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Highly Selective Reductive Cross-Amination between Aniline or Nitroarene Derivatives and Alkylamines Catalyzed by Polysilane-Immobilized Rh/Pt Bimetallic Nanoparticles

Synthesis of N-Alkylcyclohexylamines on Supported Rh/Pt Nanoparticles

Significance: Rh/Pt bimetallic nanoparticles (NPs) supported on dimethylpolysilane and alumina (Rh/Pt–DMPSi/Al₂O₃) promoted the synthesis of N-alkylcyclohexylamines from anilines and the corresponding N-alkylamines to give the corresponding alkylcyclohexylamines in up >99% yield.
N-Methylaniline and nitrobenzene also underwent the reductive coupling with octylamine to afford N-octylcyclohexanamine in yields of 89% and 87%, respectively.

Comment: The authors previously reported the preparation of Rh/Pt–DMPSi/Al₂O₃ and its application in arene hydrogenation (J. Am. Chem. Soc. 2018, 140, 11325). In the reaction of aniline with octylamine, the catalyst was used four times without significant loss of its catalytic activity (fresh: 92% yield; fourth reuse: 90%).

**Results:**
- **N-Methylaniline**
  - 93% yield
  - 89% yield (N-methylaniline was used instead of aniline)
- **Nitrobenzene**
  - 87% yield (nitrobenzene was used instead of aniline)
- **Aniline**
  - 97% yield (for 38 h)
- **Octylamine**
  - 92% yield (for 72 h)
  - >99% yield
- **Benzylamine**
  - 85% yield
- **N-Octylcyclohexanamine**
  - >99% yield

**Key words**
rhodium catalysis
platinum catalysis
aniline
alkylcyclohexylamines