Supporting Information for Manuscript Entitled

The first insoluble polymer-bound palladium complexes of 2-pyridyldiphenylphosphine: highly efficient catalysts for the alkoxycarbonylation of terminal alkynes

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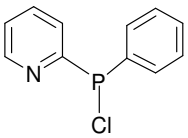
Experimental

General Procedures: All manipulations involving air-sensitive materials were carried out in an inert atmosphere glovebox or using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Diethyl ether and hexane were distilled from potassium/sodium alloy, tetrahydrofuran from potassium, toluene from sodium, dichloromethane and acetonitrile from calcium hydride. Deuteriochloroform was pre-dried with calcium hydride, vacuum-transferred, and stored over 4 Å molecular sieves. Chemicals were purchased from Aldrich, Fluka, Lancaster and Strem and used as received unless otherwise stated and 2-pyridyldiphenylphosphine was prepared according to a previously published procedure.[1]

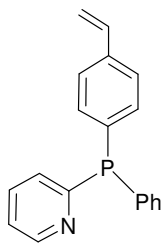
^{1}H NMR spectra were recorded on Bruker AC 200, Bruker 300 and JEOL LA 500 spectrometers at ambient temperatures unless otherwise stated. ^{13}C{^{1}H} NMR spectra were recorded on a JEOL LA 500 spectrometer at ambient temperatures. ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Cryospec WM 300 (121.5 MHz) at ambient temperature. Thin layer chromatography was performed on EM reagent 0.25mm silica gel 60-F plates. Flash column chromatography was performed on Fluorochem LC3025 silica gel (40-63μm). Flame ionisation GC analysis was undertaken using a Pye Unicam series 104 chromatograph using a Silar 5CP column and Shimadzu Chromotopac C-E1B integrator for phenylacetylene carbonylation analysis, and a Pye Unicam GCD chromatograph using a 5-10% carbowax column and Shimadzu Chromotopac C-E1B integrator for propyne carbonylation analysis. All samples were run against a standardised solution of the pure material. CHN analysis was undertaken using a Carlo-Erba 1106 elemental combustion analyser. High-resolution mass spectrometry was run on a Micromass Autospec-M double focussing magnetic sector instrument. ICP-OES for Pd analysis was undertaken using a Unicam model 701 ICP-OES machine with an external Pd standard (Pd 1000μg/ml, 20% in HCl, VHG labs). GPC analysis was performed by RAPRA Technology, using a PLgel guard plus 2 x mixed bed-B column (30 cm, 10 microns) and a refractive index detector. The data was collected using 'Trisec 2000' and analysed using 'Trisec 3.0' software.

Synthesis of Compounds 2, 3, 6, 7, 8, and 9



(**2**)

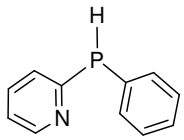
2-Pyridylphenylchlorophosphine (2): A solution of 2-bromopyridine (10.0 ml, 103 mmol) in Et_2O (10 ml) was added drop-wise to a solution of *n*-BuLi (2.5M in hexane, 41.1 ml, 103 mmol) in Et_2O (50 ml) cooled to -40°C. The resulting solution was allowed to warm to -5°C, stirred at this temperature for 15 min and then re-cooled to -40°C and a THF:pyridine (5:1, 180 ml) solution of freshly prepared anhydrous $ZnCl_2$ (14.2 g, 103 mmol) added. The reaction mixture gradually darkened in colour and an oily residue formed which solidified after approx 1h. The resulting solid was triturated to afford a fine powder which was stirred at room temperature overnight, filtered, washed with diethylether (2 x 150 ml) dried and used immediately in the next step.[2] The solid was dissolved in THF:pyridine mixture (4:1, 50 ml), cooled to -35°C and added dropwise to a solution of dichlorophenylphosphine (15.6 ml, 103 mmol) in pyridine (30 ml) cooled to -35°C. The reaction mixture was allowed to warm to room temperature and stirred for 16h after which time the solvent was removed under reduced pressure to give a yellow solid, which was triturated with hexane (2 x 150 ml) and dried *in vacuo* overnight. The resulting solid was distilled at reduced pressure (0.2 mmHg) to give a small forerun of dichlorophenylphosphine (150-155°C) followed by the product (182-185°C), which solidified overnight to give **2** as a yellow solid in 64% yield (14.6 g). The spectroscopic and analytical data acquired was consistent with that previously published. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.45 (d, *J* = 5.0 Hz, 1H, py-*H*), 7.65 (d, 1H, Ar-*H*), 7.45-7.50 (m, 3H, Ar-*H*), 7.10-7.15 (m, 3H, Ar-*H*), 6.95-7.00 (m, 1H, Ar-*H*); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 122, 124, 128, 130, 132, 136, 149, 162; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ): 67 (s); Mass spec: 186 (M^+-Cl); Anal. Calc for $C_{11}H_9ClNP$: C, 59.6%; H, 4.1%; N, 6.3%. Found: C, 59.3%; H, 4.3%; N, 6.2%.



