved in hydrogen bonding. In proton sponge systems downfield shifts up to 18 ppm are often found.[26] Similarly, the Br···Br distance in **17** and **18** (3.62 Å both) are equal to the sum of the van der Waals radii (1.85 Å);[22] the Br···Br distance is only 0.2 Å longer than in the highly strained 4,5-dibromophenanthrene.[48]

As mentioned in the introduction, crowded phosphanes with a biphenyl backbone have found widespread use in catalysis. As a preliminary experiment all four Pd complexes **15**–**18** were tested as (pre)catalysts in the Suzuki–Miyaura cross coupling of 2-bromotoluene as a non-activated substrate with phenylboronic acid. Reactions were monitored by successive investigation of small samples using ^{1}H NMR spectroscopy with acetyl ferrocene as an internal standard.[49–52] Figure 3 depicts the results of time course experiments. After 60 min in every case, quantitative conversions had been achieved. Complex **16** (R = NMe_2, R′ = *i*Pr) was the most active catalyst in the series and enabled > 90% conversion after only 20 min. The activities observed for these complexes follow the expected trend that

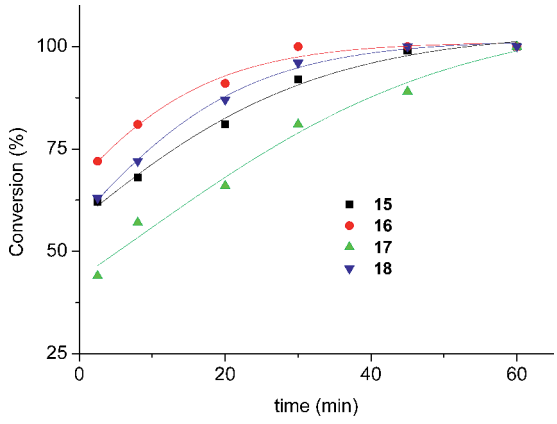


Figure 3. Time course of the Suzuki–Miyaura cross coupling of 2-bromotoluene with phenylboronic acid [reaction conditions: 1 mmol 2-bromotoluene, 1.2 mmol phenylboronic acid, 3 mmol base, 0.5 mol-% palladium complex, 10 mL of dioxane/water (2:1), 85 °C].

crowded and electron-rich phosphane ligands, as in **12**, afford complexes with higher activity in Suzuki–Miyaura cross couplings. The reduced activity of bromo-substituted complexes **17** and **18** might also be attributed to deactivation by an oxidative addition to the C–Br bond. For example, Leroux reported a phosphanylation of biphenyls that involved very similar intermediates but at temperatures substantially higher than 100 °C.[32] However, thus far we have not found C–Br bond activation in the Pd^{2+} complexes. Further investigations will be necessary to evaluate this point and to test the catalytic activities in detail.

Conclusions

New 6,6′-dibromo- and 6,6′-bis(dimethylamino)-substituted 2,2′-diphosphanylbiphenyls were prepared by a multistep synthesis. Depending on the phosphanyl groups used the resulting nickel, palladium and platinum complexes show different symmetry and coordination spheres. Free rotation of the isopropyl groups is remarkably hindered with C_2 symmetry being found in the solid state for complexes employing diphenylphosphanyl-substituted ligands. Conversely, complexes with isopropyl-substituted phosphanes were found to be C_1-symmetric in the solid state as well as in solution. These differences in steric hindrance and complex symmetries seem to minimally influence catalytic activity. Further work to evaluate the catalytic scope of these complexes is underway.

Experimental Section

General: All reactions handling sensitive chemicals were carried out under argon using standard Schlenk and cannula techniques. NMR spectra were recorded with a Bruker Avance III 500 spectrometer; chemical shifts for ^{1}H and ^{13}C NMR are referenced internally to the residual protons and to the ^{13}C NMR signal of the deuterated solvent.[53] Elemental analyses were performed by using a Thermo FlashAE 1112 analyzer. Infrared spectra were recorded with a Nicolet IR200 FT-IR spectrometer. Mass spectra were recorded with a Bruker micrOTOF-QIIa mass spectrometer operating in ESI mode. CCDC-932246 (**14**), -932247 (**15**), -932248 (**16**), -932249 (**17**), -932250 (**18**) and -932251 (**19**) contain 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.

