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New Concept for the Short, Facile and High Yield Synthesis of Extremely Efficient Pincer-Type Suzuki-Catalysts Bearing Aminophosphine Substituents

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General procedures. All synthetic operations were carried out in oven-dried glassware using a combination of glovebox (M. Braun 150B-G-II) and Schlenk techniques under a dinitrogen atmosphere. Solvents were reagent grade or better, freshly distilled under N_2 atmosphere by standard procedures and were degassed by freeze-thaw cycles before use. Deuterated solvents were purchased from Armar, stored in a Schlenk tube (Teflon tap) over P_4O_{10} distilled and degassed prior to use. All the chemicals were purchased from Aldrich Chemical Co. or Fluka and used without further purification. Phenylboronic acid was purchased from Aldrich Chemical Co.

Analysis. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data were recorded at 500.13, 125.76 and 202.46 MHz, respectively, on a Bruker DRX-500 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm) coupling constants (*J*) are in Hz. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane; the resonance of the residual protons of the solvents were used as internal standard for ^{1}H (δ 7.15 benzene; 7.26 chloroform; 3.58 and 1.73 THF-d_8) and *all-d* solvent peaks for ^{13}C (δ 128.0 benzene; 77.0 chloroform; 67.4 and 25.2 THF-d_8). ^{31}P{^{1}H} NMR data are reported downfield relative to external 85% H_3PO_4 at in D_2O at δ 0.0 ppm. All measurements were carried out at 298 K. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, duplet; t, triplet; m, multiplet; v, virtual. IR spectra were obtained by ATR methods with a Bio-Rad FTS-45 FTIR spectrometer. Elemental analyses were performed on a Leco CHNS-932 analysator at the University of Zurich, Switzerland.

Preparation of $P(NC_5H_{10})_3$. 5 ml (7.87 g, 57.31 mmol) of phosphorus trichloride and 40 ml (287 mmol, 5.0 equiv.) of triethyl amine were dissolved in 100 ml of diethyl ether and cooled in an ice bath to 0°C. 17 ml (171.9 mmol, 3 equiv.) of piperidine was slowly added drop wise, during which the formation of a white precipitate ($C_5H_{10}N{\bullet}HCl$) was observed. After complete addition, the suspension was allowed to warm up to room temperature and was stirred for an additional hour. The reaction mixture was filtrated. The solid was washed with 100 ml of diethyl ether. The combined pale yellow filtrates were dried *in vacuo* giving 12.36 g (43.61 mmol, 76%) of an off-white solid.

$^{31}P\{^1H\}$-NMR (C_6D_6; δ, ppm): 117.3 (s, $P(NC_5H_{10})_3$). ^1H NMR (C_6D_6; δ, ppm): 2.95 (t, $^3J_{HH}$ = 5.0 Hz, 12H, NCH_2), 1.45 (broad s, 18H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 47.3 (d, $^2J_{PC}$ = 64.4 Hz, NCH_2), 27.5 (d, $^3J_{PC}$ = 19.6 Hz, NCH_2CH_2), 26.1 (s, $NCH_2CH_2CH_2$).

Preparation of $[PdCl_2\{P(NC_5H_{10})_3\}_2]$ (1). To a yellow suspension of 0.680 g (2.38 mmol) of $[PdCl_2(COD)]$ in 10 ml of THF, 1.350 g (4.78 mmol, 2.03 equiv.) of $P(NC_5H_{10})_3$ (dissolved in 10 ml of THF) was added and stirred for 5 minutes. Removal of the solvent under reduced pressure and addition of 10 ml of cold pentane, followed by filtration, gave a pale yellow solid, which was washed five times with 5 ml portions of cold pentane. The product was dried *in vacuo*, resulting in 1.555 g (2.09 mmol, 88%) of $[PdCl_2\{P(NC_5H_{10})_3\}_2]$ (**1**) as a pale yellow powder. The combined pentane extractions were well dried, giving additional ~0.23 g of **1**.

