Supplementary Information

Diazaphospholidine terminated Polyhedral Oligomeric Silsesquioxanes in the hydroformylation of vinyl acetate

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General

All experiments were carried out in oven-dried glassware using standard Schlenk techniques under an atmosphere of nitrogen. Nitrogen was dried through a Cr(II)/silica packed glass column.

All chemicals were purchased from Sigma-Aldrich, Acros Organics or ABCR and used as received unless otherwise stated. All gases were purchased from BOC. Toluene and THF were purified using a solvent purification system from Innovative Technologies, UK. They were dried by passing through an activated alumina column and degassed in a second column containing copper catalyst, except in the case of THF where the second column also contained activated alumina. THF was degassed by repeated freeze-pump-thaw cycles. Dichloromethane was distilled over CaH_2 under nitrogen. Hexane was distilled over sodium under inert atmosphere. Water was distilled and stored under nitrogen.

Optical rotations were measured on a PERKIN ELMER (MODEL 341) polarimeter at $\lambda = 589$ nm.

Proton, carbon and phosphorus NMR spectra were recorded on a Bruker AM 300 NMR spectrometer (^{1}H, 300.13 MHz; ^{13}C, 75.5 MHz; ^{31}P, 121.5 MHz) or Bruker Advance II 400 NMR spectrometer (^{1}H, 400.13 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz, ^{29}Si, 79.5 MHz).

Chemical analysis was performed by the University of St-Andrews Microanalysis service on a Carl Erba model 1106 analyser.

Procedure for vinylacetate hydroformylation

A Hastelloy^{TM} autoclave of internal capacity 225 cm^3 was used for vinylacetate The reactor was purged three times with CO/H_2 (1/1); subsequently, the catalytic solution containing $[Rh(acac)(CO)_2]$ (5.4 mg, 2.4×10^{-5} mol), toluene (4 cm^3), vinyl acetate (1 cm^3) and the ESPHOS functionalised dendrimer was added *via* cannula. The autoclave was then pressurised with syngas at 40 bar and heated at 80 °C for 20 hours. At the end of the reaction, the autoclave was rapidly cooled and the unreacted gases were vented. The liquid products were analyzed by GC with a flame ionization detector (quantitative) and GC-MS (qualitative). Both analysis methods employed a Supelco^{TM} beta-DEX^{TM} [nonbonded phase with 25 % 2,3-di-O-acetyl-6-O-TBDMS-β-cyclodextrin in SPB-20 poly(20 % phenyl / 80 % dimethylsiloxane)] fused silica capillary column (60 m (2 x 30 m) x 0.25 mm x 0.25 μm). The enantioselectivity of the reaction was determined by comparison with authentic product samples.