Materials: Diethyl ether and thf were purified by distillation from sodium/benzophenone ketyl. Ethanol was purified by distillation from magnesium and acetonitrile by distillation from calcium hydride. Diphosphane **14** (6,6′-dibromo-4,4′-dimethyl-1,1′-biphenyl-2,2′-diyl)bis(diisopropylphosphane) was synthesized according to published procedures.[21] All other chemicals were purchased by commercial suppliers and were used without further purification.

Synthesis of 2-Bromo-4-methyl-6-nitroaniline (2) (Modification from Refs.[36,37]): 4-Methyl-2-nitroaniline (**1**, 61.5 g 0.40 mol) was dissolved in acetic acid (470 mL, 98%) in a 2 L flask by gentle heating. The flask was placed in an ice bath, and bromine (71.5 g 0.45 mol) dissolved in acetic acid (100 mL) was added over 30 min with a dropping funnel; during the addition the temperature was kept below 10 °C. After addition of about 1/3 of the bromine, an orange

solid started to precipitate (protonated **1**). After completed addition, the reaction mixture was stirred at 0 °C for additional 20 min and at ambient temperature for another 2 h. Completeness of the reaction was checked by sampling a small quantity and recording the ^{1}H NMR spectrum. To the reaction mixture $NaHCO_3$ (20 g, 0.24 mol) was carefully added (gas develops with delay), then water (500 mL) and another portion of $NaHCO_3$ (20 g, 0.24 mol) were added. The crude product precipitated from the solution and was separated by suction filtration and carefully washed with water to remove acetic acid completely. The crude product was dissolved in CH_2Cl_2, the organic phase was washed with water (200 mL), dried with $MgSO_4$, and the solvent was removed by rotary evaporation to yield pure **2** as orange solid (88.2 g, 0.38 mol, 94% based on **1**). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.94 (dd, ^4J(H,H) = 2.0 Hz, ^4J(H,H) = 0.9 Hz, Ar-*H*, 1 H), 7.55 (dd, ^4J(H,H) = 2.0 Hz, ^4J(H,H) = 0.9 Hz, Ar-*H*, 1 H), 6.45 (br s, NH_2, 2 H), 2.27 (s, CH_3, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 140.32, 140.08, 132.7, 126.56, 125.58, 112.02, 20.01 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3484 (s, $\nu_{N\text{-}H}$), 3368 (s), 1576 (s), 1509 (s, $\nu_{N\text{-}O}$), 1347 (s, $\nu_{C\text{-}N}$), 1085 (m) cm^{-1}. $C_{14}H_{14}Br_2N_2O_2$ (231.05): calcd. C 36.93, H 3.05, N 12.12; found C 36.40, H 3.01, N 12.13. M.p. 67–69 °C (ref.[37] 68.6–68.9 °C).

Synthesis of 1-Bromo-2-iodo-5-methyl-3-nitrobenzene (3) (Modification from Ref.[36]): Fairly grinded **2** (88.1 g, 0.38 mol) was suspended in diluted sulfuric acid (63 mL of concd. acid in 300 mL of water) at 0 °C. To this mixture $NaNO_2$ (43 g, 0.623 mol) dissolved in H_2O (120 mL) was added slowly with vigorous stirring during 45 min. The suspension was stirred at ambient temperature for another 30 min. The solution was filtered, and the filtrate was directly poured into a well-stirred solution of KI (120 g, 0.72 mol) dissolved in water (100 mL). The filter cake was washed with water, extracted with dichloromethane, filtered through silica gel and was recrystallized from ethanol to yield 25 g of unreacted aniline derivative **2**. The aqueous solution containing the diazonium salt and KI was stirred at 70 °C for 1 h. The cooled solution was then extracted with dichloromethane (3 × 100 mL). The organic phases were combined and washed with bicarbonate solution, sodium sulfite solution, and water, then dried with $MgSO_4$. Evaporation of the solvent yielded **3** (68.2 g, 0.20 mol, 52%) as a yellow to brown crystalline solid of sufficient purity. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (dd, ^4J(H,H) = 1.9 Hz, ^4J(H,H) = 0.7 Hz, Ar-*H*, 1 H), 7.35 (dd, ^4J(H,H) = 1.9 Hz, ^4J(H,H) = 0.7 Hz, Ar-*H*, 1 H), 2.37 (s, CH_3, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 156.28, 141.32, 136.20, 133.02, 123.64, 90.66, 20.75 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3075 (s, $\nu_{Ar\text{-}H}$), 1530 (s, $\nu_{N\text{-}O}$) 1347 (s, $\nu_{C\text{-}N}$), 1259 (s), 1048 (s) cm^{-1}. M.p. 70–73 °C.