$^{31}P\{^1H\}$-NMR (C_6D_6; δ, ppm): 92.5 (s, $P(NC_5H_{10})_3$). ^1H NMR (C_6D_6; δ, ppm): 3.35 (s, 24H, NCH_2), 1.50 (s, 24H, NCH_2CH_2), 1.46 (s, 12H, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6; δ, ppm): 48.5 (s, NCH_2), 27.0 (s, NCH_2CH_2), 25.7 (s, $NCH_2CH_2CH_2$). Elemental analysis: Calc. for $C_{30}H_{60}Cl_2N_6P_2Pd$: C, 48.43; H, 8.13; N, 11.29. Found: C, 48.71; H, 8.29; N, 11.36.

Preparation of [{(C_6H_3)(NHP(NC_5H_{10})$_2$)$_2$}Pd(Cl)] (2). 72.4 mg (0.67 mmol) of 1,3-diaminobenzene were added to a toluene solution (100 ml) of **1** (488.5 mg; 0.66 mmol). The reaction mixture was placed in an oil bath and heated up to 80°C and stirred for 45 minutes under nitrogen atmosphere. The solvent was removed under reduced pressure. The pale yellow residue was extracted with 40 ml of diethyl ether. Removal of the solvent gave 290.5 mg (0.45mmol, 69%) of pure **2** as colorless powder.

$^{31}P\{^1H\}$-NMR ($CDCl_3$; δ, ppm): 120.8 (s, $P(NC_5H_{10})_2$). ^1H NMR ($CDCl_3$; δ, ppm): 6.81 (tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{PH}$ = 1.9 Hz, 1H, Ar_{para}), 6.10 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Ar_{meta}), 4.41 (s, 2H, NH), 3.19 (s, 16H, PNCH_2), 1.56 (s, 24H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ, ppm): 151.4 (vt, J_{PC} = 16.2 Hz, *Ar*NHP), 127.7 (s, Ar_{para}), 123.3 (unresolved t, Ar_{ipso}), 101.6 (vt, $^3J_{PC}$ = 9.6 Hz, Ar_{meta}), 46.7 (vt, $^2J_{PC}$ = $^4J_{PC}$ = 3.9 Hz, NCH$_2$), 26.4 (s, NCH_2CH_2), 24.9 (s, $NCH_2CH_2CH_2$). The assignment of the ^1H and $^{13}C\{^1H\}$ NMR signals was confirmed by COSY and $^{13}C\{^1H\}$ DEPT experiments. Elemental analysis: Calc. for $C_{26}H_{45}ClN_6P_2Pd$: C, 48.33; H, 7.03; N, 13.02. Found: C, 48.51; H, 6.99; N, 12.98.

Preparation of [{(C_6H_3)(OP(NC_5H_{10})$_2$)$_2$}Pd(Cl)] (3). 41.0 mg (0.37 mmol) resorcinol were added to a toluene solution (30 ml) of 268.5 mg (0.36 mmol) of **1**. The reaction mixture was stirred under nitrogen for 15 minutes at 80°C during which the solution decolorized. The solvent was removed under reduced pressure, and the solid was extracted with 20 ml of diethyl ether. After removal of the solvent *in vacuo*, 180.0 mg (0.28 mmol, 77%) of **3** was obtained as colorless powder.

$^{31}P\{^1H\}$-NMR ($CDCl_3$; δ, ppm): 146.1 (s, $P(NC_5H_{10})_2$). ^1H NMR ($CDCl_3$; δ, ppm): 7.04 (tt, $^3J_{HH}$ = 7.9 Hz, $^5J_{PH}$ = 1.5 Hz, 1H, Ar_{para}), 6.56 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Ar_{meta}), 3.25 (t, $^3J_{HH}$ = 4.3 Hz, 16H, NCH_2), 1.56 (t, $^3J_{HH}$ = 4.3 Hz, 16H, NCH_2CH_2), 1.56 (overlapped s, 8H, $NCH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ, ppm): 160.1 (vt, J_{PC} = 10.2 Hz, *Ar*OP), 128.9 (s, *Ar*$_{para}$), 128.6 (t, $^2J_{PC}$ = 7.8 Hz, *Ar*$_{\text{ipso}}$), 106.0 (vt, J_{PC} = 8.4 Hz, *Ar*$_{meta}$), 46.3 (d, $^2J_{PC}$ = 4.1 Hz, N*C*H$_2$), 26.4 (s, NCH$_2$*C*H$_2$), 24.6 (s, NCH$_2$CH$_2$*C*H$_2$). The assignment of the ^{1}H and ^{13}C{^{1}H} NMR signals was confirmed by COSY and ^{13}C{^{1}H} DEPT experiments. Elemental Analysis: Calc. for $C_{26}H_{43}ClN_4O_2P_2Pd$: C, 48.23; H, 6.69; N, 8.65. Found: C, 48.13; H, 6.65; N, 8.41.

