Supplementary Material

New Linker Systems for Superior Immobilized Catalysts

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Scheme 1. Synthesis of 3 and 4, the immobilized linkers 3i and 4i, and the catalysts 5i and 6i.

Experimental Procedures and Data

All reactions were performed by using standard Schlenk techniques or in a glove-box in an oxygen-free nitrogen atmosphere. The solvents were dried by boiling over Na, distilled and kept under nitrogen. All the immobilization experiments were carried out with Merck silica 40 (specific surface area 750 m²/g; average pore size 40 Å; particle size 0.063-0.2 mm) that was dried at 600 °C in vacuo (10⁻² Pa) for at least two days in order to condense surface silanol groups.
The molecular compounds were characterized by mass spectrometry and NMR spectroscopy. The liquids NMR spectra were recorded on the instruments Bruker AC-300, Varian Inova-300, and Bruker DRX-500. The signal assignments have been obtained by $^1$H, $^1$H COSY, $^{29}$Si,$^1$H COSY, $^{13}$C,$^1$H COSY, and $^{13}$C,$^3$P NMR measurements. All solid-state NMR spectra were recorded on a Bruker DSX-400 spectrometer, equipped with a 4 mm broadband MAS probehead and ZrO₂ rotors. The modified silica was filled loosely into the rotors under nitrogen. The relaxation delays were 10 s for all surface-immobilized compounds. All spectra were recorded at room temperature (298 K). The $^{31}$P MAS NMR spectra were referenced with respect to 85% H₃PO₄ (aq) by setting the $^{31}$P NMR peak of solid NH₄H₂PO₄ to +0.81 ppm. The $^{29}$Si and $^{119}$Sn Hartmann-Hahn and external chemical shift standards were Si(SiMe)₃ and SnPh₄, respectively. The single crystals were obtained by recrystallizing in CHCl₃.

**Si(p-C₆H₄Br)₄ (1):** 1,4-Dibromobenzene (6.58 g, 27.88 mmol) is dissolved in 70 ml of ether and cooled to -15 °C. Then 11.15 ml of a 2.5 m solution of $^n$BuLi (27.88 mmol) in hexane is added dropwise. After stirring for 15 min 0.80 ml (6.97 mmol) of SiCl₄ is added dropwise. After stirring for 15 min, the mixture is allowed to warm to ambient temperature and is stirred for 1 h. After adding 20 ml of 1 m HCl the product is extracted with ether. The organic phase is washed with H₂O and dried with MgSO₄. Si(p-C₆H₄Br)₄ is obtained after filtration, removal of the solvent in vacuo, and recrystallization with CHCl₃ as a colorless crystalline powder in 54.1 % yield (2.46 g, 3.77 mmol). mp 219-220 °C (open capillary). $^1$H NMR (CDCl₃, 500.1 MHz): δ = 7.56 (d, $^3$J(H-H) = 8.0 Hz; SiCCCH), 7.33 (d, $^3$J(H-H) = 8.1 Hz; SiCCCH); $^{13}$C NMR (CDCl₃, 125.8 MHz): δ = 137.61 (SiCCH), 136.36 (SiC), 131.44 (BrCCH), 125.44 (BrC); $^{29}$Si NMR (CDCl₃, 99.4 MHz): δ = -13.76 ppm. HR-MS (FAB⁺): [M]⁺ (21.6 %) 647.7657 (calcld. 647.7755), [M-Br]⁺ (82.4 %) 568.8695 (calcld. 568.8571), [M-C₆H₄Br]⁺ (56.8 %) 492.8249 (calcld. 492.8258).

**Sn(p-C₆H₄Br)₄ (2):** 1,4-Dibromobenzene (5.89 g, 24.97 mmol) is dissolved in 60 ml of ether and cooled to -15 °C. Then 15.6 ml of a 1.6 m solution of $^n$BuLi (24.97 mmol) in hexane is added in a dropwise manner. After stirring for 15 min the reaction mixture is cooled to -78 °C and 0.73 ml (4.12 g, 5.56 mmol) of SnCl₄ is added dropwise. After stirring for 12 h at ambient temperature, 20 ml of 1 m HCl is added and the product is extracted with ether. The organic phase is washed with H₂O and dried with MgSO₄. Sn(p-C₆H₄Br)₄ is obtained after filtration, removal of the solvent in vacuo, and recrystallization with CHCl₃ as a colorless crystalline powder in 89.0 % yield (4.12 g, 5.56 mmol). mp 214 °C (open capillary). $^1$H NMR (CDCl₃, 500.1 MHz): δ = 7.53 (d, $^3$J(H-H) = 8.0 Hz; SiCCCH), 7.33 (d, $^3$J(H-H) = 8.1 Hz; SiCCCH); $^{13}$C NMR (CDCl₃, 125.8 MHz): δ = 137.61 (SiCCCH), 136.36 (SiC), 131.44 (BrCCH), 125.44 (BrC); $^{29}$Si NMR (CDCl₃, 99.4 MHz): δ = -13.76 ppm. HR-MS (FAB⁺): [M]⁺ (21.6 %) 647.7657 (calcld. 647.7755), [M-Br]⁺ (82.4 %) 568.8695 (calcld. 568.8571), [M-C₆H₄Br]⁺ (56.8 %) 492.8249 (calcld. 492.8258).