Synthesis of 2,2′-Dibromo-4,4′-dimethyl-6,6′-dinitro-1,1′-biphenyl (4) (Modification from Refs.[35,36]): Compound **3** (68 g, 0.2 mol) was dissolved in dry DMF (80 mL) under argon. To the stirred solution copper powder (84 g, 1.3 mol) was added at 100 °C in three portions in 30 min intervals. After cooling to ambient temperature, dichloromethane (160 mL) was added, and the reaction mixture was filtered, the filter cake was washed several times with additional portions of dichloromethane, the combined organic phases were washed with 2.5 M hydrochloric acid (5 × 100 mL). The solvents were removed by rotary evaporation; the crude product was washed with ethanol (100 mL) under heating and stirring to yield the desired product **4** in analytical purity as yellow solid (31 g, 0.072 mol, 72.5%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.01 (d, ^4J(H,H) = 2.0 Hz, Ar-*H*, 2 H), 7.80 (d, ^4J(H,H) = 2.0 Hz, Ar-*H*, 2 H), 2.52 (s, CH_3, 6H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 149.44, 141.47, 138.62, 131.34, 125.16, 124.83, 21.13 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3075 (s, $\nu_{C\text{-}H}$), 1528 (s, $\nu_{N\text{-}O}$), 1352 (s, $\nu_{C\text{-}N}$), 1040 (s). M.p. 202–207 °C.

Synthesis of 2,2′-Diamino-6,6′-dibromo-4,4′-dimethyl-1,1′-biphenyl (5) (Modification from Ref.[36]): The dinitrobiphenyl **4** (30.9 g, 0.072 mol) was suspended in methanol (150 mL), and zinc dust (33 g, 0.505 mol) was added. The reaction mixture was refluxed for a few minutes, and concentrated hydrochloric acid was added dropwise until a clear solution with small residues of zinc dust had formed. The completeness of the reaction was checked by means of ^{1}H NMR spectroscopy. To the cooled solution ammonia (25% in water) was added until the solution became basic and was subsequently extracted with dichloromethane (2 × 100 mL) to yield a clear organic phase. The combined extracts were washed with diluted ammonia (10% in water) and dried with $MgSO_4$. The solvent was removed by rotary evaporation, and the crude product was dissolved in diethyl ether (100 mL), the solution was then filtered through aluminum oxide and once again concentrated to dryness to yield diamine **5** as white solid (23.7 g, 0.064 mol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.95 (d, ^4J(H,H) = 2.0 Hz, Ar-*H*, 2 H), 6.56 (d, ^4J(H,H) = 2.0 Hz, Ar-*H*, 2 H), 3.54 (br. s, NH_2, 4 H), 2.28 (s, CH_3, 6H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ = 145.99, 140.89, 125.56, 123.40, 120.73, 115.24, 32.2 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 3361 (s, $\nu_{N\text{-}H}$), 3010 (s, $\nu_{C\text{-}H}$), 1612 (s), 1549 (s), 1302 (s, $\nu_{C\text{-}N}$), 1034 (s) cm^{-1}. ESI-TOF MS: calcd. for $[C_{14}H_{14}Br_2N_2+nH]^+$ 370.957; found 370.955. $C_{14}H_{14}Br_2N_2$ (370.082): calcd. C 45.44, H 3.81, N 7.57; found C 46.04, H 3.80, N 7.66. M.p. 131–134°C (ref.[36] 135–136 °C).