G1-8SemiEsphos

n-butyllithium (2.10 cm^{-3}, 2.5 mol dm^{-3} in hexane, 5.25 mmol) was added dropwise to a stirred solution of 3-(bis(dimethylaminophosphine))bromobenzene [1] (1.44 g, 5.25 mmol) in diethylether (30 cm^{-3}) cooled at -78 °C. The reaction mixture was warmed gradually to -20 °C and maintained for 30 minutes at this temperature before being cooled to -78 °C. This solution was then slowly transferred via canula to a Schlenk flask containing **G1-8Cl** [2] (810 mg, 0.58 mmol) in THF (30 cm^{-3}) and allowed to warm to room temperature overnight with constant stirring. A saturated solution of $NaHCO_3$ was subsequently added to quench the reaction, followed by CH_2Cl_2 (10 cm^{-3}). The aqueous layer was extracted twice with CH_2Cl_2 (2 x 10 cm^{-3}) and the combined organic fractions washed with brine (20 cm^{-3}), before being dried over $MgSO_4$. After filtration, the solvent was evaporated and the resulting yellow oil was used without any further purification in the next step. An oven-dried flask equipped with a condenser and a magnetic stirring bar was charged under nitrogen with the residue (1.29 g, 0.48 mmol) and (S)-2-(Phenylaminomethyl)pyrrolidine [3] (923 mg, 5.25 mmol) in toluene (40 cm^{-3}). The solution was refluxed for 5 days until no more release of $HNMe_2$ was detected as indicated by damp litmus paper. The solvent was then removed leading to a waxy solid, which was purified by precipitation in hexane (60 cm^{-3}) after dissolution in toluene (3 cm^{-3}). This procedure was repeated twice affording the desired compound as a white powder (1.23 g, 63 %); $[\alpha]_D$ = -0.5 (c = 1.0, $CHCl_3$); (Found: C, 59.7; H, 7.3; N, 6.9. $Si_{16}O_{12}N_{16}P_8C_{168}H_{224}$ requires C, 60.1; H, 6.7; N, 6.7%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 0.16 (48 H, br, $Si(C\mathit{H}_3)_2$), 0.51 (16 H, m, $O_3SiCH_2C\mathit{H}_2Si$), 0.73 (16 H, m, $O_3SiC\mathit{H}_2CH_2Si$) 1.69-2.06 (32 H, m, -$C\mathit{H}_2$-), 2.95-3.03 (8 H, m, -$C\mathit{H}_2$-), 3.27 (16 H, m, -$C\mathit{H}_2$-), 3.41 (8 H, m, -$C\mathit{H}_2$-), 3.97 (8 H, m, NC*H*), 6.73 (8 H, m, Ar*H*), 6.85 (16 H, m, Ar*H*), 7.07-7.20 (32 H, m, Ar*H*), 7.33 (8 H, m, Ar*H*) and 7.56 (8 H, m, Ar*H*); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) -2.1 ($Si(\mathit{C}H_3)_2$), 4.9 ($O_3SiCH_2\mathit{C}H_2Si$), 7.5 ($O_3Si\mathit{C}H_2CH_2Si$), 26.3 (d, J_{CP} 6.3, -$\mathit{C}H_2$-), 31.3 (-$\mathit{C}H_2$-), 53.1 (-$\mathit{C}H_2$-), 53.5 (d, J_{CP} 4.7, -$\mathit{C}H_2$-), 64.8 (d, J_{CP} 8.5, N*C*H), 115.6 (d, J_{CP} 13.4), 118.3, 127.9, 129.5, 129.6, 129.7, 134.4, 139.0 (*ipso* Si*C*), 141.9 (d, J_{CP} 26.3, *ipso* P*C*) and 147.9 (d, J_{CP} 15.3, *ipso* N*C*); δ_P(162.0 MHz; $CDCl_3$) 100.6; δ_{Si}(79.5 MHz; $CDCl_3$; Me_4Si) -66.9 ($\mathit{Si}O_3$) and -1.3 ($\mathit{Si}(CH_3)_2$).

G1-16SemiEsphos

Was similarly prepared from n-butyllithium (1.53 cm^{-3}, 2.5 mol dm^{-3} in hexane, 3.82 mmol), 3-(bis(dimethylaminophosphine))bromobenzene [1] (1.05 g, 3.82 mmol) and **G1-16Cl** [2] (330 mg, 0.21 mmol) in THF (20 cm^{-3}), followed by the use of the product of this reaction (737 mg, 0.18 mmol) and (S)-2-(Phenylaminomethyl)pyrrolidine [3] (673 mg, 3.82 mmol) in toluene (30 cm^{-3}). The waxy solid, was purified by precipitation in hexane (60 cm^{-3}) after dissolution in toluene (2 cm^{-3}). This procedure was repeated twice affording the desired compound as a white powder (834 mg, 72 %); $[\alpha]_D$ = -0.8 (c = 1.0, $CHCl_3$); (Found: C, 64.9; H, 6.2; N, 8.2. $Si_{16}O_{12}N_{32}P_{16}C_{296}H_{344}$ requires C, 64.8; H, 6.3; N, 8.2%); δ_H(300.13 MHz; $CDCl_3$; Me_4Si) 0.08 (24 H, m, $SiC\mathit{H}_3$), β hydrosilylation (<25 %, m, 0.21-0.60), 0.62-0.74 (16 H, m, $O_3SiCH_2CH_2Si$), 1.01-1.16 (16 H, m, $O_3SiCH_2CH_2Si$), 1.46-2.06 (64 H, m, -$C\mathit{H}_2$-), 2.84-3.04 (16 H, m, -$C\mathit{H}_2$-), 3.11-3.41 (48 H, m, -$C\mathit{H}_2$-), 3.74-3.98 (16 H, m, NC*H*), 6.61-6.86 (48 H, m, Ar*H*), 7.00-7.21 (64 H, m, Ar*H*) and 7.31-7.66 (32 H, m, Ar*H*); δ_C(75.5 MHz; $CDCl_3$; Me_4Si) -5.2 ($Si\mathit{C}H_3$), 4.6 ($O_3SiCH_2CH_2Si$), 5.5 ($O_3SiCH_2CH_2Si$), 25.8 (d, J_{CP} 5.3, -$\mathit{C}H_2$-), 31.4 (-$\mathit{C}H_2$), 52.6 (-$\mathit{C}H_2$-), 52.9 (d, J_{CP} 4.7, -$\mathit{C}H_2$-), 64.2 (d, J_{CP} 8.7, N*C*H), 115.1 (d, J_{CP} 13.5), 117.8, 127.7, 129.2, 129.3, 129.9, 135.1, 139.3 (*ipso* Si*C*), 141.1 (d, J_{CP} 26.6, *ipso* P*C*) and 146.8 (d, J_{CP} 15.3, *ipso* N*C*); δ_P(162.0 MHz; $CDCl_3$) 100.1; δ_{Si}(79.5 MHz; $CDCl_3$; Me_4Si) -66.1 ($\mathit{Si}O_3$) and -6.3 ($\mathit{Si}CH_3$).