**Si(p-C₆H₄PPh₂)₄ (3):** 0.260 g (0.40 mmol) of 1 is dissolved in 100 ml of ether and cooled to -78 °C. After adding 2.0 ml of a 1.6 m solution of $^n$BuLi (3.20 mmol) in hexanes in a dropwise manner the mixture is allowed to warm to ambient temperature within 2.5 h. Then the reaction mixture is again cooled to -78 °C and 0.57 ml (3.20 mmol) of ClPPh₂ is added. After warming to room temperature and stirring overnight the formed precipitate is allowed to settle down and the supernatant is decanted. The product is extracted from the solid with three 15 ml aliquots of
toluene and recrystallized from the toluene solution. The silane 3 is obtained in 55 % yield (0.089 g, 0.08 mmol) as a colorless powder. mp 130-132 °C (sealed capillary). 1H NMR (C6D6, 500.1 MHz): δ = 7.45 (dd, 3J(H-H) = 7.9 Hz, 4J(P-H) = 0.9 Hz; SiCCH), 7.42-7.38 (m; PPh2, PCCCH), 7.33 (tr, 3J(H-H) = 7.9 Hz, 3J(P-H) = 7.4 Hz, SiCCHCH); 13C NMR (C6D6, 125.8 MHz): δ = 141.78 (d, 1J(P-C) = 14.3 Hz; SiCCHCH), 137.21 (d, 1J(P-C) = 11.6 Hz; PPh2, PCS), 135.49 (d, 1J(P-C) = 6.1 Hz; SiCCH), 134.37 (d, 2J(P-C) = 20.1 Hz; PPh2, PCCCH), 133.41 (d, 2J(P-C) = 18.6 Hz; SiCCHCH), 129.10 (s; PPh2, PCCCHCHCH), 128.90 (d, 3J(P-C) = 7.1 Hz; PPh2, PCCCHCH) ppm; 31P NMR (C6D6, 202.5 MHz): δ = -5.19 ppm; 31P CP/MAS: δiso = -5.5 ppm (νrot = 4 kHz); 29Si NMR (C6D6, 79.5 MHz): δ = -14.42 ppm, no rotational sidebands (νrot = 5 kHz). HR-MS (FAB+): [M]+ (26.3 %) 1072.3114 (calcd. 1072.3102), [M-C6H5]+ (16.6 %) 995.1943 (calcd. 995.2711), [M - C6H3P]+ (12.0 %) 964.2365 (calcd. 964.2973).

Alternative Synthesis of Si(p-C6H4PPh2)4 (3): 2.38 g (6.97 mmol) Ph2P(p-C6H4Br) (synthesis and data see below) is dissolved in 150 ml of Ether and cooled to -60 °C. Then 2.79 ml of a 2.5 m solution of 6BuLi (6.97 mmol) in hexanes is added in a dropwise manner and the solution is allowed to warm to ambient temperature. After cooling again to -60 °C 0.20 ml (1.74 mmol) of SiCl4 is added. After stirring the reaction mixture overnight at room temperature the solvents are removed in vacuo and the product is extracted with three 30 ml aliquots of toluene. Removal of the solvent yields 1.31 g (1.22 mmol, 70 %) of 3 as a colorless powder.