Synthesis of 6,6′-Dibromo-2,2′-diiodo-4,4′-dimethyl-1,1′-biphenyl (6) (Modification from Ref.[36]): Diamine **5** (12 g, 0.032 mol) was suspended in diluted sulfuric acid (18 mL of concd. acid in 100 mL of water) and cooled to 0 °C. Sodium nitrite (6.9 g, 0.10 mol) dissolved in water (60 mL) was added dropwise within 30 min. The diazonium salt solution was added to a vigorously stirred solution of KI (20 g) in water (60 mL). After complete addition, the reaction mixture was stirred at 70 °C for 90 min and chilled to ambient temperature. The reaction mixture was extracted with dichloromethane (5 × 80 mL) and washed with $NaHCO_3$ solution and Na_2SO_3 solution. The combined extracts were concentrated to dryness, and the crude product was purified by column chromatography (SiO_2; hexane/dichloromethane 5:1) to yield the crude product as white solid, which was recrystallized from hexane to yield the pure product **6** as colorless crystalline solid (6.37 g, 0.011 mol, 33.2%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (dd, ^4J(H,H) = 1.5 Hz, ^4J(H,H) = 0.7 Hz, Ar-*H*, 2 H), 7.51 (dd, ^4J(H,H) = 1.5 Hz, ^4J(H,H) = 0.7 Hz, Ar-*H*, 2 H), 2.37 (br. s, CH_3, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.4, 141.7, 139.0, 133.5, 100.0, 67.1, 20.6 (*C*H$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2906 (m, $\nu_{C\text{-}H}$), 1612 (s), 1580 (s), 1521 (s), 1030 (s) cm^{-1}. $C_{14}H_{10}Br_2I_2$ (591.846): calcd. C 28.41, H 1.70; found C 29.00, H 1.69. M.p. 205 °C (ref.[36] 212–213 °C).

Synthesis of 2,2′-Dibromo-6,6′-bis(dimethylamino)-4,4′-dimethyl-1,1′-biphenyl (7) (Modification from Ref.[27]): Diamine **5** (11 g, 0.03 mol) was dissolved in thf (200 mL), sodium hydride (4.4 g, 0.18 mol) and dimethyl sulfate (15.1 mL, 0.18 mol) were added. The reaction mixture was refluxed for 35 h; after cooling to ambient temperature, an excess of ammonia (10% in H_2O) was added. The mixture was extracted with dichloromethane (3 × 60 mL). The combined organic extracts were filtered through silica and reduced to dryness to afford the crude product. Recrystallization from methanol yielded the desired product **7** as white semi-crystalline solid (8.9 g, 0.021 mol, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15 (s, Ar-*H*, 2 H), 6.85 (s, Ar-*H*, 2 H), 2.49 (s, N-CH_3, 12H), 2.34 (s, Ar-CH_3, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.0,

139.3, 132.6, 127.2, 126.9, 119.8, 43.8, 21.4 (CH_3) ppm. ESI-TOF MS: calcd. for $[C_{18}H_{22}Br_2N_2 + H]^+$ 427.02; found 427.02. IR (KBr): $\tilde{\nu}$ = 3053 (s), 1593 (s), 1544 (s), 1346 (s), 1303 (m), 1210 (m), 1046 (m), 738 (s) cm^{-1}. $C_{18}H_{22}Br_2N_2$ (426.19): calcd. C 50.73, H 5.20, N 6.57; found C 50.72, H 5.27, N 6.41. M.p. 137–140 °C.