G1-24SemiEsphos

Was similarly prepared from n-butyllithium (3.10 cm^{-3}, 2.5 mol dm^{-3} in hexane, 7.75 mmol), 3-(bis(dimethylaminophosphine))bromobenzene [1] (2.13 g, 7.75 mmol) in diethylether (35 cm^{-3}) and **G1-24Cl** [2] (493 mg, 0. 29 mmol) in THF (20 cm^{-3}) with the product of this reaction (1.26 g, 0.23 mmol) being reacted with (S)-2-(Phenylaminomethyl)pyrrolidine [3] (1.36 g, 7.75 mmol) in toluene (40 cm^{-3}). The waxy solid, which was purified by precipitation in hexane (60 cm^{-3}) after dissolution in toluene (10 cm^{-3}). This procedure was repeated twice affording the desired compound as a white powder (1.32 g, 60%);$[\alpha]_D$ = -1.0 (c = 1.01, CHCl$_3$); (Found: C, 66.6; H, 6.7; N, 8.3. $Si_{16}O_{12}N_{48}P_{24}C_{424}H_{464}$ requires C, 66.9; H, 6.1; N, 8.8%); δ_H(300.13 MHz; CDCl$_3$; Me$_4$Si) 0.62 (16 H, m, O$_3$SiCH$_2$CH$_2$Si), 1.28 (16 H, m, O$_3$SiCH$_2$CH$_2$Si), 1.46-1.93 (96 H, m, -C*H*$_2$-), 2.74-2.93 (24 H, m, -C*H*$_2$-), 2.98-3.30 (72 H, m, -C*H*$_2$-), 3.68 (24 H, m, NC*H*), 6.51-6.82 (72 H, m, Ar*H*), 6.92-7.21 (96 H, m, Ar*H*) and 7.26-7.75 (48 H, m, Ar*H*); δ_C(75.5 MHz; CDCl$_3$; Me$_4$Si) 4.2 (O$_3$SiCH$_2$CH$_2$Si), 5.1 (O$_3$SiCH$_2$CH$_2$Si), 25.8 (d, J_{CP} 5.3, -*C*H2-), 31.3 (-*C*H2-), 52.5 (-*C*H2-), 52.9 (d, J_{CP} 4.7, -*C*H2-), 64.3 (d, J_{CP} 8.7, N*C*H), 115.0 (d, J_{CP} 13.3), 117.7, 127.7, 129.1, 129.3, 130.2, 134.6, 139.2, 141.1(*ipso* Si*C*) (d, J_{CP} 26.9, *ipso* P*C*) and 146.8 (d, J_{CP} 15.3, *ipso* N*C*); δ_P(162.0 MHz; CDCl$_3$) 99.1; δ_{Si}(79.5 MHz; CDCl$_3$; Me$_4$Si) -66.7 (*Si*O$_3$) and -10.1 (*Si*Ar).

References

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