(**3**)

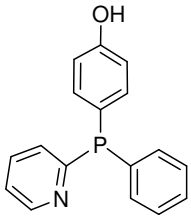
2-Pyridyl-4-vinylphenylphenylphosphine (3):[3,4] Approximately 2-3 ml of a solution of 4-chlorostyrene (0.90 ml, 6.9 mmol) in THF (10ml) was added slowly to suspension of magnesium powder (0.36 g, 15.1 mmol) and a crystal of iodine in THF (20 ml). The resulting mixture was heated gently to initiate Grignard formation after which the remaining the 4-chlorostyrene solution was added at a rate that maintained gentle reflux. After heating at 60°C for a further 4h, the mixture was allowed to cool to room temperature and then added dropwise to a solution of 2-pyridylphenylchlorophosphine (1.33 g, 6 mmol) in THF (10ml) at 0 °C. The resulting mixture was stirred at room temperature overnight, quenched by addition of water (20 ml) and extracted in to dichloromethane (2 x 50 ml). The extracts were combined dried over magnesium sulphate and the solvent removed under reduced pressure to afford **3** as a white solid in 82 % yield (1.31g). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.65 (d, *J* = 4.9 Hz, 1H, Ar-*H*), 7.40-7.50 (m, 5H, Ar-*H*), 7.10-7.20 (m, 5H, Ar-*H*), 7.00 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 6.60 (dd, *J* = 10.9, 17.6 Hz, 1H, =C*H*), 5.75

(dd, *J* = 0.8, 17.6 Hz, 1H, =C*H*H), 5.10 (dd, *J* = 0.8, 10.9 Hz, 1H, =CH*H*); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 500 MHz): 115.3, 126.6, 128.1, 128.4, 128.9, 129.1, 129.5, 134.7, 135.4, 136.0, 136.2, 136.7, 138.7, 150.8, 164.4; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, δ): -4.1 (s); Mass spec: 289.102745 (M^+, calculated for $C_{19}H_{16}NP$ = 289.102038); IR (ν_{max}, cm^{-1}): 3387 (OH), 1613, 1638 (C=C); Anal. Calc for $C_{19}H_{16}NP$: C 78.9, H 5.9, N 4.8% Found: C 79.2, H 5.8, N 4.7%.



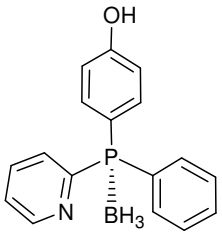
(**6**)

2-Pyridylphenylphosphine (6): A solution of **2-**pyridylphenylchlorophosphine (3.65 g, 16.5 mmol) in *ca*. 25 ml of THF was added dropwise to a suspension of magnesium powder (0.80 g, 32.9 mmol) in THF (50 ml) at 0°C. The reaction mixture was maintained at 0°C for 30 min during which time the solution turned intense red, indicating the presence of the magnesium phosphide. After stirring at room temperature overnight the solution was quenched by addition of degassed water (5 ml), which resulted in the immediate dissipation of the colour. The organic layer was separated dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure to give **6** as a colourless oil (3.35g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.50 (d, *J* = 5.0 Hz, 1H, py-*H*), 7.40-7.50 (m, 3H, Ar-*H*), 7.20-7.30 (m, 4H, Ar-*H*), 7.00-7.05 (m, 1H, Ar-*H*), 5.35 (d, J_{P-H} = 224 Hz, 1H, P-*H*); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ): 122, 127, 128, 129, 131, 135, 136, 149, 162; ^{31}P NMR (121.5 MHz, $CDCl_3$, δ, ^{1}H coupled): -37.8 (d, J_{P-H} = 225.1Hz); Mass spec: 187.054264 (M^+ -H, calculated for $C_{11}H_{10}PN$ = 187.055088); Anal. calculated for $C_{11}H_{10}NP$: C, 70.5; H, 5.4; N, 7.5% Found: C, 70.1; H, 5.3; N, 7.1%.



