Dendritic effects in catalysis by Pd complexes of bidentate phosphines on a dendronized support: Heck vs. carbonylation reactions

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Supporting Information

General

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring. Solvents were dried prior to use. Dry NMP was purchased from Sigma-Aldrich. Reagents were obtained from Sigma-Aldrich, Fluka, Strem Chemicals or Merck at the highest available purity and used as received. $Pd(dba)_2$ was prepared according to known procedure.[1] All resins used are 1% crosslinked divinylbenzene-styrene copolymer, 100-200 mesh, with loading 0.77-1.30 mmol/g and were purchased from Novabiochem. HPLC grade acetonitrile and water were purchased from Bio-Lab and Merck respectively and used after filtration. HPLC experiments were carried out using an Inertsil ODS-3v column on a Jasco chromatograph equipped with a UV/Vis detector with acetonitrile and water as the eluting solvents.
^{1}H NMR (200, 400 MHz), ^{13}C NMR (100.8 MHz) and ^{31}P NMR (162.6 MHz) spectra were recorded on Bruker AVANCE-200 and AVANCE-400 spectrometers, in $CDCl_3$ or $CDCl_3$/TFA (1:1) using residual $CHCl_3$ (^{1}H, 7.26 ppm), or $CDCl_3$ (^{13}C, 77.0 ppm) as an internal standard. Gel-phase ^{13}C NMR (100.8 MHz) and ^{31}P NMR (162.6 MHz) spectra were recorded in benzene-d_6, on a Bruker AVANCE-400 instrument using the solvent (^{13}C, 126.0 ppm) as an internal standard or H_3PO_4, 85% (^{31}P, 0.0 ppm) as an external standard. The yields of the polymer-bound ligands and complexes were determined using gel-phase ^{31}P NMR with an internal phosphorus-containing resin standard.[2]

Characterization of Gn(CO_2Me) resins

G1(CO_2Me)
Prepared from Wang Bromo PS (0.76 mmol/g).
Yield >99%, purity >99%, loading 0.69 mmol/g.
Gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 165.8, 159.3, 158.0, 132.4, 129.5, 123.3, 120.4, 115.0, 70.0, 51.9. Following TFA-induced cleavage: ^{1}H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 8.35 (t, *J* = 1.3 Hz, 1H), 7.86 (d, *J* = 1.3 Hz, 2H), 4.06 (s, 6H). ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 168.4, 154.8, 130.9, 123.8, 121.5, 53.1.

G2(CO_2Me)
Prepared from **G1(Cl)** (0.50 mmol/g).
Yield >99%, purity >95%, loading 0.42 mmol/g.
Partial Gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 165.7, 158.9, 138.0, 132.3, 123.4, 120.2, 114.1, 69.8, 51.9.
Following TFA-induced cleavage: ^{1}H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 8.35 (s, 2H), 7.93 (s, 4H), 7.20 (s, 1H), 7.05 (s, 2H), 5.20 (s, 4H), 4.06 (s, 12H). ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 168.6, 158.4, 157.0, 138.1, 130.7, 123.6, 121.0, 119.5, 114.0, 69.6, 53.1.

G3(CO_2Me)
Prepared from **G2(Cl)** (0.30 mmol/g).
Yield >99%, purity >95%, loading 0.26 mmol/g.
Partial gel-phase ^{13}C NMR (100.8 MHz, C_6D_6): δ 165.5, 158.9, 138.5, 132.2, 123.2, 120.0, 113.6, 69.7, 51.9.
Following TFA-induced cleavage: ^{1}H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 8.33 (s, 4H), 7.91 (s, 8H), 6.98-7.21 (m, 9H), 5.16 (s, 12H), 4.04 (s, 24H). ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 168.5, 158.5, 158.4, 138.5, 137.8, 130.7, 123.6, 120.9, 119.7, 119.4, 114.0, 113.8, 69.9, 69.7, 53.1.

Characterization of Gn(serinol-OH) resins

G1(serinol-OH)
Prepared from **G1(Cl)** (0.50 mmol/g).
Yield >99%, purity >99%, loading 0.47 mmol/g.
Following TFA-induced cleavage: ^{1}H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 7.19 (m, 3H), 4.73 (m, 2H), 4.43 (s, 4H), 4.29-4.04 (m, 8H). ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 156.7, 132.2, 131.8, 119.1, 62.9, 58.1, 55.8.

G2(serinol-OH)
Prepared from **G2(Cl)** (0.30 mmol/g).
Yield 90%, purity >95%, loading 0.25 mmol/g.
Following TFA-induced cleavage: ^{1}H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 7.56 (br, NH), 7.21-6.62 (m, 9H),

4.92 (m, 4H), 4.74 (m, 4H), 4.45 (m, 8H), 4.11 (m, 16H-xH), 3.70 (m, xH) . Partial ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 132.0, 117.9, 114.2, 112.3, 69.5, 62.9, 58.0, 55.6.

G3(serinol-OH)
Prepared from **G3(Cl)** (0.26 mmol/g).
Yield >99%, purity >95%, loading 0.23 mmol/g.
Following TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 7.6 (br, NH), 7.24-7.07 (m, 21H), 5.08 (m, 8H), 4.78 (m, 8H), 4.50 (m, 16H), 4.20-3.96 (m, 32H). Partial ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 132.0, 117.9, 69.6, 63.3, 58.0, 55.7.

Characterization of Gn(serinol-Cl) resins

G1(serinol-Cl)
Prepared from **G1(serinol-OH)** (0.47 mmol/g).
Yield >99 %, purity >99%, loading 0.44 mmol/g.
Following TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 8.04 (br, NH), 7.25 (m, 3H), 4.50 (s, 4H), 4.03 (s, 10H). ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 156.5, 131.5, 124.3, 119.2, 59.9, 50.1, 39.3. MS: found (m/z), 373.1; calcd for $C_{14}H_{22}{}^{35}Cl_4N_2O$ (MH^+) 373.1.

G2(serinol-Cl)
Prepared from **G2(serinol-OH)** (0.25 mmol/g).
Yield >99 %, purity >95%, loading 0.23 mmol/g.
Following TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 8.09 (br, NH), 7.20-6.70 (m, 9H), 5.20 (m, 4H), 4.46 (m, 8H), 4.01 (m, 20H). ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 159.8, 138.1, 134.0, 124.4, 119.3, 118.7, 114.3, 69.8, 60.0, 52.9, 39.6.

G3(serinol-Cl)
Prepared from **G3(serinol-OH)** (0.23 mmol/g).
Yield 53 %, purity >95%, loading 0.11 mmol/g.
Following TFA-induced cleavage: ^1H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 8.12 (br, NH), 7.13-6.99 (m, 21H), 5.09 (m, 12H), 4.50 (m, 16H), 4.01 (m, 40H). Partial ^{13}C NMR (100.8 MHz, $CDCl_3$/TFA 1:1): δ 159.9, 132.3, 132.1, 131.5, 129.3, 129.1, 69.9, 59.8, 50.3, 39.5.

References

1. L. S. Hegedus in *Organometallics in synthesis*, ed. M. Schlosser, Wiley, 1994.
2. B. Ben-Aroya Bar-Nir and M. Portnoy, *Tetrahedron*, 2002, **58**, 5147.