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Supporting Information

Modular Functionalized Polyphosphines for Supported Materials: Previously Unobserved ^{31}P-NMR « Through-Space » ABCD Spin Systems and Heterogeneous Palladium-Catalysed C–C and C–H Arylation

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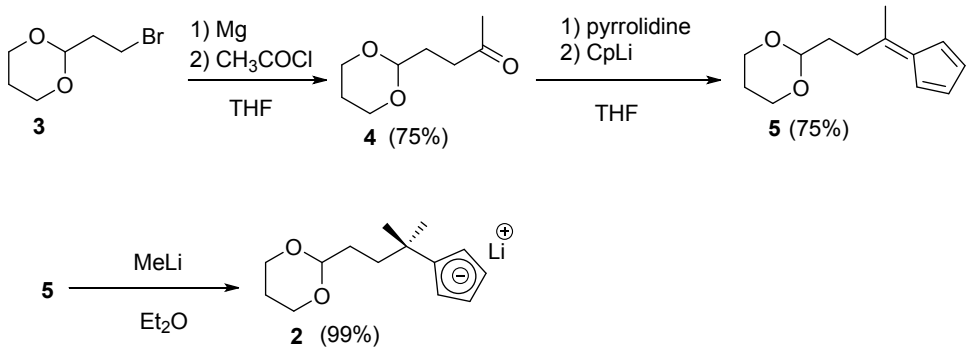
Content

General Procedures

All reactions were performed under argon atmosphere using Schlenk techniques. Toluene, THF, heptane and Et_2O, were degassed and distilled from sodium benzophenone treatment under argon atmosphere prior to use. Dichloromethane was distilled from calcium hydride under argon. THF-d_8 was distilled from NaK under argon. The identity and purity of the products were established at the "*Chemical Analysis platform and Molecular Synthesis University of Burgundy*" using multinuclear NMR, elemental analysis and high-resolution mass spectrometry. Elemental analysis was performed on an Analyzer CHNS/O Thermo Electron Flash EA 1112 Series and ICP-AES iCAP Thermo. The exact masses were obtained from a LTQ-Orbitrap XL (THERMO). ^{1}H(300.13, 500.13, or 600.13 MHz) and ^{13}C NMR (δ in ppm) spectra (75.5, 125.8,or 150.9 MHz) were recorded at 298 K on a Bruker 300 Avance, Bruker 500 Avance DRX, or Bruker 600 Avance II spectrometer. CP-MAS ^{31}P NMR spectra were recorded on the 500 MHz spectrometer with a 4mm BB-CPMAS probe at a working frequency of 202.4 MHz. The spectra were acquired using the cross-polarization sequence under magic angle spinning at a spinning rate of 14 kHz. The 90° pulse was 3.5 µs and the contact pulse was 2 ms. Spectra were collected after 10000 scans with a recycle delay of 2 s and a line broadening of 100 Hz. FT-IR analyses were achieved on a Bruker Vector 22.



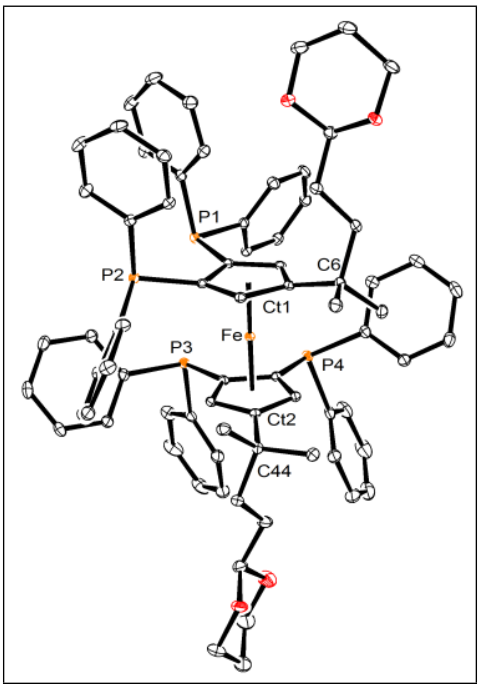
Synthesis of 4-(1,3-dioxan-2-yl)butan-2-one (4). This compound can be synthesized following two methods. **Method A**: To a suspension of magnesium ribbon (1.10 g, 46.3 mmol) in 10 mL of THF was added dropwise a solution of commercially available 2-(2-bromoethyl)-1,3-dioxane (3.20 g, 16.4 mmol) in 20 mL of THF. After the addition the Grignard solution formed was dropwise added *via* a cannula bridge into a solution of acetylchloride (1.76 g, 22.4 mmol) in 20 mL of THF. The mixture was stirred for 15 h at 20 °C and then quenched by a saturated aqueous solution of NH_4Cl. The THF solvent was removed under reduced pressure, and the aqueous layer was extracted with 2x30 ml of dichloromethane. The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent AcOEt/heptane 1:5) to yield 2.02 g (75%) of **4** as pale yellow oil. **Method B:** zinc powder (0.23 g, 3.5 mmol) and LiCl (0.11 g, 2.6 mmol) were degassed and dried at 150 °C under reduced pressure for 5 min. After cooling, 5 ml of THF were added, and the zinc powder was activated by addition of 5 mol% of 1,2-dibromoethane and 1 mol% of chlorotrimethylsilane. Then, 2-(2-iodoethyl)-1,3-dioxane (0.63 g, 2.6 mmol) was introduced. The mixture was refluxed for 20 h, and after cooling was filtered off on cotton to remove zinc excess. The filtrate was dosed according to the literature method.[1] To this solution, was added 2 mol% of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and 8 mol% PPh_3 in 1 ml CH_2Cl_2, and acetylchloride (0.25 mL, 3.5 mmol) at –20 °C. The mixture was stirred for 2 h at 20 °C and quenched by a saturated aqueous solution of NH_4Cl, then extracted with 2x10 mL of CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The crude product obtained was purified as above described to yield 0.31 g (75%) of **4** as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) : δ 4.50 (t, 1 H, *J* = 5 Hz), 4.01 (m, 2 H), 3.67 (m, 2 H), 2.49 (t, 2 H, *J* = 7 Hz), 2.08 (s, 3 H), 1.98 (m, 1 H), 1.80 (td, 2 H, *J* = 5 Hz, *J* = 7 Hz), 1.26 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 208.3 (s, 1 C), 100.8 (s, 1 C), 66.8 (s, 2 C), 37.6 (s, 1 C), 29.9 (s, 1 C), 29 (s, 1 C), 25.7 (s, 1 C).

Synthesis of [3-(cyclopenta-2,4-dienylidene)butyl]-1,3-dioxane (5). To a solution of the ketone **4** (3.8 g, 24 mmol) in 30 mL of dried THF was added dropwise at room temperature pyrrolidine (1.9 g, 26.8 mmol). After 5 min, a solution of CpLi (2.25 g, 31.2 mmol) in 30 mL of dried THF was added dropwise via a cannula bridge into the reaction mixture. After 1 h at 20 °C, the reaction mixture was quenched by a saturated aqueous solution of NH_4Cl. THF solvent was removed under reduced pressure, and the aqueous layer was extracted with 3x50 mL of dichloromethane. The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent AcOEt/heptane 1:3) to yield 3.8 g (75%) of **5** as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) : δ 6.49 (m, 4 H), 4.51 (t, 1 H, *J* = 5 Hz), 4.11 (m, 2 H), 3.74 (m, 2 H), 2.63 (t, 2 H, *J* = 7 Hz), 2.20 (s, 3 H), 2.08 (m, 1 H), 1.83 (td, 2 H, *J* = 5 Hz, *J* = 7 Hz), 1.34 (m, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.7 (s, 1 C), 143.2 (s, 1 C), 131.1, 130.8 (s, 1 C each), 120.8, 120.7 (s, 1 C each), 101.3 (s, 1 C), 66.9 (s, 2 C), 34.2 (s, 1 C), 31.2 (s, 1 C), 25.9 (s, 1 C), 20.9 (s, 1 C). FT-IR υ(cm^{-1}): C=C 1639.2 (spectrum in SI).