Ph2P(p-C6H4Br): 10 ml of a 2.5m solution of 6BuLi (25.05 mmol) in hexanes is added dropwise to a solution of 5.91 g (25.07 mmol) of 1,4-dibromobenzene in 100 ml of ether at -50 °C. Then the mixture is allowed to warm up to ambient temperature within 2.5 h. The mixture is again cooled to -50 °C and 4.50 ml of ClPPh2 is cooled to -60 °C. Then 2.79 ml of a 2.5m BuLi (25.05 mmol) in hexanes is added dropwise in a dropwise manner. After warming the mixture to ambient temperature and stirring overnight the solvent is removed in vacuo and the product is extracted with three 15 ml aliquots of toluene. After removal of the solvent the product is obtained in 98 % yield as a colorless powder (8.42 g, 24.68 mmol). mp 79 °C (open capillary). 1H NMR (acetone-d6, 500.1 MHz): δ = 7.58 (d, BrCCCH, 3J(H-H) = 8.2 Hz), 7.41-7.39 (m, PPh2, PCCCH, PCCCHCHCH), 7.31-7.28 (m, PPh2, PCCCH), 7.21 (tr, BrCCCHCH, 3J(H-H) = 8.2 Hz, 3J(P-H) = 8.1 Hz). 13C NMR (acetone-d6, 125.8 MHz): δ = 138.92 (d, BrCCCHCH, 1J(P-C) = 13.6 Hz), 138.49 (d, PPh2, PC, 1J(P-C) = 11.4 Hz), 137.09 (d, BrCCCHCH, 2J(P-C) = 20.2 Hz), 135.39 (d, PPh2, PCCCH, 2J(P-C) = 20.0 Hz), 133.51 (d, BrCCCH, 3J(P-C) = 6.7 Hz), 130.94 (s, PPh2, PCCCHCHCH), 130.59 (d, PPh2, PCCCHCH, 3J(P-C) = 7.0 Hz), 124.79 (s, BrC). 31P NMR (202.5 MHz, acetone-d6): δ = -5.66 (s). HR-MS (FAB+): [M]+ (98.1 %) 339.9985 (calcd. 340.0017), [M-Br]+ (16.0 %) 261.0842 (calcd. 261.0833), [M-C6H4Br]+ (26.7 %) 185.0493 (calcd. 185.0520).

Sn(p-C6H4PPh2)4 (4): 0.400 g (0.54 mmol) of 2 is dissolved in 150 ml of ether and cooled to -60 °C. After adding 1.72 ml of a 2.5m solution of 6BuLi (4.31 mmol) in hexanes in a dropwise manner the mixture is allowed to warm to ambient temperature within 2.5 h and it is stirred for 15 min. Then the reaction mixture is again cooled to -60 °C and 0.77 ml (4.31 mmol) of CIPPh2 is added. After warming to room temperature and stirring overnight the formed precipitate is allowed to settle down and the supernatant is decanted. The product is extracted from the solid with three 20 ml aliquots of toluene and recrystallized from the toluene solution. The stannane 4 is obtained in 79 % yield (0.494 g, 0.42 mmol) as a colorless powder. Melting range 175-250 °C (sealed capillary). 1H NMR (C6D6, 500.1 MHz): δ = 7.42-7.40 (m; PPh2, PCCCH), 7.40 (d,
overlapping; SnCCH), 7.35 (tr, $^3J$(H-H) = 7.4 Hz, $^3J$(P-H) = 7.4 Hz; SnCCHCH), 7.04-7.02 (m; PPh$_3$, PCCHCHCH, PCCHCH); $^{13}$C NMR (C$_6$D$_6$, 125.8 MHz): $\delta$ = 139.56 (d, $^1J$(P-C) = 13.3 Hz; SnCCHCH), 138.33 (s, SnC), 137.68 (d, $^1J$(P-C) = 12.1 Hz; PPh$_3$, PC), 137.61 (d, $^3J$(P-C) = 6.2 Hz; $^2J$(Sn-C) = 81.3 Hz, SnCCH), 134.29 (d, $^2J$(P-C) = 19.8 Hz; PPh$_3$, PCCH), 134.14 (d, $^2J$(P-C) = 18.9 Hz, $^3J$(Sn-C) = 50.3 Hz; SnCCHCH), 128.97 (s; PPh$_3$, PCCHCHCH), 128.85 (d, $^3J$(P-C) = 6.9 Hz; PPh$_3$, PCCHCH) ppm; $^{31}$P NMR (C$_6$D$_6$, 121.5 MHz): $\delta$ = -5.23 ppm; $^{31}$P CP/MAS: $\delta_{iso}$ = -7.3 ppm ($\nu_{rot}$ = 2 kHz), $\delta_{11}$ = 12 ppm, $\delta_{22}$ = 2 ppm, $\delta_{33}$ = -37 ppm ($\nu_{rot}$ = 0 kHz); $^{119}$Sn NMR (C$_6$D$_6$, 99.4 MHz): $\delta$ = -127.59 ppm. LIFDI-MS: [M]$^+$ (100 %) 1164.2373 (calcd. 1164.2355).