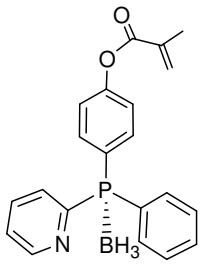
(**7**)

4-Hydroxyphenyl-2-pyridylphenylphosphine (7):[5] A DMA solution of **6** (0.57 g, 3.03 mmol) was transferred via cannula into a solution of 4-iodophenol (0.67 g, 3.05 mmol), palladium acetate (0.007 g, 0.03 mmol) and potassium acetate (0.5 g, 3.64 mmol) in DMA (3 ml) and the reaction heated at 130°C for 4h, then cooled to room temperature and stirred overnight. The resulting mixture was then diluted with dichloromethane (50 ml), washed with water (3 x 50ml) to remove excess DMA. The organic layer was dried over magnesium sulphate, filtered and the solvent removed to afford an off-white solid which was crystallised from dichloromethane to give **7** as white crystals in 69% yield (0.59 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 9.10 (br s, 1H, O*H*), 8.50 (d, 1H, *J* = 4.2 Hz, Ar-*H*), 7.50 (m, 1H, Ar-*H*), 7.20 (m, 6H, Ar-*H*), 7.15 (m, 1H, Ar-*H*), 7.00 (m, 3H, Ar-*H*), 6.40 (d, *J* = 7.8 Hz, 2H, Ar-*H*); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, δ): 114.1 (*C*HCOH), 119.8, 125.2, 126.3, 131.7, 133.4, 134.1, 135.0, 147.6, 156.2 (*C*OH), 163.2; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, δ): -6.5 (s); Mass spec: 279.080589 (M^+, calculated for $C_{17}H_{14}NOP$ = 279.081303) IR (ν_{max}) 3450 (OH); Anal. calculated for $C_{17}H_{14}NOP$: C, 73.1; H, 5.1; N, 5.0% Found: C, 72.8; H, 5.2; N, 5.0%.



(**8**)

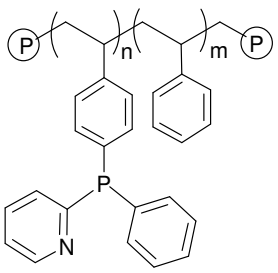
4-Hydroxyphenyl-2-pyridylphenylphosphine borane complex (8):[6] A THF solution of BH_3 (1.0 M in THF, 3.5 ml) was added dropwise to a solution of 4-hydroxy-phenyl-2-pyridylphenylphosphine (0.91 g, 3.26 mmol) in THF (10 mL) at 0°C over a period of *ca*. 30 min. The resultant solution was allowed to stir for 4h at room temperature after which time the solvent was removed and the crude product purified by column chromatography (SiO_2, 95:5 CH_2Cl_2:MeOH) to give **8** as a flocculent white solid in 95% yield (0.91 g). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.70 (d, *J* = 4.8 Hz, 1H, py-*H*), 8.00-8.05 (m, 1H, Ar-*H*), 7.70-7.75 (m, 1H, Ar-*H*), 7.60-7.65 (m, 2H, Ar-*H*), 7.20-7.40 (m, 7H, Ar-*H*), 6.50 (dd, 2.0, 8.7 Hz, 2H, Ar-*H*), 0.80-1.80 (br s, 3H, B*H*$_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 114.1 (*C*HCOH), 125.4, 128.7, 129.8, 130.1, 130.5, 132.0, 134.9, 136.3, 137.4, 153.1 (*C*OH), 159.4; ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ): 19.8 (br s;) Mass spec: 279.080620 (M^+ -BH_3, calculated for $C_{17}H_{14}NOP$ = 279.081303) IR (ν_{max}) 3450 (OH), 2380 (BH_3); Anal. calculated for $C_{17}H_{17}BNOP$: C, 69.7; H, 5.9; N, 4.8%. Found: C, 69.4; H, 5.6; N, 4.5%.