Synthesis of 1,2-bis(diphenylphosphino)-3-[4-(1,3-dioxan-2-yl)-2-methylbutyl] cyclopentadienyl lithium (6). To a solution of **5** (3.8 g, 18.5 mmol) in 40 mL of dry Et_2O was added dropwise at –20 °C a commercial solution of MeLi (13.5 mL, 20.3 mmol). After 24 h at 20 °C, a white precipitate was formed and filtered off, then washed with dry Et2O under argon and dried under reduced pressure, to yield 4.0 g (99%) of 1-[4-(1,3-dioxan-2-yl)-2-methylbutyl]cyclopentadienyl lithium (**2**), as an air-sensitive white powder (^{1}H NMR (THF-d_8, 300 MHz): δ 5.63 (m, 4 H), 4.32 (t, 1 H, J = 5 Hz), 4.11 (m, 2 H), 3.72 (m, 2 H), 2.09 (m, 1 H), 1.52-1.73 (m, 4 H), 1.35 (m, 1 H), 1.28 (s, 6 H)). To a solution of **2** (2.0 g, 8.77 mmol) in 20 mL of toluene was added dropwise at –95 °C chlorodiphenylphosphine (2.13 g, 9.65 mmol). The reaction mixture was stirred 4 h allowing temperature to reach room temperature. A solution of *n*-BuLi 1.6 M in hexane (6 ml, 9.65 mmol) was then added dropwise at –95 °C. The reaction mixture was stirred 15 h at room temperature and a white precipitate was formed. A second equivalent of chlorodiphenylphosphine was then introduced and the mixture was treated according to the previous procedure. The resulting solution was filtered off on Celite® under argon. The filtrate was treated with *n*-BuLi (6 ml, 9.65 mmol) at –95 °C. The white precipitate formed was filtered off, washed with 2x20 mL of heptane and dried under reduced pressure to yield 5.0 g (96%) of **6** as an air-sensitive white powder. Due to the one-pot synthesis, less than 10% traces of other Cp-phosphines are occasionally detected. ^{1}H NMR (THF-d_8, 300 MHz): δ 7.47-7.08 (m, 20 H), 5.96 (m, 2 H), 4.34 (m, 1 H), 4.02 (m, 2 H), 3.69 (m, 2 H), 2.02

(m, 1 H), 1.73-1.51 (m, 4 H), 1.38 (m, 1 H), 1.27 (s, 6 H). $^{31}P\{^{1}H\}$ NMR (THF-d_8, 121.4 MHz): δ –25.2 (s).

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-di[4-(1,3-dioxan-2-yl)-2-methylbut-2-yl]ferrocene (7). To a suspension of $FeCl_2$ (0.45 g, 3.55 mmol) in 5 mL of toluene was added dropwise at 20 °C a solution of **6** (3.1 g, 5.2 mmol) in 10 mL of toluene. The reaction mixture was then refluxed overnight and filtered off. Solvents were removed under reduced pressure and the residue was washed with cold ethanol. When impurities were still present, purification by flash column chromatography on silica gel (eluent AcOEt/heptane 1:4) was performed to yield 3.2 g. (50%) of **7** as an orange-red powder. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.42-6.45 (m, 40 H, Ph), 4.47 (m, 2 H, OCH_1), 4.15-4.06 (m, 8 H, 4HCP+ 4OC$H_{6eq,8eq}$), 3.79 (m, 4 H, OC$H_{6ax,8ax}$), 2.11 (m, 2 H, CH_{7eq}), 1.51-1.21 (m, 10 H, 2 CH_{7ax} + 4H_2, 4H_3), 0.94, 0.10 (s, 6 H each, Me). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 242.9 MHz): δ –30.4 (AA' spin system, 2 P), –34.4 (BB' spin system, 2 P). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 137.5-127.1 (m, 48 C), 105.4 (s, 2 C), 102.8 (s, 2 C), 87.9 (dd, 2 C, J_{CP} = 35.5 Hz, J_{CP} = 13 Hz), 79.4 (m, 2 C), 72.7, 72.0 (s, 2 C each), 67.0 (s, 4 C), 41.7 (s, 2 C), 32.8 (s, 2 C), 31.0 (s, 2 C), 26.9, 28.7 (s, 2 C each), 26.0 (s, 2 C). $C_{76}H_{78}FeO_4P_4$ (1235.17). Exact mass [M+Na^+]: m/z = 1257.4037, simulated = 1257.4092, σ = 0.030, err[ppm] = 4.42.



Molecular structure of the acetal functionalized tetraphosphine **7** (CCDC 988196).

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-di(4-oxo-2-methylbut-2-yl)ferrocene (1). To a solution of **7** (0.3 g, 0.24 mmol) in 15 mL of THF were added 5 mL of a hydrochloric acid solution (2N). The reaction mixture was stirred for 20 min under microwave irradiation (125 W), quenched by a solution of saturated aqueous sodium hydrogenocarbonate and extracted with 2x25 mL of CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent AcOEt/heptane 1:4) to yield 0.245 g (90%) of **1** as a red powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.77 (s, 2 H), 8.37-6.48 (m, 40 H), 4.18 (s, 2 H), 4.04 (s, 2 H), 2.20 (m, 4 H), 1.54 (m, 4 H), 0.97, 0.21 (s, 6 H each). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.48 MHz) : δ –31.0 (AA', 2 P), –35.0 (BB', 2 P). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 202.0 (s, 2 C), 138.7-127.4 (m, 48 C), 105.1 (s, 2 C), 88.8 (m, 2 C), 80.0 (m, 2 C), 72.4, 71.7 (s, 2 C each) 40.2 (s, 2 C), 37.7 (s, 2 C), 32.8 (s, 2 C), 28.0, 27.4 (s, 2 C each). FT-IR υ (cm^{-1}): CO, 1721.8 (full spectrum in SI). Due to the reactivity of the formyl function proper mass analyses were not obtained.

