Supplementary

Catalyst preparation and characterisation

Catalysts were prepared (see Table 1) by dissolving an *in situ* mixture of Pd(CF₃CO₂)₂, 1,1'-bis(diphenylphosphino)ferrocene ¹⁵⁰ (DPPF) and CF₃SO₃H (TfH) in 1-ethyl-3-methyl-imidazolium trifluoromethane sulphonate (EMIm), 1-butyl-3-methyl-imidazolium trifluoromethane sulphonate (BMIm) or 1-hexyl-2,3-dimethyl-imidazolium trifluoromethane sulphonate (HM₂Im). Silica (aerosil 355 by Degussa, 150 m²/g) was ground to particle size 60-200 µm ¹⁵⁵ and impregnated with the solution to obtain a free flowing powder.

| Table 1 Amounts used in the preparation of the supported cat |
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| Ionic liquid | Ionic liquid | Pd(CF ₃ CO ₂) ₂ | Pd contents | DPPF | TfH | Silica |
|--------------|-------------------------|---|--|------|------|--------|
| - | / ml | / mg | $/ \text{mmol}_{Pd^{2+}} g_{Cat}^{-1}$ | / mg | / mg | / g |
| EMIm | 2.5 | 33 | 0.011 | 83 | 150 | 5.0 |
| | 2.5 | 66 | 0.023 | 166 | 150 | 5.0 |
| | 2.5 | 133 | 0.044 | 333 | 150 | 5.0 |
| BMIm | 2.5 | 33 | 0.012 | 83 | 150 | 5.0 |
| | 2.5 | 66 | 0.023 | 166 | 150 | 5.0 |
| | 2.5 | 133 | 0.042 | 333 | 150 | 5.0 |
| HM_2Im | 3.5 ^{<i>a</i>} | 33 | 0.012 | 83 | 150 | 5.0 |
| | 3.5 ^{<i>a</i>} | 66 | 0.024 | 166 | 150 | 5.0 |
| | 3.5 ^{<i>a</i>} | 133 | 0.041 | 333 | 150 | 5.0 |
| | | | - | | | |

^{*a*} quantity in g, as HM₂Im is a solid at RT.

Determination of the absorption constant for aniline and styrene A fixed bed reactor was filled with 50 mg catalyst and glass beads

(remaining volume). A constant flow of heptane (1 mlmin⁻¹) was ¹⁶⁰ passed over the catalyst bed and the temperature of the reactor and feed increased to 120°C. The concentration of aniline was then increased stepwise to 1.85⁻10⁻⁴, 2.27⁻10⁻⁴ and 2.70⁻10⁻⁴ mol⁻1⁻¹. The concentration of aniline at the exit was followed with UV spectroscopy. The uptake was calculated from the time-¹⁶⁵ concentration diagram by comparison with an experiment, where the reactor had been filled only with glass beads. Aniline absorption was only observed in the first step. The experiment was repeated with styrene, but no absorption was observed.

170 Catalytic testing in batch mode

Catalytic experiments were performed in an inert atmosphere of nitrogen using a 12-batch reactor (Radleys). The catalyst (0.25 g) was suspended in octane (15 cm³) and heated to reflux at 125°C. Aniline (1 mmol), styrene (1.5 mmol) and undecane (internal GC

¹⁷⁵ standard) were added. Samples (50 µl) were taken periodically and analyzed by gas chromatography.

Tests on leaching of palladium complex

(i) Samples were taken during the experiments performed in the 180 batch mode and analysed for palladium contents. The amount of palladium leached into the reaction solution was below the detection limit of AAS.

(ii) No further reaction was observed, when the reaction mixture was filtered and the filtrate maintained at 125°C.

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Catalytic testing in fixed bed reactor

A fixed bed reactor was filled with catalyst (50 mg) and glass beads (remaining volume) and a solution of aniline $(0.10 \text{ mol} \Gamma^1)$ and styrene $(0.15 \text{ mol} \Gamma^1)$ in heptane passed over the catalyst (flow 0.2

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¹⁹⁰ ml min⁻¹). The temperature was increased stepwise from 150°C to 300°C. After steady state was obtained, samples of the product mixture were collected for gas chromatography. The temperature was then reduced to 150°C and confirmed that the initial activity was obtained.