1. Experimental Procedure

1.1. General details

All operations were performed in a Vacuum Atmospheres or MBraun dry box under purified nitrogen or using Schlenk techniques under a nitrogen atmosphere. Silica gel (60-200 mesh, Aldrich) was dried under reduced pressure (10^{-2} torr) and heated to 300 °C for 6 h (BET surface area 474 m²/g). Alumina (Fluka), Celite (Aldrich), and activated carbon (Aldrich) were dried in vacuo at 150 °C. The complex N-(3-triethoxysilylpropyl)-4,5-dihydroimidazol (I) (Gelest) was used as received. The ionic liquids 1-butyl-3-methyl-imidazolium tetrafluoroborate, [bmim][BF₄], and 1-butyl-3-methyl-imidazolium hexafluorophosphate, [bmim][PF₆], have been synthesized following literature preparations. The following chemicals have been purchased from Aldrich: Anhydrous pentane, anhydrous diethyl ether, anhydrous chloroform, anhydrous dichloromethane, anhydrous acetonitrile, 1-chlorobutane, 1-methyl-imidazol, sodium tetrafluoroborate, and sodium hexafluorophosphate. Acetonitrile-d₃ was purchased from Cambridge Isotopes and was degassed and dried over 4 Å molecular sieves. All chemicals were used as received unless otherwise stated. The high-resolution ¹H and ¹³C NMR spectra were recorded on a Varian Unity 400 spectrometer at room temperature. Chemical shifts were referenced to an internal standard (tetramethylsilane). Solid-state Bloch decay and cross-polarization magic-angle spinning (CPMAS) ¹³C NMR spectra were recorded on a Chemagnetics CMXII-200 spectrometer. Chemical shifts are reported on TMS (external) scale, using hexamethylbenzene as a secondary reference. Infrared spectra were measured with a Jasco FT/IR-620 FT-IR spectrometer. BET surface area analysis was performed using a Micromeritics ASAP 2400. Galbraith Laboratory performed elemental analyses.

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1.2. Synthesis of 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (2)

A mixture of N-(3-triethoxysilylpropyl)-4,5-dihydroimidazol (13.7 g, 0.05 mol) (1) and 1-chlorobutane (13.9 g, 0.15 mol) was refluxed at 78 °C for 21 h. The reaction mixture was cooled to room temperature and the volatiles evaporated under reduced pressure (10⁻² torr). The resulting material consisted of a brown colored paste, which was washed with pentane (3 x 100 mL) and dried in vacuo. Extraction of the material into dichloromethane (100 mL) and filtration through a bed of activated carbon and alumina gave a yellow colored solid after the removal of the volatile components under reduced pressure (10⁻² torr). Yield of complex (2): 17.4 g, 0.048 mol, 95%. ¹H NMR (400 MHz, CD₃CN): 0.61 (m, 2H, CH₂-C₃H₂-Si), 0.95 (tr, 3H, J = 7.4 Hz, CH₂-CH₂-C₃H₃), 1.19 (tr, 9H, J = 7.0 Hz, CH₃-CH₂-O), 1.36 (m, 4H, Si-CH₂-CH₂, CH₂-CH₂-CH₃), 3.68 (m, 8H, Si-CH₂-CH₂-CH₂-N, N-CH₂-CH₂-N-Bu), 3.82 (m, 6H, CH₃-C₃H₂-O), 4.14 (m, 4H, N-CH₂-CH₂-CH₂-CH₃, N-CH₂-CH₂-N-Bu), 10.40 (s, 1H, N-CH-N) ppm. ¹³C{¹H} NMR (101 MHz, CD₃CN): 7.5 (Si-C₃H₂-CH₂), 13.8 (CH₂-CH₂-C₃H₃), 18.6 (CH₃-CH₂-O), 19.6 (CH₂-CH₂-CH₂), 19.8 (Si-CH₂-CH₂), 21.4 (Si-CH₂-CH₂), 29.5 (CH₂-CH₂-CH₃), 47.6, 48.8, 49.0, 50.1 (CH₂-CH₂-N-Bu, Bu-N-CH-N-CH₂, Bu-N-CH₂, CH₃(CH₂)₂-CH₂), 58.6 (CH₂-CH₂-O), 158.9 (N-CH-N) ppm. FT-IR (KBr): 3441 b, 2950 s, 2883 s, 2791 s, 2447 w, 1663 s, 1528 w, 1442 m, 1313 w, 1252 w, 1203 m, 1093 s, 958 m, 786 m, 700 m, 467 m cm⁻¹. MS (Electrospray): m/z 331 (M⁺ - Cl). Anal. Calcd for C₁₆H₃₅N₂ClO₃Si: C, 52.37; H, 9.61; N, 7.63; Si, 7.65. Found: C, 51.64; H, 9.94; N, 7.60; Si, 7.65.