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-di(4-hydroxy-2-methyl but-2-yl)ferrocene (8). To a suspension of $LiAlH_4$ (40 mg, 1.05 mmol) in 5 ml of dry THF was added dropwise at 0 °C a solution of dialdehyde **1** (0.3 g, 0.27 mmol) in 5 mL of dry THF. The reaction mixture was stirred 1 h at 20 °C and then quenched by 5 mL of a saturated aqueous solution of NH_4Cl. THF was removed under reduced pressure, and the aqueous layer was extracted with 3x10 mL of dichloromethane. The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure to yield without further purification 0.3 g (99%) of **8** as a red-orange powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.39-6.48 (m, 40 H), 4.04, 4.18 (s, 2 H each), 3.62 (br s, 4 H), 1.46-1.13 (m, 10 H), 0.97, 0.17 (s, 6 H each). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz) : δ –30.5 (m, 2 P), –34.5 (m, 2 P). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.0-127.3 (m, 48 C), 105.8 (s, 2 C), 88.0 (dd, 2 C, J_{CP} = 30.0 Hz, J_{CP} = 12.8 Hz), 79.6 (pt, 2 C, J_{CP} = 19.5 Hz, J_{CP} = 18.8 Hz), 71.9, 72.5 (br s, 2 C each), 63.6 (s, 2 C), 42.7 (s, 2 C), 33.0 (s, 2 C), 28.7 (s, 2 C), 28.4 (s, 2 C), 27.0 (s, 2 C). $C_{70}H_{70}FeO_2P_4$ (1123.04). Exact mass [M$^+$]: *m*/*z* = 1122.36232, simulated 1122.36722, σ = 0.073, err[ppm] = 4.19.

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-bis[2-methyl-6-(4-vinylphenyl)hex-5-en-2-yl]ferrocene (9). To a suspension of triphenyl(4-vinylbenzyl)phosphonium iodide (0.68 g, 1.33 mmol) in 15 ml of THF and NaH (32 mg, 1.35 mmol) was added dropwise at 20 °C a solution of **1** (0.50 g, 0.45 mmol) in 5 ml of THF. The reaction mixture was stirred for 30 min at 20 °C and then quenched by 15 mL of a saturated aqueous solution of NH_4Cl. THF was removed under reduced pressure, and the aqueous layer was extracted with 2x20 mL of dichloromethane. The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure to yield after purification by flash column chromatography on silica gel (AcOEt/hexane 1:4) 0.30 g (50%) of pure **9** as a red powder. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.44-6.41 (m, 50 H), 6.42 (d, 2 H, *J* = 16.8 Hz), 6.22 (m, 2 H), 5.77 (d, 2 H, *J* = 17.4 Hz), 5.25 (d, 2 H, *J* = 11.4 Hz), 4.10, 4.23 (s, 2 H each), 1.94, 2.12 (m, 2 H), 1.28, 1.38 (m, 2 H), 1.07, 0.18 (s, 6 H each). ^{31}P NMR ($CDCl_3$, 121.48 MHz): δ –30.8 (AA', 2 P), –34.9 (BB', 2 P). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 139.0-126.1 (m, 60 C), 136.5 (s, 2 C), 131.2 (s, 2 C), 129.4 (s, 2 C), 113.4 (s, 2 C), 105.5 (s, 2 C), 88.1 (m, 2 C, J_{CP} = 34.5 Hz, J_{CP} = 12.0 Hz), 79.7 (m, 2 C), 72.6, 72.1 (s, 2 C each), 46.7 (s, 2 C), 33.3 (s, 2 C), 28.8 (s, 2 C), 28.6, 27.1 (s, 2 C each). FT-IR υ(cm^{-1}): 1476.2, 1433.2 (see spectrum in SI). $C_{88}H_{82}P_4Fe$ (1319.33). Exact mass [M+H$^+$]: *m*/*z* = 1319.48325, simulated 1319.47892, σ = 0.083, err[ppm] = 3.29.

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-[2-methyl-5-(4-vinylbenzyl amino)pent-2-yl]ferrocene (10). To a mixture of sodium triacetoxyborohydride (0.40 g, 1.88 mmol) and *p*-vinylbenzylamine (0.25 g, 1.88 mmol) in 30 mL of dichloroethane was added dropwise at 20 °C a solution of **1** (0.63 g, 0.57 mmol) in 10 ml of dichloroethane. The reaction mixture was stirred 15 h at room temperature and quenched by 15 mL of a solution of NaOH (1 M). The aqueous layer was extracted with 2x30 ml of CH_2Cl_2, the organic layer was dried over MgSO4, and the solvent were removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent MeOH/CH_2Cl_2 5:95) to yield 0.42 g (55%) of a red powder. ^{1}H NMR ($CDCl_3$, 600 MHz): 8.36-6.46 (m, 50 H), 5.75 (d, 2 H, *J* = 16.2 Hz), 5.25 (d, 2 H, *J* = 12.0 Hz) 4.01, 4.16 (s, 2 H each), 3.84 (s, 4 H), 2.62 (m, 4 H), 1.27 (m, 2 H), 1.45-1.10 (m, 8 H) 0.93, 0.16 (s, 6 H each). ^{31}P{^{1}H} NMR ($CDCl_3$, 242.9 MHz): δ –30.5 (AA', 2 P), –34,4 (BB', 2 P). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 138.0-127.2 (m, 48 C), 136.4 (s, 2 C), 126.4 (s, 8 C), 113.8 (s, 2 C), 106.0 (s, 2 C), 88.0 (dd, 2 C, J_{CP} = 33.0 Hz, J_{CP} = 12.0 Hz), 79.6 (pt, 2

C, J_{CP} = 19.5 Hz, J_{CP} = 18.8 Hz), 71.8, 72.4 (br s, 2 C each), 53.4 (s, 2 C), 49.7 (s, 2 C), 44.1 (s, 2 C), 33.1 (s, 2 C), 28.5 (s, 2 C), 27.0 (s, 2 C), 25.0 (s, 2 C). $C_{88}H_{88}P_4FeN_2$ (1353.39). Exact mass [M+H$^+$]: *m/z* = 1353.53492; simulated 1353.53202, σ = 0.105, err[ppm] = 2.14.

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-bis{5-[(3-triethoxysilyl)propylcarbamoyloxy]-2-methyl}pent-2-ylferrocene (11). Tetraphosphine **1** (50 mg, 44 µmol) was solubilized in 1 mL of CH_2Cl_2. The addition of (3-isocyanatopropyl)triethoxysilane (24 µl, 44 µmol) to the reaction mixture was complemented with one drop of triethylamine. After 20 h at 20 °C, the solvent of the reaction was evaporated under reduced pressure to yield 70 mg (99%) of **11** as a red powder. ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ 8.42-6.45 (m, 40H), 4.7 (s, 2H), 4.17, 4.04 (s, 2 H each), 4.02 (t, 4 H, ^3J = 6.5 Hz), 3.82 (q, 12 H, ^3J = 7 Hz), 3.20 (q, 4 H, ^3J = 6.5 Hz), 1.65 (m, 4 H), 1.30 (m, 4H), 1.24 (t, 18 H, ^3J = 7 Hz), 0.99, 0.13 (s, 6 H each), 0.87 (m, 4H), 0.63 (s, 4 H). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.5MHz, 298 K) : δ(ppm) –30.7 (AA', 2P), –34.6 (BB', 2P). ^{13}C NMR ($CDCl_3$, 125.7 MHz, 298 K): δ (ppm) 157.1 (s, 2 C), 139.1-127.5 (m, 48 C, Ph), 105.8 (s, 2 C), 88.5 (dd, 2 C, J_{CP} = 13.8 Hz, 35.2 Hz), 79.9 (t, 2 C, J_{CP} = 18.9 Hz), 72.7, 72.2 (s, 2 C each), 65.6 (s, 2 C), 58.8 (s, 6 C), 43.8 (s, 2 C), 43.3 (s, 2 C), 35.7 (s, 2 C), 28.9, 27.2 (s, 2 C each), 25.1 (s, 2 C), 23.7 (s, 2 C), 18.6 (s, 6 C), 8.0 (s, 2 C). $C_{90}H_{112}P_4FeO_{10}N_2Si_2$(1617.77). Exact mass [M$^+$]: *m/z* = 1616.61284, simulated 1616.61537, σ = 0.1892, err[ppm] = 1.3.