(**9**)

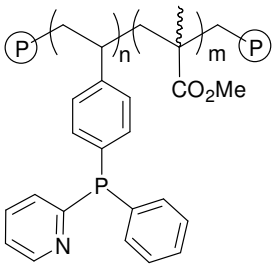
4-(Phenylmethacrylate)-2-pyridylphenylphosphine borane complex (9): 4-Hydroxyphenyl-2-pyridylphenylphosphine borane complex (**8**) (0.71 g, 2.43 mmol) and *t*-butyl catechol (10 mg) were dissolved in CH_2Cl_2 (10 ml), NEt_3 (0.36 ml, 2.55 mmol) and DMAP (3.0 mg, 25 μmol) were added and the solution cooled -78°C. Freshly distilled methacryloyl chloride (0.26 ml, 2.67 mmol) was added drop-wise and the mixture was stirred at -78°C for 2h, at 0°C for an additional 2h and then finally at room temperature overnight. The resulting solution was washed with water (2 x 25 ml), dried over magnesium sulphate, filtered and the solvent removed to afford **9** as a thick viscous oil (0.78 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.70 (d, *J* = 4.7 Hz, 1H, py-*H*), 8.00 (t, *J* = 6.6 Hz, 1H, Ar-*H*), 7.60-7.75 (m, 5H, Ar-*H*), 7.20-7.40 (m, 4H, Ar-*H*), 7.10 (dd, *J* = 1.9, 8.6 Hz, 2H, Ar-*H*), 6.20 (d, *J* = 1.5 Hz, 1H, =C*H*H), 5.70 (d, *J* = 1.5 Hz, 1H, =CH*H*), 1.95 (s, 3H, =CHC*H*$_3$), 0.70-1.80 (br s, 3H, B*H*$_3$); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, δ): 18.2 (=C*C*H$_3$), 122.0, 124.1, 125.6 (=*C*H$_2$), 127.5, 128.7, 129.1, 130.8, 131.6, 133.4, 134.1 (=*C*CH$_3$), 135.6, 150.2, 153.5 (*C*-O-C=O), 154.7, 165.3 (*C*=O); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ): 18.5 (br s); Mass spec: 347.106277 (M^+ -BH_3, calculated for $C_{20}H_{18}NO_2P$ = 347.107517); IR (ν_{max}) 3450 (OH), 3057 (=CH_2), 2380 (BH_3), 1737 (C=O), 1692 & 1637 (C=C); Anal. calculated for $C_{20}H_{21}BNO_2P$: C, 69.8; H, 5.9; N, 3.9% Found: C, 69.4; H, 5.8; N, 5.6%.

Polymerisation Procedures[7]



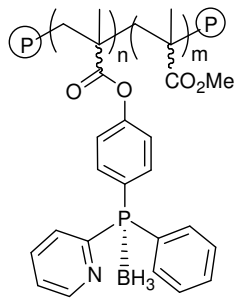
(**4**)

Polystyrene homopolymer 4: A solution of 2-pyridyl-4-vinylphenylphenylphosphine (**3**) (1.3 g, 4.5 mmol) and styrene (2.1 ml, 18.1 mmol) in benzne (10 mL) was treated with AIBN (2 mol%, 0.074 g, 0.45 mmol) and heated at 60°C overnight, after which time a further portion of AIBN (1 mol%, 0.037 g, 0.23 mmol) was added and heating continued for a further 2h. The polymer was precipitated by dropwise addition in to methanol (50 ml). The resulting white solid was filtered, washed with methanol (2 x 50 ml) and dried *in vacuo* to afford **4** as a fine white powder in 89% yield (2.85 g). GPC (average over 2 runs): M_w = 15,750 M_n = 7,375, PDI = 2.1; Anal. Found: C, 68.9; H, 7.4; N, 1.6% (approx. ^{31}P monomer content 15.1 mol%, 1.14 mmol per gram); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ): -5.0 (s).