1.2. Synthesis of 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium tetrafluoroborate (3)

The complex 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (2) (10 g, 0.028 mol) was dissolved in acetonitrile (200 mL) and treated with one equivalent of sodium tetrafluoroborate (3.1 g, 0.028 mol). The resulting slurry was stirred for 5 d at room temperature. After the removal of the precipitate by filtration through a bed of Celite the volatiles were evaporated under reduced pressure (10⁻² torr) to give a brown liquid. Extraction of the material into dichloromethane (100 mL) and filtration through a bed of activated carbon and alumina gave a brown liquid solid after the removal of the volatile components under reduced pressure (10⁻² torr). Yield of complex (3): 10.0 g, 0.024 mol, 85%. ¹H NMR (400 MHz, CD₃CN): 0.58 (m, 2H, CH₂-C₃H₂-Si), 0.94 (tr, 3H, J = 7.4 Hz, CH₂-CH₂-CH₃), 1.12 (tr, 9H, J = 7.0 Hz, CH₃-CH₂-O), 1.33 (m, 2H, CH₂-CH₂-CH₂), 1.60 (m, 2H, Si-CH₂-CH₂), 1.69 (m, 2H, CH₂-CH₂-CH₃), 3.48 (m, 4H, Si-CH₂-CH₂-CH₂-N, N-CH₂-CH₂-N-Bu), 3.78 (m, 6H, CH₃-C₃H₂-O), 3.88 (m, 4H, N-CH₂-CH₂-CH₂-CH₃, N-CH₂-CH₂-N-Bu), 8.91 (s, 1H, N-CH-N) ppm. ¹³C{¹H} NMR (101 MHz, CD₃CN): 7.6 (Si-C₃H₂-CH₂), 13.8 (CH₂-CH₂-CH₂), 18.7 (CH₃-CH₂-O), 20.0 (CH₂-CH₂-CH₃), 21.6 (Si-CH₂-CH₂), 29.7 (CH₂-CH₂-CH₂), 48.2, 48.9, 49.0, 50.7 (CH₂-CH₂-N-Bu, Bu-N-CH-N-CH₂, Bu-N-CH₂, CH₃(CH₂)₂-CH₂), 59.0 (CH₃-CH₂-O), 158.8 (N-CH-N) ppm. FT-IR (KBr): 3447 b, 2981 s, 2883 s, 1657 s, 1522 m, 1455 m, 1307 m, 1252 w, 1093 s, 958 m, 786 s, 523 m, 474 m cm⁻¹. MS (Electrospray): m/z 331 (M⁺ - BF₄⁻). Anal. Calcd for C₁₆H₃₅N₂BF₄O₃Si: C, 45.94; H, 8.43; N, 6.70; B, 2.58; F, 18.16. Found: C, 45.95; H, 8.52; N, 6.88; B, 2.24; F, 17.86.
1.3. Synthesis of 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium hexafluorophosphate (4)

The complex 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride (2) (25.07 g, 68.0 mmol) was dissolved in acetonitrile (200 mL) and treated with one equivalent of sodium hexafluorophosphate (11.49 g, 68.0 mmol). The resulting slurry was stirred for 5 d at room temperature. After the removal of the precipitate by filtration through a bed of Celite the volatiles were evaporated under reduced pressure (10⁻² torr) to give a brown liquid. Extraction of the material into dichloromethane (100 mL) and filtration through a bed of activated carbon and alumina gave a brown liquid after the removal of the volatile components under reduced pressure (10⁻² torr). Yield of complex (4): 26.7 g, 0.056 mol, 82%. ¹H NMR (400 MHz, CD₃CN): 0.59 (m, 2H, CH₂-C₃H₂-Si), 0.93 (tr, 3H, J = 7.4 Hz, CH₂-CH₂-C₃H₃), 1.19 (tr, 9H, CH₃-CH₂-O), 1.33 (m, 2H, CH₂-C₃H₂), 1.61 (m, 2H, Si-CH₂-CH₂), 1.70 (m, 2H, CH₃-CH₂-CH₃), 3.41 (m, 4H, Si-CH₂-CH₂-N, N-C₃H₂-CH₂-N-Bu), 3.80 (m, 6H, CH₃-CH₂-O), 3.88 (m, 4H, N-C₃H₂-CH₂-CH₂-N-Bu), 7.83 (s, 1H, N-C₃H₂-N) ppm. ¹³C{¹H} NMR (101 MHz, CD₃CN): 7.5 (Si-C₃H₂-CH₂), 13.6 (CH₂-CH₂-C₃H₃), 18.6 (CH₃-CH₂-O), 19.9 (CH₂-CH₂-CH₃), 21.4 (Si-CH₂-CH₂), 29.4 (CH₂-CH₂-CH₃), 48.3, 48.9, 48.9, 50.7 (CH₂-CH₂-N-Bu, Bu-NCH-N-CH₂, Bu-N-C₃H₂-CH₂), 58.9 (CH₂-CH₂-O), 157.6 (N-CH-N) ppm. FT-IR (KBr): 2981 s, 2938 s, 2883 s, 1675 s, 1534 w, 1460 m, 1313 m, 1258 w, 1166 s, 964 s, 835 s, 559 s, 467 s cm⁻¹. Anal. Calcd. for C₁₆H₃₄N₂F₆PO₃Si: C, 40.47; H, 7.22; N, 5.90; F, 23.87; Si, 5.91. Found: C, 40.08; H, 7.57; N, 5.89; F, 22.15; Si, 5.68.