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4,4'-bis[2-(2-methylpent-4-enyl)]ferrocene (12).

The synthesis of the cyclopentadiene precursor 1-[2-(2-methyl)pent-4-enyl]cyclopentadiene, **2a'** was conducted as follows. To a solution of 6,6-dimethylfulvene (7.7 g, 72.5 mmol) in 60 mL of THF was dropwise added a commercial solution (2M in THF) of allylmagnesium chloride (40 mL, 80 mmol) at 20 °C. After 2 h, the reaction mixture was quenched with water. THF was removed under reduced pressure and the residue was extracted with 2×50 mL of Et_2O. The aqueous phase was treated with HCl (2N), and then extracted with 50 mL of Et_2O. The organic layers were collected and dried over $MgSO_4$, then concentrated under reduced pressure. Distillation of the crude product under reduced pressure (67 °C under 25 mbar) afforded 6.3 g (60%) of **2a'** as a pale yellow oil.

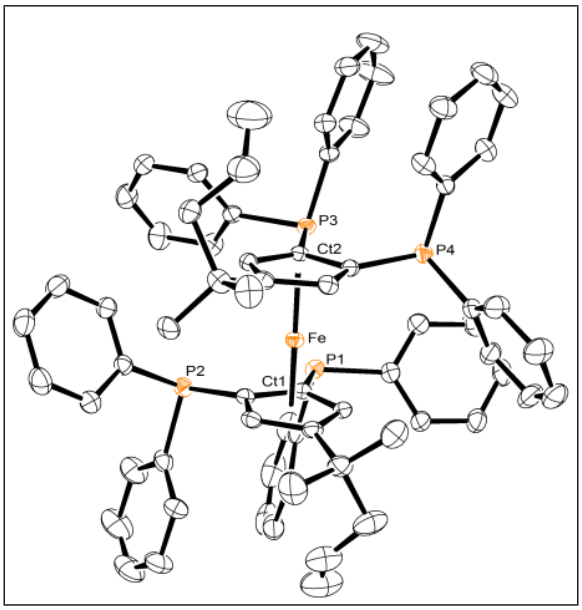
The salt 1-[2-(2-methyl)pent-4-enyl]cyclopentadienyl lithium, **2b**, was obtained from **2a'**. The diene **2a'** (6.3 g, 42.6 mmol) was solubilized in 60 mL of hexane, then a solution of *n*-BuLi (27 mL, 42.6 mmol, 1.6 M in hexane) was dropwise added at –80 °C. The reaction mixture was allowed to reach 20 °C and was stirred for 4 h. The precipitate formed was filtered, washed with hexane and dried under reduced pressure to yield 5.1 g (78 %) of **2b** as a white powder. ^{1}H NMR (THF-d_8, 300 MHz) 5.92 (m, 1 H), 5.65 (m, 4H), 5.03 (dd, 1 H, J = 2 and 10 Hz), 4.91 (dd, 1 H, J = 2 and 17 Hz), 2.28 (d, 2 H, J = 2.5 Hz), 1.21 (s, 6H).

The salt 1-diphenylphosphino-3-[2-(2-methyl)pent-4-enyl]cyclopentadienyl lithium, **2c**, was obtained from **2b**. To a solution of 1-[2-(2-methyl)pent-4-enyl]cyclopentadienyl lithium **2b** (3.0 g, 20.1 mmol) in 50 mL of toluene was dropwise added a solution of chlorodiphenylphosphine (4.6 g, 21.1 mmol) in 50 mL of toluene at –80 °C. The reaction mixture was allowed to reach 20 °C and was stirred 15 h. The reaction mixture was then filtered over Celite® and concentrated to dryness. Hexane was added (50 mL) and a solution of *n*-BuLi (13.8 mL, 22.1 mmol) was dropwise added at –20 °C. The precipitate formed was filtered, washed with hexane and dried under reduced pressure to yield 6.5 g (90%) of **2c** as a white powder. ^{1}H NMR (THF-d_8, 300 MHz) 7.36-7.21 (m, 10 H), 5.91 (m, 1 H), 5.63 (m, 3 H), 5.02 (dd, 1 H, J = 2 Hz and 10 Hz), 4.91 (dd, ^{1}H, J = 2 Hz and 17 Hz), 2.29 (d, 2H, J = 2.5 Hz), 1.22 (s, 6 H). ^{31}P NMR (THF-d_8, 121.4 MHz) –21.1 (s).

The salt 1,2-bis(diphenylphosphino)-4-[2-(2-methyl)pent-4-enyl]cyclopentadienyl lithium, **2 d**, was obtained from **2c**. A solution of chlorodiphenylphosphine (7.1 g, 32.3 mmol) in toluene was dropwise added to a solution of 1-diphenylphosphino-3-[2-(2-methyl)pent-4-enyl] cyclopentadienyl lithium **2c** (9 g, 26.9 mmol) in 50 mL of toluene at –80 °C. The reaction mixture was allowed to reach 20 °C and was then

stirred 15 h. The reaction mixture was then filtered over Celite® and evaporated to dryness. Hexane was added (50 mL) and a solution of *n*-BuLi (20 mL, 32 mmol) was dropwise added at –20 °C. The precipitate formed was filtered, washed with hexane and dried under reduced pressure to yield 11 g (80%) of **2d** as a white powder. ^{1}H NMR (THF-d_8, 300 MHz) 7.34-6.93 (m, 20 H), 5.92 (m, 1 H), 5.6 (m, 2 H), 5.02 (dd, 1 H, J = 2 Hz and 10 Hz), 4.93 (dd, 1 H, J = 2 Hz and 17 Hz), 2.28 (d, 2 H, J = 2.5 Hz), 1.22 (s, 6 H). ^{31}P NMR (THF-d_8, 121.4 MHz) –22.5 (s).

To a suspension of $FeCl_2$ (1.56 g, 12.3 mmol) in DME (10 mL) was dropwise added at room temperature a solution of **2d** (11 g, 22.4 mmol) in toluene (50 mL). Reaction mixture was refluxed 24 h and filtered over silica. The crude product was purified by column chromatography on silica gel (eluent toluene/hexane 1:1) to afford 3 g (20%) of **12** as a red powder. ^{1}H NMR ($CDCl_3$, 300 MHz) 6.35-8.32 (m, 40H), 5.51 (m, 2H), 5.10 (dd, 2H, J = 10 and 2 Hz), 5.01 (dd, 2H, J = 17 and 2 Hz), 3.95, 4.08 (s, 2H each), 1.77 (m, 4H), 0.13, 0.91 (s, 6H each). ^{31}P NMR ($CDCl_3$, 121.4 MHz) –30.6 (m), –34.5 (m). ^{13}C NMR ($CDCl_3$, 75 MHz) 127.2-138.5 (m, 40C), 135.7 (s, 2C), 117.3 (s, 2C), 105.7 (s, 2C), 88.1 (dd, 2C, J = 34.5 and 13.5 Hz), 79.3 (p-t, 2C, J = 20.5 and 19.5 Hz), 72.4, 72.7 (s, 2C each), 50.8 (s, 2C), 33.4 (s, 2C), 27.3, 28.3 (s, 2C each). $C_{70}H_{66}P_4Fe$ (1087.03). Exact mass [M+H$^+$]: m/z = 1087.35558, simulated 1087.35392, err[ppm] = 1.7.