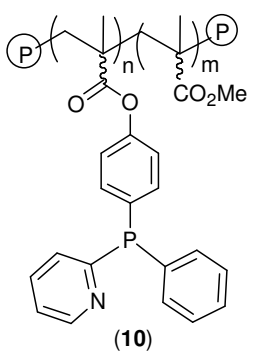
(**5**)

Polymethacrylate-styrene copolymer 5: A solution of 2-pyridyl-4-vinylphenylphenylphosphine (**3**) (1.5 g, 5.2 mmol) and methyl methacrylate (2.2 ml, 21.0 mmol) in benzene (10 mL) was treated with AIBN (2 mol%, 0.085 g, 0.52 mmol) and heated at 60°C overnight, after which time a further portion of AIBN (1 mol%, 0.043 g, 0.26 mmol) was added and heating continued for a further 2h. The polymer was precipitated by dropwise addition of the reaction mixture into methanol and the resulting solid filtered, washed with methanol and dried *in vacuo* to afford **5** in 83% yield (2.95 g). GPC (average over 2 runs): M_w = 6,645 M_n = 3,405, PDI = 2.0; Anal. Found: C 84.5%, H 6.7%, N 2.0% (approx. ^{31}P monomer content 19.6 mol%, 1.43 mmol per gram); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ): -5.0 (s).



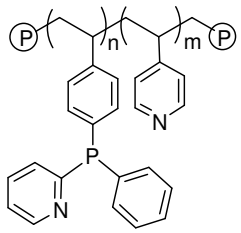
(**9**)

Borane protected polymethacrylate homopolymer 9: A solution of 4-(phenylmethacrylate)-2-pyridylphenyl-phosphine borane complex **9** (0.73 g, 2.0 mmol) and methyl methacrylate (0.85 ml, 8.0 mmol) in C_6H_6 (5 ml) treated with AIBN (2 mol%, 0.017 g, 0.1 mmol) and heated at 60°C overnight after which time a second portion of AIBN (1mol%, 0.008 g, 0.05 mmol) was added and the heating continued for a further 2h. The polymer was precipitated by dropwise addition to methanol (35 ml), filtered, washed with methanol (2 x 50ml) and dried *in vacuo* overnight to afford **9** as a white powder (1.2 g, 78%). Anal. Found: C, 66.0; H, 7.0; N, 1.8% (approx. ^{31}P monomer content 19.4 mol%, 1.29 mmol per gram); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ): 18.6 (br s).



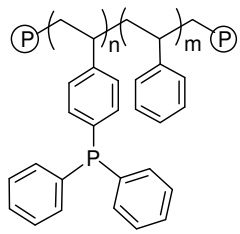
(**10**)

Deprotection Borane protected polymethacrylate homopolymer 9:[8] A dichloromethane solution of **9** (1.20 g, ~2.0 mmol ^{31}P monomer) was treated dropwise with DABCO (0.34 g, 3 mmol) and the resulting mixture stirred at room temperature overnight. The solvent was removed under reduced pressure to give a white solid that was washed with methanol (5 x 50 ml) and dried *in vacuo* overnight to afford **10** (1.1 g, 97%). GPC (averaged over 2 runs): M_w = 4,705 M_n = 1,185, PDI = 3.95; Anal. Found: C, 63.8; H, 6.7; N, 2.0% (approx. ^{31}P monomer content 22.1 mol%, 1.43 mmol per gram); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ): -4.3 (s).



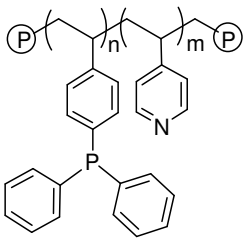
(**11**)

Poly(pyridine-styrene) copolymer 11: A solution of **3** (0.61 g, 2.1 mmol) and 4-vinylpyridine (0.9 ml, 8.45 mmol) in benzene (5 ml) was treated with AIBN (5 mol%, 0.09 g, 0.55 mmol) and heated at 60^{o}C overnight after which time a second portion of AIBN (1 mol%, 0.017 g, 0.1 mmol) was added and heating continued for a further 2h. The solvent was removed under reduced pressure, the resulting solid triturated, washed with methanol (2 x10 ml) dried *in vacuo* to afford **11** as a light brown powder in 72% yield (0.99g). GPC (averaged over 2 runs): M_w = 2,370 M_n = 900, PDI = 2.1; Anal. Found: C, 72.0; H, 6.3; N, 9.0% (Approx. ^{31}P monomer content 27.4 mol%, 1.76 mmol per gram); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, δ): -4.3 (s).