1.5. Synthesis of 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium tetrafluoroborate anchored on silica gel giving the modified support material (5)

The complex 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium tetrafluoroborate (3) (2.0 g, 4.8 mmol) was dissolved in chloroform (50 mL) and treated with silica gel (3.0 g). After heating the slurry under reflux condition for 24 h the solid was isolated by filtration and washed with pentane (50 mL). Additional washings were carried out with acetonitrile (100 mL) and diethyl ether (100 mL) before the material was dried under reduced pressure (10⁻² torr) to give a slightly yellow colored powder (5). ¹³C NMR (solid state): 9 (Si-CH₂-CH₂-CH₂), 13 (CH₃-CH₂-CH₂), 18-20 (CH₃-CH₂-O, Si-CH₂-CH₂-CH₂, CH₃-CH₂-CH₂), 29-31 (CH₃-CH₂-CH₂), 48-52 (CH₂-N-CH₂-CH₂-N-CH₂), 58-65 (CH₃-CH₂-O), 156-158 (N-CH-N) ppm. FT-IR (Photoacoustic): 3097 w, 2967 m, 2928 m, 1876 m, 1786 m, 1655 s, 1525 w, 1458 m, 1196 s, 1130 s, 802 s cm⁻¹. Anal. Found: C, 5.39; H, 1.32; N, 0.78.

1.6. Synthesis of 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium hexafluorophosphate anchored on silica gel giving the modified support material (6)

The complex 1-butyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium hexafluorophosphate (4) (4.0 g, 8.4 mmol) was dissolved in chloroform (200 mL) and treated with silica gel (40.0 g). After heating the slurry under reflux condition for 18 h the solid was isolated by filtration and washed with diethyl ether (3x 50 mL). The resulting material was dried under reduced pressure (10⁻² torr) to give a slightly yellow colored powder (6). ¹³C NMR (solid state): 9 (Si-CH₂-CH₂-
CH$_2$), 13 (CH$_3$-CH$_2$-CH$_2$), 18-20 (CH$_3$-CH$_2$-O, Si-CH$_2$-CH$_2$, CH$_3$-CH$_2$-CH$_2$), 29-31 (CH$_3$-CH$_2$-CH$_2$), 48-52 (CH$_2$-N-CH$_2$-CH$_2$-N-CH$_2$), 58-65 (CH$_3$-CH$_2$-O), 156-158 (N-CH-N) ppm. Anal. Found: C, 5.61; H, 1.42; N, <0.5.

1.7. Catalyst preparation: Surface modified support material (5) treated with 3-butyl-1-methyl-imidazolium tetrafluoroborate and catalyst precursors

The complex dicarbonylacetylacetonate rhodium (3 mg, 0.01 mmol) and tri(m-sulfonyl)triphenyl phosphine tris(1-butyl-3-methyl-imidazolium) salt (tppti) (68.5 mg, 0.1 mmol) were dissolved in acetonitrile (3 mL). To this solution was added the ionic liquid 3-butyl-1-methyl-imidazolium tetrafluoroborate (0.8 g) to give a clear yellow solution. The resulting mixture was treated with the surface modified support material (5) (3 g). After stirring the mixture for 1 h the volatile organic components of the slurry were evaporated under reduced pressure (10$^{-2}$ torr) to give a free flowing powder with a slight yellow coloration. (The preparation of the corresponding catalyst containing the ligand tppts was carried out in the same manner).

1.8. Catalyst preparation: Surface modified support material (6) was treated with 3-butyl-1-methyl-imidazolium hexafluorophosphate and catalyst precursor

The complex dicarbonylacetylacetonate rhodium (3 mg, 0.01 mmol) and tri(m-sulfonyl)triphenyl phosphine tris(1-butyl-3-methyl-imidazolium) salt (tppti) (68.5 mg, 0.1 mmol) were dissolved in acetonitrile (3 mL). To this solution was added the ionic liquid 3-butyl-1-methyl-imidazolium hexafluorophosphate (0.8 g) to give a clear yellow solution. The resulting mixture was treated with the surface modified support material (6) (3 g). After stirring the mixture for 1 h the volatile organic components of the slurry were evaporated under reduced pressure (10$^{-2}$ torr) to give a free flowing powder with a slight yellow coloration.