Molecular structure of the vinyl-functionalized tetraphosphine **12** (disorder of 1,1-dimethylbut-3-enyl groups and hydrogen atoms are omitted for clarity (CCDC 988195).

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4-[4-(1,3-dioxan-2-yl)-2-methylbut-2-yl]-butyl-4'-*tert*-butylferrocene (13). To a suspension of $FeCl_2$ (0.45 g, 3.54 mmol) in 20 mL of toluene and 5 mL of THF was added at –80 °C a solution of **6** (2.05 g, 3.47 mmol) in 30 mL of toluene. The solution was allowed to reach room temperature and was stirred for 1 h. A solution of 1,2-bis(diphenylphosphino)-4-*tert*-butylcyclopentadienyl lithium (1.75 g, 3.52 mmol) in 20 ml of toluene was then added at –80 °C. After reaching 20 °C, the deep-red solution was refluxed for 4 h. The solution was filtered off on silica, the filtrate was concentrated under reduced pressure and the crude product was purified by flash column chromatography on silica gel (eluent AcOEt/heptane 1:3) to afford 0.98 g (25%) of an orange powder. ^{1}H NMR ($CDCl_3$, 300 MHz, 303 K): δ(ppm) 6.30-8.42 (m, 40H), 4.34 (m, 1H), 3.88-4.05 (m, 6H), 3.69 (m, 2H), 2.01 (m, 1H), 1.21-1.51 (m, 5H), 0.84 (s, 3H), 0.6 (s, 9H), 0.05 (s, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.49 MHz, 303 K) : δ(ppm) –30.0 (m, 2P), –33.8 (m, 2P). ^{13}C NMR ($CDCl_3$, 75.46 MHz, 303 K): δ(ppm) 127.4-139.4 (m, 48C), 107.7 (s, 1C), 105.7 (s, 2C), 103.1 (s, 2C), 88.3 (m, 2C), 79.7 (m, 2C), 73.0, 72.5, (m, 2C each), 72.0, 71.2 (d, 2C each, JCP = 5.3 Hz), 67.3, 61.2 (s, 1C each), 41.0 (s, 1C), 33.2 (s, 1C), 31.9 (s, 3C), 31.1, 30.7 (s, 1C each), 28.9, 27.3 (s, 1C each), 26.3 (s, 2C). $C_{71}H_{70}P_4FeO_2$ (1135.05). Exact Mass [M+H$^+$]: *m*/*z* = 1135.37669, simulated 1135.37505, σ = 0.0351, err[ppm] = 1.4.

1,1',2,2'-tetrakis(diphenylphosphino)-4-(4-oxo-2-methylbut-2-yl)-4'-tert-butylferrocene, (14). A procedure similar to the one used for synthesizing compound **1** from **7** was achieved. To a solution of **13** (0.3 g, 0.26 mmol) in 15 mL of THF were added 5 mL of a hydrochloric acid solution (2N). The reaction mixture was stirred for 20 min under microwave irradiation (125 W), quenched by a solution of saturated aqueous sodium hydrogenocarbonate to yield after workup procedure 0.25 g of **14** (90%, NMR yield) as a red powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.78 (s, 1 H, C*H*O), 8.40-6.53 (m, 40H, Ph), 4.21, 4.18, 4.12, 4.04 (s, 1H each, *H*-Cp), 2.25 (m, 2H), 1.5 (m, 2H), 0.91 (s, 3H), 0.74 (s, 9H, *t*-Bu), 0.23 (s, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.49 MHz, 303 K): δ(ppm) –30.1 (m, 2P), –34.1 (m, 2P). Due to the reactivity of the formyl function proper mass analyses were not obtained and this intermediate was engaged quickly in further reaction.

Synthesis of 1,1',2,2'-tetrakis(diphenylphosphino)-4-[2-methyl-5-(4-vinylbenzylamino)pent-2-yl]-4'-*tert*-butylferrocene (15). To a mixture of sodium triacetoxyborohydride (0.08 g, 0.36 mmol) and *p*-vinylbenzylamine (0.05 g, 0.36 mmol) in 5 mL of dichloroethane was added at room temperature a solution of **14** (0.25 g, 0.24 mmol) in 5 ml of dichloroethane. The reaction mixture was stirred 15 h at room temperature and quenched by 15 mL of a solution of NaOH (1 M). The aqueous layer was extracted with 2x30 ml of CH_2Cl_2, the organic layer was

dried over $MgSO_4$, and the solvent were removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent $MeOH/CH_2Cl_2$ 5:95) to yield 0.13 g of **15** (45%) as a red powder. ^1H NMR ($CDCl_3$, 500MHz, 300 K): δ(ppm) 6.45-8.42 (m, 45H), 5.75 (dd, 1H, ^3J = 10.5 Hz, ^2J <1 Hz), 5.25 (dd, 1H, ^3J = 6.5 Hz, ^2J <1 Hz), 4.18, 4.16, 4.08, 4.02 (s, 1H each), 3.83 (s, 2H), 2.60 (t, 2H, ^3J = 3.5 Hz), 1.21-1.51 (m, 4H), 0.98, 0.15 (s, 3H each), 0.71 (s, 9H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.45 MHz, 300 K) : δ(ppm) –30.2 (m, 2P), –33.8 (m, 2P). ^{13}C NMR ($CDCl_3$, 125.75 MHz, 300 K): δ(ppm) 140.6 (s, 1C), 137.0 (s, 2C), 136.8 (s, 1C), 128.7 (s, 2C), 127.1-137.5 (m, 48C), 126.4 (s, 1C), 113.9 (s, 1C), 107.7, 106.2 (s, 1C each), 88.2 (m, 2C), 79.7 (m, 2C), 72.8, 72.6, 71.9, 71.3 (s, 1C each), 54.4 (s, 1C), 50.7 (s, 1C), 44.9 (s, 1C), 33.4, 30.7 (s, 1C each), 31.9 (s, 1C), 28.8, 27.5 (s, 1C each), 26.1 (s, 1C). $C_{77}H_{75}P_4FeN$ (1194.17). Exact Mass [M+H$^+$]: *m/z* 1194.4250, simulated 1194.4275, σ = 0.0482, err[ppm] = 1.9.