Preparation of [{(C_6H_3)(NHP(NC_5H_{10})$_2$)$_2$}Pd(CO)][BF_4] (4). 13.0 mg (0.06 mmol) of $AgBF_4$ was added to a methylene chloride solution (10 ml) of 43.0 mg (0.06 mmol) **2**. The reaction mixture was stirred for 15 minutes under rigorous exclusion of light. The reaction mixture was filtered over celite. The solvent was removed under reduced pressure. Dissolution of [{(C_6H_3)(NHP(NC_5H_{10})$_2$)$_2$}Pd][BF_4] in THF-*d*$_8$ subsequent by treatment with an excess (~50 equiv.) of CO gas yielded quantitatively complex **4**. CO release was observed under reduced pressure, hence an elemental analysis was not obtained.

^{31}P{^{1}H}-NMR (THF-*d*$_8$; δ, ppm): 119.29 (s, *P*(NC_5H_{10})$_2$). ^{1}H NMR (THF-*d*$_8$; δ, ppm): 6.96 (broad s, 2H, N*H*), 6.82 (broad t, $^3J_{HH}$ = 7.8 Hz, 1H, *Ar*$_{para}$), 6.26 (broad d, $^3J_{HH}$ = 7.8 Hz, 2H, *Ar*$_{meta}$), 3.16 (s, 16H, PNC*H$_2$*), 1.60 (s, 24H, C*H$_2$*). ^{13}C{^{1}H} NMR (THF-*d*$_8$; δ, ppm): 183.9 (t, J_{PC} = 15.1 Hz, *C*O), 153.4 (vt, J_{PC} = 16.6 Hz, *Ar*NHP), 132.5 (s, *Ar*$_{para}$), 130.8 (unresolved t, *Ar*$_{\text{ipso}}$), 104.1 (vt, $^3J_{PC}$ = 18.5 Hz, *Ar*$_{meta}$), 48.0 (s, N*C*H$_2$), 27.4 (s, NCH$_2$*C*H$_2$), 25.0 (s, NCH$_2$CH$_2$*C*H$_2$). IR (ATR; cm^{-1}) ν 2106 cm^{-1} (s, CO).

Preparation of [{(C_6H_3)(OP(NC_5H_{10})$_2$)$_2$}Pd(CO)][BF_4] (5). 13.6 mg (0.07 mmol) of $AgBF_4$ was added to a methylene chloride solution (10 ml) of **3** (48.4 mg; 0.07 mmol). The reaction mixture was stirred for 15 minutes under rigorous exclusion of light. The reaction mixture was filtered over celite. The solvent was removed under reduced pressure. Dissolution of [{(C_6H_3)(OP(NC_5H_{10})$_2$)$_2$}Pd][BF_4] in THF-*d*$_8$ subsequent by treatment with an excess (~50 equiv.) of CO gas yielded quantitatively complex **5**. CO release was observed under reduced pressure, hence an elemental analysis was not obtained.

$^{31}P\{^{1}H\}$-NMR (THF-d_8; δ, ppm): 140.75 (s, $P(NC_5H_{10})_2$). ^{1}H NMR (THF-d_8; δ, ppm): 7.22 (broad t, $^{3}J_{HH}$ = 8.3 Hz, 1H, Ar_{para}), 6.72 (broad d, $^{3}J_{HH}$ = 8.3 Hz, 2H, Ar_{meta}), 3.25 (s, 16H, PNCH_2), 1.57 (s, 24H, CH_2). $^{13}C\{^{1}H\}$ NMR (THF-d_8; δ, ppm): 181.0 (t, J_{PC} = 11.6 Hz, *C*O), 160.7 (vt, J_{PC} = 11.1 Hz, *Ar*OP), 133.7 (s, Ar_{para}), 133.2 (unresolved t, Ar_{ipso}), 107.8 (vt, $^{3}J_{PC}$ = 8.1 Hz, Ar_{meta}), 47.3 (s, NCH_2), 27.4 (s, NCH_2CH_2), 25.2 (s, $NCH_2CH_2CH_2$). IR (ATR; cm^{-1}) ν 2133 cm^{-1} (s, CO).