Synthesis of 6,6′-Bis(diphenylphosphanyl)-*N*²,*N*²,*N*²′,*N*²′,4,4′-hexamethyl-1,1′-biphenyl-2,2′-diamine (11): To a solution of **7** (400 mg, 0.94 mmol) in diethyl ether (8 mL) *n*BuLi (1.6 M, 1.76 mL, 2.8 mmol) was added at 0 °C, and the reaction mixture was stirred at this temperature for 3 h. The solution was cooled to –40 °C, and chlorodiphenylphosphane (723 mg, 3.3 mmol) in diethyl ether (4 mL) was added in one portion. The reaction mixture was stirred for 72 h, and subsequently water (5 mL) was added. The reaction mixture was extracted with dichloromethane (3 × 5 mL), the combined organic extracts were washed with water and dried with $MgSO_4$. The organic phase was filtered through silica gel and concentrated to dryness. The resulting solid was washed with ethanol to afford **11** as white solid (370 mg, 0.51 mmol, 54%). The product can be further purified by recrystallization from ethanol/dichloromethane (1:2). ^1H NMR (500 MHz, C_6D_6, 25 °C): δ = 7.32–7.37 (m, PPh_2, 8 H), 7.28 (d, J = 7 Hz, 2H, Ar-*H*), 7.07 (m, 6 H), 6.95 (t, PPh_2, J(P,H) = 6 Hz, 4 H), 6.80 (br. s, PPh_2, 4 H), 2.27 (s, CH_3, 6 H), 2.08 (s, $N(CH_3)_2$, 12 H) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = –11.60 ppm. IR (KBr): $\tilde{\nu}$ = 3051 (m, $\nu_{C\text{-}H}$), 1589 (s), 1545 (m), 1476 (m), 1309 (s), 1429 (s), 1130 (s) cm^{-1}. ESI-TOF MS: calcd. for $[C_{42}H_{42}N_2P_2 + H]^+$ (100%) 637.289; found 637.275. $C_{42}H_{42}N_2P_2{\cdot}CH_2Cl_2$ (636.74): calcd. C 71.56, H 6.15, N 3.88; found C 71.32, H 6.49, N 3.65. M.p. 229 °C (dec.).

Synthesis of 6,6′-Bis(diisopropylphosphanyl)-*N*²,*N*²,*N*²′,*N*²′,4,4′-hexamethyl-1,1′-biphenyl-2,2′-diamine (12): To a solution of **7** (498 mg, 1.16 mmol) in diethyl ether (15 mL) *n*BuLi (1.6 M, 2.4 mL, 3.84 mmol) was added at 0 °C and the solution was stirred at this temperature for 2.5 h. After a few minutes a white precipitate had formed. To the reaction mixture chlorodiisopropylphosphane (1.15 g, 7.6 mmol) dissolved in diethyl ether (3 mL) was added at 0 °C. The reaction mixture was stirred at ambient temperature overnight and concentrated to dryness. Degassed sodium hydrogen carbonate solution was added, and the reaction mixture was extracted with dichloromethane (3 × 30 mL). The combined organic extracts were dried with $MgSO_4$, and the solution was subjected to flash chromatography on SiO_2 (dichloromethane). Evaporating the solvent to dryness afforded a colorless oil that solidified upon stirring with ethanol. The crude product was recrystallized from ethanol (10 mL) to yield the pure compound **12** as white, slightly air-sensitive solid (240 mg, 0.48 mmol, 41%). $^1H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.00 (s, Ar-H, 2 H), 6.71 (s, Ar-H, 2 H), 2.26 (s, biphen-CH_3, 6 H), 2.30 (s, $N(CH_3)_2$, 12 H), 2.23 (sept, ^3J(H,H) = 6.9 Hz, $CH(Me)_2$, 2 H), 1.71 (sept, ^3J(H,H) = 7.2 Hz, $CH(Me)_2$, 2 H), 1.10 (d, ^3J(H,H) = 6.9 Hz, $CH(CH_3)_2$, 6 H), 0.98 (d, ^3J(H,H) = 7.2 Hz, $CH(CH_3)_2$, 6 H), 0.97 (d, ^3J(H,H) = 6.6 Hz, $CH(CH_3)_2$, 6 H), 0.79 (d, ^3J(H,H) = 7.23 Hz, $CH(CH_3)_2$, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.8 (dd, J(P,C) = 8.8, 2.0 Hz), 139.2 (d, J(P,C) = 14.3 Hz), 136.1, 135.2 (dd, J(P,C) = 32.0, 5.4 Hz), 125.9 (d, J(P,C) = 2.2 Hz), 119.8, 43.17, 25.0 (d, J(P,C) = 16.9 Hz), 23.6 (d, J(P,C) = 16.3 Hz), 23.2 (d, J(P,C) = 23.5 Hz), 22.0 (d, J(P,C) = 20.8 Hz), 21.8, 19.3 (d, J(P,C) = 13.9 Hz), 18.2 (d, J(P,C) = 9.0 Hz) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$): δ = –1.4 ppm. $C_{30}H_{50}P_2N_2$ (500.68): calcd. C 71.97, H 10.70, N 5.60; found C 71.67, H 10.32, N 5.63.