Synthesis of 1,2-diphenylphosphino-1'-diisopropylphosphino-4-[4-(1,3-dioxan-2-yl)-2-methylbut-2-yl]-butylferrocene (17a). To a suspension of $FeCl_2$ (0.45 g, 3.54 mmol) in 20 mL of THF was added at –80 °C a solution of **6** (2.08 g, 3.48 mmol) in 30 mL of THF. The solution was allowed to reach room temperature and was stirred for 1 h. A solution of di*iso*propylphosphino cyclopentadienyl lithium (0.65 g, 3.45 mmol) in 20 ml of THF was then added at –80 °C. After having reached 20 °C the deep-red solution was refluxed for 4 h. The solution was filtered off over silica, the filtrate was concentrated under reduced pressure and the crude product was purified by flash column chromatography on silica gel (eluent AcOEt/heptane 1:3) to afford 0.8 g (30%) of **17a** as an orange powder. ^1H NMR ($CDCl_3$, 600 MHz): δ 6.93-7.70 (m, 20 H), 4.55 (m, 2 H), 4.17 (m, 2 H), 4.12 (s, 4 H), 3.90 (s, 2 H), 3.81 (m, 2 H), 2.14 (m, 1 H), 1.57 (m, 4 H), 1.47 (m, 2 H), 1.39 (m, 1 H), 1.33 (s, 6 H), 0.88, 0.62 (dd, 6 H each, *J* = 7 and 13 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.5 MHz): δ –3.5 (s, 1 P), –25.5 (s, 2 P). ^{13}C NMR ($CDCl_3$, 100 MHz) : δ 127.8-138.9 (m, 12 C), 105.8 (s, 1 C), 102.9 (s, 1 C), 81.6 (p-t, 2 C, J_{CP} = 12 Hz), 80.7 (d, 1 C, J_{CP} = 11 Hz), 73.8 (d, 2 C, J_{CP} = 10 Hz), 72.5 (s, 2 C), 71.3 (s, 2 C), 67.0 (s, 2 C), 40.5 (s, 1 C), 33.8 (s, 1 C), 31.2 (s, 1 C), 28.2 (d, 2 C, $^{TS}J_{CP}$ = 6 Hz), 26.0 (s, 1 C), 23.2 (d, 2 C, J_{CP} = 11 Hz), 20.0, 20.2 (d, 1 C each, J_{CP} = 11 Hz). $C_{49}H_{57}P_3FeO_2$ (826.74). Exact Mass [M+H$^+$]: *m/z* = 827.30045, simulated 826.29936, σ = 0.093, err[ppm] = 1.31.

Synthesis of 1,2-bis(diphenylphosphino)-1'-diisopropylphosphino-4-(4-oxo-2-methylbut-2-yl)ferrocene (18a). To a solution of **17a** (0.1 g, 0.12 mmol) in 2 ml of THF was added 1 ml of a 2N HCL acidic solution. After 2 h refluxing the reaction mixture was quenched with a saturated aqueous solution of sodium hydrogenocarbonate and extracted with 2x10 mL of CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product

was purified by flash column chromatography on silica gel (eluent AcOEt/heptane 1:4) to afford 0.09 g (95%) of **18a** as an orange powder. ^{1}H NMR ($CDCl_3$, 600 MHz, 298 K): δ(ppm) 9.82 (s, 1H) 6.91-7.68 (m, 20H), 4.14 (s, 2H), 4.11 (s, 2H), 3.91 (s, 2H). 3.81 (m, 2H), 2.14 (m, 1H), 1.57 (m, 4H), 1.47 (m, 2H), 1.39 (m, 1H), 1.33 (s, 6H), 0.88, 0.62 (dd, 6H each, J = 7 and 13 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz, 298 K) : δ(ppm) −3.5 (s, 1P), −25.2 (s, 2P). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K) : δ(ppm) 202.5 (s, 1C), 127.1-142.8 (m, 36C), 105.1 (s, 1C), 81.9 (dd, 2C, $^{1}J_{CP}$ = 13.5 Hz, $^{2}J_{CP}$ = 8.5 Hz), 80.8 (d, 1C, $^{1}J_{CP}$ = 21.1 Hz), 73.8 (d, 2C, $^{2}J_{CP}$ = 10 Hz), 72.3 (s, 2C), 71.5 (s, 2C), 40.3 (s, 1C), 37.9 (s, 1C), 33.8 (s, 1C), 28.2 (d, 2C, $^{TS}J_{CP}$ = 9 Hz), 23.2 (d, 2C, $^{1}J_{CP}$ = 12 Hz), 20.0, 20.2 (d, 1C each, $^{2}J_{CP}$ = 13.5 Hz). Due to the reactivity of the formyl function proper mass analyses were not obtained.

Synthesis of 1,2-diphenylphosphino-1'-diisopropylphosphino-4-[2-methyl-5-(4-vinylbenzylamino)pent-2-yl]ferrocene (19a). To a mixture of sodium triacetoxyborohydride (0.3 g, 1.41 mmol) and *p*-vinylbenzylamine (0.19 g, 1.41 mmol) in 20 mL of dichloroethane was added at 20 °C a solution of **18a** (0.72 g, 0.94 mmol) in 10 ml of dichloroethane. The reaction mixture was stirred 15 h at 20 °C and quenched by 15 mL of a solution of NaOH (1 M). The aqueous layer was extracted with 2x30 ml of CH_2Cl_2, the organic layer was dried over $MgSO_4$, and the solvent were removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluent MeOH/CH_2Cl_2 5:95) to yield 0.42 g (50%) of **19a** as a red powder. ^{1}H NMR ($CDCl_3$, 300 MHz, 303 K): δ(ppm) 6.85-7.70 (m, 24H), 6.69 (dd, 1H, ^{3}J = 18 Hz, ^{3}J = 11 Hz), 5.73 (dd, 1H, ^{3}J = 18 Hz, ^{2}J = 1.5 Hz), 5.24 (dd, 1H, ^{3}J = 10.8 Hz, ^{2}J = 1.5 Hz), 4.11 (m, 4H), 3.89 (m, 4H), 2.75 (m, 2H), 1.58 (m, 4H), 1.45 (hd, 2H, $^{3}J_{HH}$ = 7 Hz, $^{2}J_{HP}$ = 3 Hz), 1.30 (s, 6H), 0.84 (dd, 6H, $^{3}J_{HP}$ = 13 Hz, $^{3}J_{HH}$ = 7 Hz), 0.60 (dd, 6H, $^{3}J_{HP}$ = 13 Hz, $^{3}J_{HH}$ = 7 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.49 MHz, 303 K) : δ(ppm) −3.4 (s, 1P), −25.0 (s, 2P). ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ(ppm) 127.5-139.0 (m, 24C), 136.3 (s, 1C), 127.5 (s, 2C), 126.5 (s, 2C), 114.2 (s, 1C), 106.4 (s, 1C), 81.5 (d, 1C, $^{1}J_{CP}$ = 21 Hz,), 81.5 (s, 1C), 80.5 (d, 1C, $^{1}J_{CP}$ = 22 Hz), 73.8, 73.7 (s, 1C each), 72.2, 71.3 (s, 2C each), 52.6 (s, 1C), 48.9 (s, 1C), 43.3 (d, 1C, $^{TS}J_{CP}$ = 4 Hz), 33.9 (s, 1C), 28.1 (d, 2C, $^{TS}J_{CP}$ = 4 Hz), 24.2 (m, 1C), 23.1 (d, 2C, $^{1}J_{CP}$ = 16 Hz), 20.0, 20.2 (d, 2C each, $^{2}J_{CP}$ = 14 Hz). $C_{55}H_{62}P_3FeN$ (885.85). Exact Mass [M+H^{+}]: m/z = 886.34967, simulated 886.35185, σ = 0.574, err[ppm] = 2.3.

The analogues **17b, 18b** and **19b** were synthesized in 40, 88 and 55% yield, respectively, following the same procedures. Their characterization is given below. NMR data are consistent with reported non-functionalized (homogeneous) analogous compounds.