Preparation of [{(C_6H_3)(NHP(NC_5H_{10})$_2$)$_2$}Pd(Br)]. To an orange suspension of 0.709 g (1.89 mmol) of [$PdBr_2$(COD)] in 15ml of THF, 1.077 g (3.80 mmol, 2.01 equiv.) of $P(NC_5H_{10})_3$ (dissolved in 10 ml of THF) was added and stirred for 5 minutes at room temperature, which quantitatively yielded [$Pd(Br)_2\{P(NC_5H_{10})_3\}_2$]. To THF solutions (10 ml) of 260 mg (0.31 mmol) of [$Pd(Br)_2\{P(NC_5H_{10})_3\}_2$], 36.0 mg (0.33 mmol, 1.07 equiv.) of 1,3-diaminobenzene was added. The reaction mixture was placed in an oil bath and heated up to 80°C and stirred for 45 minutes under nitrogen atmosphere. The solvent was removed under reduced pressure. The pale yellow residue was extracted with 40 ml of diethyl ether. Removal of the solvent gave 153.9 mg (0.223 mmol, 67%) of pure [{(C_6H_3)(NHP(NC_5H_{10})$_2$)$_2$}Pd(Br)] as pale yellow powder.

Data of [$Pd(Br)_2\{P(NC_5H_{10})_3\}_2$]: $^{31}P\{^{1}H\}$-NMR (C_6D_6; δ, ppm): 93.9 (s, $P(NC_5H_{10})_3$). ^{1}H NMR (C_6D_6; δ, ppm): 3.32 (s, 24H, NCH_2), 1.52 (s, 24H, NCH_2CH_2), 1.40 (s, 12H, CH_2). $^{13}C\{^{1}H\}$ NMR (C_6D_6; δ, ppm): 49.1 (s, NCH_2), 26.8 (s, NCH_2CH_2), 25.6 (s, $NCH_2CH_2CH_2$). Elemental analysis: Calc. for $C_{30}H_{60}Br_2N_6P_2Pd$: C, 43.26; H, 7.26; N, 10.09. Found: C, 43.31; H, 7.11; N, 10.01. Data of [{(C_6H_3)(NHP(NC_5H_{10})$_2$)$_2$}Pd(Br)]: $^{31}P\{^{1}H\}$-NMR (C_6D_6; δ, ppm): 122.7 (s, $P(NC_5H_{10})_2$). ^{1}H NMR (C_6D_6; δ, ppm): 7.00 (tt,

$^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{PH}$ = 1.8 Hz, 1H, *Ar*$_{para}$), 6.06 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H, *Ar*$_{meta}$), 3.96 (s, 2H, N*H*), 3.18 (s, 16H, PNC*H*$_2$), 1.41 (m, 16H, C*H*$_2$), 1.36 (m, 8H, C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6; δ, ppm): 151.7 (vt, J_{PC} = 16.2 Hz, *Ar*NHP), 127.9 (s, *Ar*$_{para}$), 126.7 (unresolved t, *Ar*$_{ipso}$), 102.2 (vt, $^{3}J_{PC}$ = 9.8 Hz, *Ar*$_{meta}$), 47.1 (vt, $^{2}J_{PC}$ = $^{4}J_{PC}$ = 3.8 Hz, N*C*H$_2$), 26.7 (s, NCH$_2$*C*H$_2$), 25.2 (s, NCH$_2$CH$_2$*C*H$_2$). The assignment of the ^{1}H and ^{13}C{^{1}H} NMR signals was confirmed by COSY and ^{13}C{^{1}H} DEPT experiments. Elemental analysis: Calc. for $C_{26}H_{43}BrN_6P_2Pd$: C, 45.26; H, 6.57; N, 12.18. Found: C, 45.39; H, 6.90; N, 12.09.