Synthesis of 6,6′-Dibromo-4,4′-dimethyl-1,1′-biphenyl-2,2′-diylbis(diphenylphosphane) (13): To a solution of **6** (300 mg, 0.506 mmol) in diethyl ether (6 mL) was added at –95 °C within 5 min a solution of *n*BuLi (0.665 mL, 1.6 M in *n*-hexane, 1.06 mmol). The resulting slightly opaque mixture was stirred at –95 °C for 25 min, and then a solution of Ph_2PCl (232.6 mg, 1.06 mmol) in diethyl ether (5 mL) was added. The mixture was allowed to attain room temperature within 2 h. At ca. –65°, the precipitation of a white solid occurred. After stirring at ambient temperature for 4 h, the mixture was concentrated to dryness under reduced pressure (oil pump vacuum) for 1 h, then a new portion of Et_2O (5 mL) was added. The mixture was quenched by addition of 10 mL of degassed H_2O, extracted with dichloromethane (3 × 10 mL) under Ar. The combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The crude material obtained was filtered through silica gel by using DCM as eluent and then concentrated under reduced pressure. The resulting colorless oil was recrystallized from EtOH to yield 204 mg (56%) of the title compound as white crystals. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.38 (d, Ar-H, 2 H), 7.08–7.70 (m, Ph, 20 H) 6.97 (s, Ar-H, 2 H), 2.01 (s, biphen-CH_3, 6 H) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C): δ = –12.0 ppm. IR (KBr): $\tilde{\nu}$ = 3051 (s, $\nu_{C\text{-}H}$, Aryl-H), 1580 (m), 1478 (m, ν_{CH3}, Aryl-CH_3), 1434 (s), 1208 (s), 1068 (s, $\nu_{C\text{-}Br}$, Aryl-Br) cm^{-1}. ESI-TOF MS: calcd. for $[C_{38}H_{30}Br_2P_2 + H]^+$ (100%) 709.25; found 709.011. $C_{38}H_{30}Br_2P_2$ (708.40): calcd. C 64.43, H 4.27; found C 64.60, H 4.59.

Synthesis of Palladium Complexes 15–18 and Platinum Complex 19: To a solution of the appropriate diphosphane (0.2 mmol) in DCM (5 mL) a solution of $[Pd(COD)Cl_2]$/$[Pt(COD)Cl_2]$ (COD = cycloocta-1,5-diene) (0.2 mmol) in DCM (5 mL) was added. This solution was stirred for 12 h and then concentrated to dryness to yield the crude products, which were subsequently crystallized by vapor diffusion of diethyl ether or pentane to a solution of the complex in DCM.

(11-κP-κP′)$PdCl_2$ (15) (R = NMe_2; R′ = Ph): The crude product was recrystallized from CH_2Cl_2/diethylether yielding a yellow powder (85.9%). M.p. 260 °C (dec.). $^1H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.92 (d, J(P,H) = 7.5 Hz, 4 H), 7.84 (d, J(P,H) = 7.5 Hz, 4 H), 7.39 (m, 6 H), 7.31 (t, J(P,H) = 7.5 Hz, 2 H), 7.17 (d, J(P,H) = 7.5 Hz, 4 H), 6.55 (s, 2 H), 6.05 (s, 2 H), 2.40 (s, $N(CH_3)_2$, 12 H), 2.02 (s, CH_3, 6 H) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C): δ = 31.6 ppm. IR (KBr): $\tilde{\nu}$ = 3057 (s, $\nu_{C\text{-}H}$, Aryl-H), 1589 (s), 1543 (s, ν_{CH3}, Aryl-CH_3), 1433 (s), 1349 (s, $\nu_{C\text{-}N}$, ArylN), 1591 (s), 1093 (s, $\nu_{C\text{-}N}$, Alkyl-N) cm^{-1}. ESI-TOF MS: calcd. for $[C_{42}H_{42}ClN_2P_2Pd_2 - Cl + H]^+$ 777.155; found 777.140. $C_{42}H_{42}N_2P_2Pd{\cdot}1.5CH_2Cl_2$ (814.07): calcd. C 55.49, H 4.82, N 2.98; found C 55.73, H 5.00, N 2.87.