(**12**)

Polystyrene homopolymer 12: A solution of 4-vinylphenyldiphenylphosphine (4.54 g, 15.7 mmol) and styrene (7.2 ml, 62.7 mmol) in tetrahydrofuran (10 ml) was treated with AIBN (2 mol%, 0.26 g, 1.6 mmol) and heated at 60^{o}C overnight after which time a second portion of AIBN (1 mol%, 0.13 g, 0.8 mmol) was added and heating continued for a further 2h. The polymer was precipitated by dropwise addition to methanol (50 ml) and the resulting white solid filtered, washed with methanol (2, x 50 ml) and dried *in vacuo* to afford **12** as a white powder (8.8 g, 77%). GPC (average of 2 runs): M_w = 29.700, M_n = 9305, PDI = 3.15; Anal Found: C, 87.0; H, 7.0%. (approx ^{31}P monomer content 34.0 mol%, 2.04 mmol per gram); ^{31}P NMR (121.5 MHz, $CDCl_3$, δ): -5.0 (s).



(**13**)

Poly(pyridine-styrene) supported PPh_3 (13): A solution of 4-vinylphenyldiphenylphosphine (0.50 g, 1.7 mmol) and 4-vinylpyridine (0.75 ml, 6.9 mmol) in benzene (10 ml) was treated with AIBN (5 mol%, 0.07 g, 0.4 mmol) and heated at 60°C overnight after which time a second portion of AIBN (1 mol%, 0.014 g, 0.08 mmol) was added and heating continued for a further 2h. The solvent was removed under reduced pressure and the resulting solid triturated, washed with methanol (2 x 10 ml) and dried *in vacuo* to afford **13** as a buff coloured powder in 77% yield (0.10 g). GPC (average over 2 runs): M_w = 2,610 M_n = 1,360, PDI = 1.9; Anal. Found: C, 79.3; H, 6.7; N, 9.2% (approx. ^{31}P monomer content 14.0 mol%, 1.07 mmol per gram); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, δ): -5.2 (s).

General procedure for palladium loading of polymers

Polystyrene homopolymer 4. A solution of palladium acetate (10 mol% based on ligand content, 0.015 g, 0.067 mmol) in dichloromethane (3-4 ml) was cannula transferred dropwise into a solution of **4** (0.59 g, 0.67 mmol of supported ligand) in dichloromethane (*ca.* 10 ml). The resulting mixture was stirred overnight, the solvent removed under reduced pressure, the resulting solid washed with methanol and dried to afford the palladium loaded polymer as a buff brown powder (0.57 g, 99%).

Polymers, **5**, **10**, **11**, **12**, and **13** were loaded with palladium acetate according to the procedure describe above for **4** and isolated a pale brown powders.

General Procedures for Catalysis

Homogeneous methoxycarbonylation of phenylacetylene: In a typical procedure, a 300 mL stainless steel bench top reactor was charged with the catalyst components, palladium acetate (2.2 mg, 0.01 mmol), 2-pyridyldiphenylphosphine (0.0262 g, 0.1 mmol), $MeSO_3H$ (19 µl, 0.3 mmol), phenylacetylene (1.09 ml, 10 mmol) and MeOH (30 ml). The reactor was flushed with argon, pressurised with carbon monoxide (40 bar) and heated at 50 ºC while maintaining a pressure of *ca*. 40 bar by the continuous feeding of CO from a gas reservoir. After stirring at 400 rpm for 1hr the reactor was allowed to cool to room temperature, vented and the resulting solution filtered though a pad of Celite. An aliquot of the reaction solution was removed and analyzed by GC, using cumene as an internal standard, from which the selectivity and averaged catalyst activity were determined. The remaining solvent was removed under reduced pressure to leave an oily residue which was purified by column chromatography (SiO_2, 4:1 hexane:ethyl acetate) to afford pure samples of methyl 2-phenylpropenoate (major) and (*E*)-methyl 3-phenylpropenoate (minor). Methyl 2-phenylpropenoate: ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.30-7-35 (m, 2H, Ar-H), 7.25-7.30 (m, 3H, Ar-H), 6.30 (d, *J* = 1.2 Hz, 1H, =CHH), 5.85 (d, *J* = 1.2 Hz, 1H, =CHH), 3.75 (s, 3H, OCH_3). (*E*)-methyl 3-phenylpropenoate: ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.60 (d, *J* = 15.9 Hz, 1H, =C*H*H), 7.45-7.50 (m, 2H, Ar-*H*), 7.30-7.35 (m, 3H, Ar-*H*), 6.35 (d, *J* = 16.0 Hz, 1H, =CH*H*), 3.75 (s, 3H, OCH_3).

