Adhesive Immobilization of Polymer-Stabilized Pd Nanoparticles on Cellulose

**Significance:** Adhesive immobilization of palladium nanoparticles on cellulose using hyperbranched polystyrene [Pd@HPS-N(C_{12}H_{25})_3Cl] was developed. The catalyst promoted efficiently the Suzuki–Miyaura coupling, the Mizoroki–Heck reaction, the intramolecular C–H bond arylation, and the hydrogenation. The catalyst was recycled by a tweezers and reused several times.

**Comment:** The catalyst was prepared as follows: A reaction of the hyperbranched polystyrenes having tri(dodecyl)ammonium chloride moieties [HPS-N(C_{12}H_{25})_3Cl] with Pd_2(dba)_3 was carried out to give the polymer-supported palladium nanoparticles Pd@HPS-N(C_{12}H_{25})_3Cl. The resulting nanocomposite Pd@HPS-N(C_{12}H_{25})_3Cl was treated with KI and filter paper (or cotton) to afford Pd@HPS-N(C_{12}H_{25})_3Cl on cellulose.

**Selected examples:**

**Suzuki–Miyaura reaction:**

\[
\begin{align*}
\text{Ph} & + \text{(HO)B} \rightarrow \text{PhB} \quad (1.5 \text{ equiv}) \\
\text{Pd@HPS-N(C}_{12}\text{H}_{25})_3\text{Cl} & + \text{K}_2\text{CO}_3 \rightarrow \text{PhB} \quad \text{(filter paper, 2.5 mol%)} \\
\end{align*}
\]

**Mizoroki–Heck reaction:**

\[
\begin{align*}
\text{PhI} & + \text{CH} = \text{CHCO} \rightarrow \text{PhCH} = \text{CHCO} \quad (4 \text{ equiv}) \\
\text{Pd@HPS-N(C}_{12}\text{H}_{25})_3\text{Cl} & + \text{K}_2\text{CO}_3 \rightarrow \text{PhCH} = \text{CHCO} \quad \text{(filter paper, 1.5 mol%)} \\
\end{align*}
\]

**Intramolecular C–H bond arylation:**

\[
\begin{align*}
\text{MeO} & + \text{I} \rightarrow \text{MeO} \quad \text{(1.5 equiv)} \\
\text{Pd@HPS-N(C}_{12}\text{H}_{25})_3\text{Cl} & + \text{AcOK} \rightarrow \text{MeO} \quad \text{(filter paper, 0.67 mol%)} \\
\end{align*}
\]

**Hydrogenation:**

\[
\begin{align*}
\text{Pd@HPS-N(C}_{12}\text{H}_{25})_3\text{Cl} & \rightarrow \text{MeO} \quad \text{(filter paper, 0.67 mol%)} \\
\end{align*}
\]