(12-κP-κP′)$PdCl_2$ (16) (R = NMe_2; R′ = *i*Pr): The crude product was recrystallized from CH_2Cl_2/diethyl ether to yield a yellow powder (75%). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.08 (d, ^3J(P,H) = 9 Hz, Ar-H, 2 H), 6.86 (s, Ar-H, 2 H), 2.56 (s, $N(CH_3)_2$, 12 H), 2.38 (s, biphen-CH_3, 6 H), 1.55 (br., $CH(Me)_2$, 12 H), 1.28 (br., $CH(Me)_2$, 6 H), 1.01 (dd, ^3J(P,H) = 15 Hz, ^3J(H,H) = 7.15 Hz, $CH(CMe_2)_2$, 6 H) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C): δ = 46.4 (br.) ppm. IR (KBr): $\tilde{\nu}$ = 2975, 2959, 2919, 2866, 2792 (s, $\nu_{C\text{-}H}$), 1589, 1540, 1486, 1456, 1403, 1229, 1061, 665, 628, 501 cm^{-1}. ESI-TOF MS: calcd. for $[C_{30}H_{50}ClN_2P_2Pd]^+$ 641.2199; found 641.2175. $C_{30}H_{50}Cl_2N_2P_2Pd$ (678.00): calcd. C 53.14, H 7.43, N 4.13; found C 52.71, H 7.45, N 4.08.

(13-κP-κP′)$PdCl_2$ (17) (R = Br; R′ = Ph): The crude product was recrystallized from CH_2Cl_2/pentane to yield a yellow powder (85.2%). M.p. 268 °C (dec.). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.01 (dd, ^3J(P,H) = 12.45 Hz, ^3J(H,H) = 7.64 Hz, Ph, 4 H), 7.81 (m, Ph, 4 H), 7.49–7.41 (m, Ph, 8 H), 7.37 (m, Ph, 4 H), 7.03 (s, Ar-H, 2 H), 6.90 (d, ^3J(P,H) = 11.74 Hz, Ar-H, 2 H), 2.05 (s,

biphen-CH_3, 6 H) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C): δ = 31.6 ppm. IR (KBr): $\tilde{\nu}$ = 3013 (m, ν_{C-H}, Aryl-H), 1586 (s, ν_{CH3}, Aryl-CH_3), 1523 (m), 1479 (m), 1435 (s), 1097 (s, ν_{C-Br}, Aryl-Br) cm^{-1}. ESI-TOF MS: calcd. for $[C_{26}H_{38}Br_2Cl_2P_2Pd - Cl + H]^+$ 850.889; found 850.866. $C_{38}H_{30}Br_2Cl_2P_2Pd$ (885.73): calcd. C 51.53, H 3.41; found C 51.05, H 3.42.