1,2-diphenylphosphino-1'-diphenylphosphino-4-[4-(1,3-dioxan-2-yl)-2-methylbut-2-yl]-butylferrocene (17b) ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ(ppm) 6.91-7.61 (m, 30H), 4.48, (t, 1H, ^{3}J = 5 Hz), 4.14-4.19 (m, 6H), 4.06 (m, 2H). 3.80 (td, 2H, ^{3}J = 12.5 Hz, ^{3}J = 2 Hz), 2.13 (m, 1H), 1.50 (m, 2H), 1.40 (m, 1H), 0.91 (s, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.4 MHz, 298 K) : δ(ppm) –20.6 (s, 1P), –25.0 (s, 2P). ^{13}C NMR ($CDCl_3$, 125.8 MHz, 298 K) : δ(ppm) 127.5-139.5 (m, 36C), 105.1 (s, 1C), 102.7 (d, 1C, $^{TS}J_{CP}$ = 4.5 Hz), 82.5 (m, 2C), 80.4 (d, 1C, $^{1}J_{CP}$ = 4 Hz), 74.6 (s,1C), 74.5 (s, 1C), 72.3 (s, 2C), 72.1 (s, 2C), 71.4 (d, 1C), 67.1 (s, 2C), 40.3 (s, 1C), 33.3 (s, 1C), 31.3 (s, 1C), 27.7, 27.7 (s, 1C each), 26.1 (s, 1C). $C_{55}H_{53}P_3FeO_2$ (894.79). Exact Mass [M+H$^+$]: *m*/*z* = 895.26962, simulated 895.26806, err[ppm] = 1.5.

1,2-bis(diphenylphosphino)-1'-diphenylphosphino-4-(4-oxo-2-methylbut-2-yl)ferrocene (18b). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K): δ(ppm) 9.78 (t, 1H, ^{3}J = 1.5 Hz) 6.91-7.68 (m, 30H), 4.22, (m, 2H), 4.18 (m, 2H), 4.11 (m, 2H), 2.33 (td, 2H, , ^{3}J = 8.5 Hz, ^{3}J = 1.5 Hz), 1.73 (t, 2H, , ^{3}J = 8.5 Hz), 1.00 (s, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.4 MHz, 298 K) : δ(ppm) –20.7 (s, 1P), –24.7 (s, 2P). ^{13}C NMR ($CDCl_3$, 125.7 MHz, 298 K) : δ(ppm) 202.3 (s, 1C), 127.1-149.7 (m, 36C), 106.1 (s, 1C), 82.8 (m, 1C), 80.8 (m, 1C), 77.0 (m, 1C), 75.7 (m, 2C), 72.3 (m, 4C), 40.3 (s, 1C), 37.9 (s, 1C), 33.8 (s, 1C), 27.7 (s, 2C).

1,2-diphenylphosphino-1'-diphenylphosphino-4-[2-methyl-5-(4-vinylbenzylamino)pent-2-yl]ferrocene (19b).

^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ(ppm) 6.70-7.70 (m, 34H), 6.69 (m, 1H), 5.77 (m, 1H), 5.26 (m, 1H), 4.43, (m, 1H), 4.13 (m, 4H), 4.04 (m, 2H), 3.81 (s, 2H),2.60 (m, 2H), 1.38 (m, 4H), 0.93 (s, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$, 202.4 MHz, 298 K) : δ(ppm) –20.7 (s, 1P), –24.7 (s, 2P). ^{13}C NMR ($CDCl_3$, 125.7 MHz, 298 K) : δ(ppm) 127.5-140.2 (m, 42C), 136.4 (s, 1C), 114.0 (s, 1C), 105.3 (s, 1C), 81.3 (m, 1C), 80.5 (m, 1C), 77.0 (m, 1C), 74.6 (m, 2C), 72.1 (m, 4C), 53.9 (s, 1C), 50.1 (s, 1C), 43.5 (s, 1C), 37.9 (s, 1C), 33.6 (s, 1C), 27.8, 27.7 (s, 1C each), 25.8 (s, 1C).

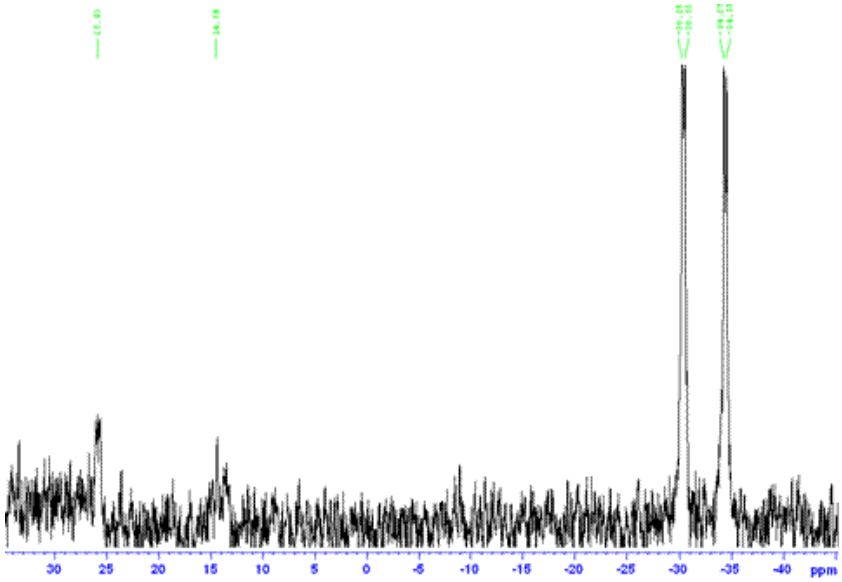
Immobilization procedures

Grafting of ligand 1 on amino-methyl polystyrene resin (PL-AMS). A standard commercially available mesoporous PL-AMS (Polymerlabs MP-Resin, 3.0 mmol g^{-1}, 150-300 μm, 100 Å) was suspended in 7 ml of DCE (0.144 g, 0.46 mmol). After 30 min stirring at 20 °C, sodium triacetoxyborohydryde (0.100 g, 0.47 mmol) was added to the suspension. A solution of ligand **1** (0.080 g, 0.073 mmol) in 3 ml of DCE was dropwise added. The mixture was stirred for 24 h at 20 °C. After addition of 1 M NaOH solution for neutralization, the mixture was filtrated over paper and the collected resin was washed several times with CH_2Cl_2 then dried under vacuum to give 0.170 g of pink colored beads (homogeneous dispersion 250-300 μm). The grafting ratio of **1** was determined by phosphorus elemental analysis and a loading of 0.99% phosphorus was achieved (0.32 mmol g^{-1}). RMN ^{31}P CP-MAS (121.48 MHz, 298 K): δ(ppm) –26.9.

Synthesis of soluble polymer resin 16. This was achieved by co-polymerization of ligand **10** with styrene. In 50 mL of toluene was poured 1.54 g of styrene (14.8 mmol) and 0.26 g of ligand **10** (0.2 mmol). After degasing of the mixture for 1 h by bubbling argon, 0.04 g of AIBN (azobisisobutyronitrile) was added to initiate the radical polymerization. The mixture was stirred (magnetic stirring) under argon at 85 °C for 48 h. Then toluene was evaporated and a minimum of THF was added to solubilize the resulting polymer. The THF solution of polymer was added dropwise to 50 mL of cold methanol maintained at 0 °C by an ice bath. The insoluble polymer slowly precipitated and was filtrated over sintered glass frit, rinsed with methanol and dried under vacuum to give 1.14 g of an orange powder. This polymer is soluble in THF, $CHCl_3$, CH_2Cl_2, toluene, Et_2O, and ethyl acetate. It is insoluble in hexane and methanol, and loosely soluble in DMF. The grafting ratio of **1** was determined by phosphorus elemental analysis and a loading of 1.05% phosphorus was achieved (0.34 mmol g^{-1} of P, or 0.085 mmol g^{-1} of ligand). RMN ^{31}P ($CDCl_3$, 298 K): δ(ppm) –34.30, –30.30 (broad).