Hetereogeneous methoxycarbonylation of phenylacetylene: In a typical procedure, a 300 mL stainless steel bench top reactor was charged with palladium loaded polymer (0.01 mmol based on palladium acetate), $MeSO_3H$ (19 µl, 0.3 mmol), phenylacetylene (1.09 ml, 10 mmol) and MeOH (30 ml). The reactor was flushed with argon and pressurised with carbon monoxide (40 bar) and heated at 50 ºC while maintaining a pressure of *ca*. 40 bar by the continuous feeding of CO from a gas reservoir. After stirring for 1 hr the reactor was allowed to cool to room temperature, vented and the resulting solution filtered though a pad of Celite. An aliquot of the reaction solution was removed and analyzed by GC (cumene internal standard) to determine selectivity and average catalyst activity. The remaining solvent was removed under reduced pressure to leave an oily residue which was purified by column chromatography (SiO_2, 4:1 hexane:ethyl acetate).

General procedure for homogeneous methoxycarbonylation of propyne: In a typical procedure, a 300 mL stainless steel bench top reactor was charged with the catalyst components, palladium acetate (2.2 mg, 0.01 mmol), 2-pyridyldiphenylphosphine (0.0262 g, 0.1 mmol), $MeSO_3H$ (19 µl, 0.3 mmol) and MeOH (30 ml). The reactor was evacuated, pressurised with 2 bar of propyne followed by 40 bar of CO and heated at 50 ºC while maintaining a pressure of *ca*. 40 bar by the continuous feeding of a CO-propyne mixture from a gas reservoir. After stirring at 400 rpm for 1 hr, the reactor was allowed to cool to room temperature and the reaction quenched by releasing the CO/propyne pressure. An aliquot of the solution was removed and analysed by GC using ±2-hexanol as internal standard and the

remaining solution was filtered though a pad of Celite, the solvent removed under reduced pressure and the resulting oily residue purified by column chromatography (SiO_2, 4:1 hexane:ethyl acetate). Methyl methacrylate: ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.15 (d, *J* = 1.4 Hz, 1H, =C*H*H), 5.60 (d, *J* = 1.4 Hz, 1H, =CH*H*), 3.75 (s, 3H, OCH_3), 1.95 (s, 3H, =CCH_3). Methyl crotonate: ^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.90 (d, *J* = 14.1Hz, 1H, =C*H*H), 5.85 (d, *J* = 14.1Hz, 1H, =CH*H*), 3.75 (s, 3H, OCH_3), 1.70 (s, 3H, =CCH_3).

General procedure for heterogeneous methoxycarbonylation of propyne: Typically, a 300 mL stainless steel bench top reactor was charged with palladium loaded polymer (0.01 mmol based on palladium), $MeSO_3H$ (19 µl, 0.3 mmol) and MeOH (30 ml). The reactor was evacuated, pressurised with 2 bar of propyne followed by 40 bar of CO and heated at 50 ºC while maintaining a pressure of *ca*. 40 bar by the continuous feeding of a CO-propyne mixture from a gas reservoir. After stirring at 400 rpm for 1 hr, the reactor was allowed to cool to room temperature and the reaction quenched by releasing the CO/propyne pressure. An aliquot of the solution was removed and analysed by GC using ±2-hexanol as internal standard and the remaining solution was filtered though a pad of Celite, the solvent removed under reduced pressure and the resulting oily residue purified by column chromatography (SiO_2, 4:1 hexane:ethyl acetate).

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