Preparation of [{(C_6H_3)(OP(NC_5H_{10})$_2$)$_2$}Pd(Br)]. To THF solutions (10 ml) of 262.8 mg (0.32 mmol) of [Pd(Br)$_2${P(NC_5H_{10})$_3$}$_2$] (see above), 36.0 mg (0.33 mmol, 1.01 equiv.) of resorcinol was added. The reaction mixture was placed in an oil bath and heated up to 80°C for 15 minutes, during which the solution decolorized. The solvent was removed under reduced pressure, and the solid was extracted with 20 ml of diethyl ether. After removal of the solvent *in vacuo*, 161.5 mg (0.24 mmol, 74%) of [{(C_6H_3)(OP(NC_5H_{10})$_2$)$_2$}Pd(Br)] was obtained as colorless powder.

^{31}P{^{1}H}-NMR (C_6D_6; δ, ppm): 147.6 (s, *P*(NC_5H_{10})$_2$). ^{1}H NMR (C_6D_6; δ, ppm): 6.96 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, *Ar*$_{para}$), 6.63 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, *Ar*$_{meta}$), 3.27 (m, 16H, NC*H*$_2$), 1.41 (m, 16H, NCH$_2$C*H*$_2$), 1.27 (m, 8H, NCH$_2$CH$_2$C*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6; δ, ppm): 160.9 (vt, J_{PC} = 10.2 Hz, *Ar*OP), 129.3 (s, *Ar*$_{para}$), 126.9 (unresolved t, *Ar*$_{ipso}$), 106.4 (vt, J_{PC} = 8.4 Hz, *Ar*$_{meta}$), 46.7 (vt, $^{2}J_{PC}$ = $^{4}J_{PC}$ = 4.1, N*C*H$_2$), 26.6 (s, NCH$_2$*C*H$_2$), 24.9 (s, NCH$_2$CH$_2$*C*H$_2$). The assignment of the ^{1}H and ^{13}C{^{1}H} NMR signals was confirmed by COSY and ^{13}C{^{1}H} DEPT experiments. Elemental Analysis: Calc. for $C_{26}H_{43}BrN_4O_2P_2Pd$: C, 45.13; H, 6.26; N, 8.10. Found: C, 45.08; H, 6.35; N, 8.13.

Procedure for the "one-pot" synthesis of catalyst solutions of 2 and 3. In a Young Schlenk 100 mg (0.35 mmol) of [Pd(COD)(Cl)$_2$] were suspended with 50 ml of toluene. After the addition of toluene solutions (20 ml) containing two equivalents of 1,1',1''-phosphinetriyltripiperidine (198.5 mg; 0.70 mmol), the reaction mixture was stirred for 10 minutes. Subsequently, an equimolar amount of resorcinol or 2,6-diaminobenzene, respectively, was added to these solutions. The reaction mixtures were heated up to 100°C and stirred until decolorizing occurred. After cooling to room temperature and precipitation of insoluble reaction products, the concentrations of the catalyst solutions were determined. Appropriate amounts from these solutions were used for catalysis.

General procedure for Suzuki cross-coupling reactions of aryl halides with phenylboronic acid (table 1). In a round bottom flask in air were placed the newly purchased or freshly recrystallized phenylboronic acid (0.732 g, 6.0 mmol), powdered, anhydrous K_3PO_4 (1.696 g, 8.0 mmol) and toluene of technical quality (12.0 ml). The mixture was vigorously stirred and heated up to 100°C. Then the aryl halide (4.0 mmol) and the correct amount of catalyst was added as a toluene solution via syringe. Samples, taken from the reaction mixture were diluted with methylene chloride and analyzed by GC/MS. At the end of catalysis the reaction mixtures were allowed to cool to room temperature, quenched with aqueous HCl (2 M, 40 ml), extracted with methylene chloride (3 x 40 ml), the combined extracts were dried ($MgSO_4$) and evaporated to dryness. The crude material was purified by flash chromatography on silica gel.