^{31}P NMR in CD_2Cl_2 solution of polystyrene-supported tetraphosphine 16.

Distinct signals for peripheral and internal phosphorus are found respectively at –30.0 ppm and –34.0 ppm. Less than 10% traces of phosphine oxide are detectable at 25.0 ppm.



Grafting of triethoxysilane ligand 11 on silica-gel (11-SiO_2). In a Dean-Stark apparatus 1.0 g (16.64 mmol) of silica-gel (Acros, 0.035-0.070 mm, 60 Å) was suspended in 50 mL of toluene and refluxed for 20 h. The silane ligand **11** (0.3 g, 185 µmol) solubilized in 15 ml of toluene was then added and the mixture was refluxed for 5 h. After evaporation of toluene, the resulting mixture was treated with 20 ml of dichloromethane, filtrated, dried and washed several times with dichloromethane, then dried under vacuum to give 1.06 g of a red powder. The grafted silica is insoluble in all the organic solvent tested (THF, $CHCl_3$, CH_2Cl_2, toluene, Et_2O, ethyl acetate, hexane, methanol, DMF, DMSO, NMP). The grafting ratio of 11 was determined and a 0.84% phosphorus loading was achieved (0.272 mmol g^{-1} of P, 0.068 mmol g^{-1} of ligand). RMN ^{31}P CP-MAS (121.48 MHz, 298 K): δ(ppm) –30.0.

Immobilization of ligand 19a: insoluble PS-resin (19a-PS). As a surfactant solution, the mixture of 4.5 g of Arabic gum and 2.8 g of NaCl in 110 mL of distilled water was boiled for 5 min. The resulting mixture was filtrated on Celite® and 45 ml of the filtrate was introduced into a 100 ml reactor with plane-ground joints. In 3 mL chlorobenzene was solubilized 3.2 ml (27.7 mmol) of styrene, 0.4 g of **19a** (0.45 mmol) and 0.41 g of divinylbenzene (3.15 mmol). Under mechanical stirring

this solution was added to the surfactant and the mixture was maintained at 85 °C before addition of 0.40 g of benzoyl peroxide as radical initiator (0.40 g, 1.65 mmol). After 20 h at 85 °C under vigorous mechanical stirring the mixture was filtrated. The polymer was washed with 2×30 ml of hot water and extracted for 24 h in methanol using a Soxhlet apparatus. After drying, 1.6 g of polymer ligand was obtained as a brown powder insoluble in THF, $CHCl_3$, CH_2Cl_2, toluene, Et_2O, ethyl acetate, hexane, methanol, DMF, DMSO, and NMP. The ratio of 19a incorporation was determined by phosphorus elemental analysis and a loading of 0.67% phosphorus was achieved (0.2163 mmol g^{-1} of P, 0.0721 mmol g^{-1} of ligand). RMN ^{31}P CP-MAS (121.48 MHz, 298 K): δ(ppm) –30.90. Immobilization of ligands **10** and **13** as insoluble PS resins was achieved following a procedure similar to the one described for immobilization of ligand **19a**.

Procedures for Pd-catalyzed C–C bond formation with immobilized polyphosphine molecular catalysts and recycling.

The cross-coupling reactions with supported ligands were carried out under the following typical conditions.

Suzuki coupling using Pd/polystyrene resin 16. A solid mixture of phenyl boronic acid (0.26 g, 2.13 mmol), potassium carbonate (0.30 g, 2.17 mmol), the polymeric supported ligand **16** (0.125 g of polymer resin containing 0.085 mmol g^{-1} of tetraphosphine ligand = 0.01065 mmol), and the palladium precursor $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.9 mg, 0.0052 mmol) was carefully degassed with stirring and placed under argon in a Schlenk tube. To this degassed solid mixture was added 1 ml of DMF distilled and degassed by sparging with nitrogen. The suspension was held at 80 °C with vigorous stirring for five minutes. Distilled and degassed bromobenzene (0.34 g, 230 µl, 2.17 mmol) was added by syringe to the reaction mixture which was held at 120 °C for 20 h. The cooled mixture was evaporated to dryness under vacuum, and the residue was dissolved in 10 mL of ethyl ether and extracted with 10 mL of water. The organic phase were dried other $MgSO_4$ and, after evaporation of the ether under vacuum, the residue was dissolved in 20 mL of methanol for separation of the palladium-complexed resin catalyst. The resulting precipitate was filtered off, and GC analysis of the solution indicated total conversion of the bromobenzene into the desired coupling product. This late was obtained in about 80% yield and isolated after separation of the supported catalyst, followed by evaporation of the organic solvent containing the product and chromatography on silica gel. The palladium catalyst isolated by filtration was immediately reused in reaction according to the same procedure by reintroducing the substrates and the base. GC analysis again shows total conversion. The isolated catalyst can be reused in this way several times without significant drop in activity, the limitation lying in the loss of polymer during filtration process.

Suzuki coupling using Pd/silica-supported 11-SiO_2. A solid mixture of phenyl boronic acid (0.26 g, 2.13 mmol), potassium carbonate (0.30 g, 2.17 mmol), bromoacetophenone (0.43 g, 2.17 mmol), silica supported ligand **11-SiO_2** (0.015 g containing 0.068 mmol g^{-1} of tetraphosphine ligand = 0.00102 mmol), was carefully degassed with stirring and placed under argon in as Schlenk tube. To this degassed solid mixture was added the palladium precursor $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1 mL of a 10 mL solution of 1.9 mg, 0.0052 mmol, in DMF). The reaction mixture was held at 120 °C for 20 h. The cooled mixture was filtered to recover the catalyst and some salt, the

mixture was carefully rinsed with degassed solvent and conserved under argon for recycling. ICP-AES analysis of the filtrate indicated no significant leaching (<10 ppm). The filtrate was evaporated to dryness under vacuum and the residue was dissolved in 10 mL of ethyl ether for extraction with addition of 10 mL of water. The organic phase were dried other $MgSO_4$. GC analysis beforehand indicated full conversion of the bromoacetophenone into the coupling product. An 85% isolated yield was obtained after evaporation and chromatography.

Direct C–H arylation of heteroaromatics with chloro-arenes using Pd/polystyrene 19a-PS. The aryl chloride (1 mmol), heteroaromatic derivative (2 mmol), KOAc (2 mmol, 196 mg), and Bu_4NBr (1 mmol, 322 mg) were introduced into a Schlenk tube equipped with a magnetic stirring bar and were purged several times with argon. In another tube $Pd(OAc)_2$ (0.005 mmol, 1.12 mg) and **19a-PS** (0.005 mmol, 69.3 mg) were mixed in 3 mL degassed DMAc and stirred for 30 min. After addition of the reagents to the catalyst, the Schlenk tube was placed in an oil bath preheated to 150°C, and the mixture was stirred for 40 h. The cooled mixture was filtered on paper to recover the catalyst. The solvent was removed by heating of the reaction vessel under vacuum and the residue was charged directly onto a silica gel column. The products were eluted using diethyl ether/pentane.