Alternative Synthesis of Sn(p-C$_6$H$_4$PPh)$_3$ (4): 2.33 g (6.82 mmol) Ph$_3$P(p-C$_6$H$_4$Br) (synthesis and data see above) is dissolved in 400 ml of Ether and cooled to -60 °C. Then 2.73 ml of a 2.5m solution of $^6$BuLi (6.82 mmol) in hexanes is added in a dropwise manner and the solution is allowed to warm to ambient temperature. After stirring again to -60 °C 0.20 ml (1.70 mmol) of SnCl$_4$ is added. After stirring the reaction mixture overnight at room temperature the solvents are removed in vacuo and the product is extract ed with two 25 ml aliquots of toluene. Recrystallization from toluene yields 1.56 g (1.34 mmol, 79 %) of 4 as a colorless powder.

Immobilization of Si(p-C$_6$H$_4$PPh)$_3$ on SiO$_2$ via one phosphonium group (3i): 1 g of rigorously dried SiO$_2$ is suspended in about 50 ml of toluene, and a solution of 20.05 mg (0.02 mmol) of 3 in 100 ml of toluene, together with 4.5 mg (0.02 mmol) Cl(CH$_2$)$_3$Si(OEt)$_3$ is added. The mixture is heated to 80 °C and stirred for 15 h. After cooling down to ambient temperature and allowing the silica to settle down, the supernatant is decanted. Then the silica is washed with three 30 ml aliquots of toluene and dried in vacuo. Since no traces of phosphorus containing substances are found in the supernatant, the surface coverage can be determined to be about 1.5 linker molecules per 100 nm$^2$ of silica surface. $^{31}$P MAS (quantitative): $\delta_{iso}$ = 23.6 ppm (PPh$_2$Et$^+$), -4.1 (PPh$_3$), intensity ratio 1:3.

Immobilization of Sn(p-C$_6$H$_4$PPh)$_3$ on SiO$_2$ via three phosphonium groups (4i): 1 g of rigorously dried SiO$_2$ is suspended in about 50 ml of toluene, and a solution of 0.080 g (0.07 mmol) of 4 in 100 ml of toluene, together with 1.686 g (7.00 mmol) of Cl(CH$_2$)$_3$Si(OEt)$_3$ is added. The mixture is heated to 90 °C and stirred for 48 h. After cooling down to ambient temperature and allowing the silica to settle down, the supernatant is decanted. Then the silica is washed with three 30 ml aliquots of toluene and dried in vacuo. Since no traces of phosphorus containing substances are found in the supernatant, the surface coverage can be determined to be about 5.5 linker molecules per 100 nm$^2$ of silica surface. $^{31}$P MAS (quantitative): $\delta_{iso}$ = 22.8 ppm (PPh$_2$Et$^+$), -4.6 (PPh$_3$), intensity ratio 3:1.

Immobilized Rh complexes 5i and 6i: The linker-modified silica 3i (4i) are suspended in about 20 ml of toluene and combined with a solution of a slight excess of ClRh(PPh$_3$)$_3$ dissolved in toluene. After stirring for 5 h at ambient temperature, the silica is allowed to settle down and the supernatant is decanted. The silica 5i (6i) is washed with three 30 ml aliquots of toluene to remove excess ClRh(PPh$_3$)$_3$ and PPh$_3$, and dried in vacuo. The surface coverages are calculated based on the fact that no signal for uncoordinated PPh$_3$ groups is visible in the $^{31}$P CP/MAS spectra, and the linker surface coverages. For 5i about 4.5 Rh complexes (three complexes per linker), for 6i about 5.5 Rh complexes are bound on 100 nm$^2$ of silica surface.
$^{31}$P CP/MAS Spectra of 6i before (top) and after (bottom) the catalytic hydrogenation of 1-dodecene. Contact time 5 ms, 4 mm rotor, 3652 (top) and 1687 (bottom) scans, rotational speed 4 kHz. The signal at 23 ppm corresponds to the phosphine ligands bound to the Rh center \textit{trans} to each other, and is overlapping with the phosphonium signal of the surface-bound linker. The resonance at about 35 ppm represents the phosphine ligand coordinated to the metal center \textit{trans} to the Cl ligand.