(14-κP-κP′)$PdCl_2$ (18) (R = Br; R′ = *i*Pr): The crude product was recrystallized from CH_2Cl_2/pentane to yield a yellow powder (77.3%). M.p. 168–171 °C. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.70 (s, Ar-H, 2 H), 7.51 (d, ^3J(P,H) = 9 Hz, Ar-H, 2 H), 3.84 (m, $CH(Me)_2$, 2 H), 2.45 (s, biphen-CH_3, 6 H), 2.35 (br. s, $CH(Me)_2$, 2 H), 1.23 (br., $CH(CMe_2)_2$, 6 H), 1.24 (br., $CH(Me)_2$, 12 H), 1.03 (dd, ^3J(P,H) = 16 Hz, ^3J(H,H) = 6.41 Hz, $CH(Me)_2$, 6 H) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C): δ = 45.0 (br.) ppm. IR (KBr): $\tilde{\nu}$ = 3030 (s, ν_{C-H}, Aryl-H), 2969 (m), 2876 (m), 1534 (m, ν_{CH3}, Aryl-CH_3), 1583 (s), 1452 (s), 1375 (s), 1221 (s), 1156 (s), 1041 (s, ν_{C-Br}, Aryl-Br) cm^{-1}. ESI-TOF MS: calcd. for $[C_{26}H_{38}Br_2Cl_2P_2Pd - Cl + H]^+$ 714.951; found 714.941. $C_{26}H_{38}Br_2Cl_2P_2Pd$ (749.66): calcd. C 41.66, H 5.12; found C 41.45, H 5.17.

(11-κP-κP′)$PtCl_2$ (19) (R = NMe_2; R′ = Ph): The crude product was recrystallized from CH_2Cl_2/diethyl ether to yield a yellow powder (91%). M.p. 218 °C (dec.). $^1H\{^{31}P\}$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.84 (d, J(H,H) = 7.8 Hz, Ph, 4 H), 7.45 (d, J(H,H) = 7.5 Hz, Ph, 4 H), 7.32 (m, Ph, 6 H), 7.23 (t, J(H,H) = 7.5 Hz, 2 H), 7.08 (t, J(H,H) = 7.8 Hz, 4 H), 6.52 (s, Ar-H, 2 H), 5.88 (s, Ar-H, 2 H), 2.31 (s, biphen-$N(CH_3)_2$, 12 H), 1.92 (s, biphen-CH_3, 6 H) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, 25 °C): δ = 11.8 (J(Pt,P)= 3600 Hz) ppm. ESI-TOF MS: calcd. for $[C_{42}H_{42}ClN_2P_2Pd_2 - Cl + H]^+$ 867.216; found 867.201. $C_{42}H_{42}N_2P_2Pt{\cdot}0.75CH_2Cl_2$ (902.73): calcd. C 53.13, H 4.54, N 2.90; found C 53.23, H 4.78, N 2.74.

Synthesis of (13-κP-κP′)$NiBr_2$ (20) (R = Br; R′ = Ph): To a suspension of $NiBr_2$ (9 mg, 0.041 mmol) in anhydrous thf (8 mL) diphosphane **13** (40 mg, 0.057 mmol) was added. The reaction mixture was refluxed for 12 h, and the resulting light green reaction mixture was filtered through Celite to remove unreacted $NiBr_2$ and then concentrated to dryness. The residue was washed with small amounts of dry DCM and diethyl ether and dried in oil pump vacuum to afford a light green-grey powder (25 mg, 0.027 mmol, 67%). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.13 (s, 6 H, CH_3), 4.17 (s, 2 H), 4.64 (s, 2 H), 6.52 (t, ^3J(H,H) = 6.7 Hz, 2 H), 7.22 (t, ^3J(H,H) = 6.6 Hz, 2 H), 7.95 (br. s, 4 H), 8.08 (s, 4 H), 8.58 (s, 4 H), 8.99 (d, ^3J(H,H) = 6.3 Hz, 4 H) ppm. IR (KBr): $\tilde{\nu}$ = 3052, 2912, 1585, 1479, 1435, 1096, 741, 694, 515, 501 cm^{-1}. ESI-TOF MS: calcd. for $[C_{38}H_{30}P_2Br_3Ni^+]$ 846.8680; found 846.8699. $C_{38}H_{30}P_2Br_4Ni$ (926.90): calcd. C 49.24, H 3.26; found C 49.02, H 3.31.

Supporting Information (see footnote on the first page of this article): Details of NMR Br/Li exchange of **7**, VT NMR spectroscopy,[53] X-ray structure analyses[54,55] on **14**–**19**, table of selected bond lengths and angles.

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