The Direct Coupling of Phenols and Amines under Rhodium Catalysis

**Significance:** A redox-neutral strategy for the dehydrative coupling of phenols and amines enabled by a dimeric cyclopentadienyl rhodium(III) complex is disclosed. The reaction proceeds under mild conditions, releasing water as the sole by-product. This method is also applicable to late-stage functionalization.

**Comment:** Starting from readily available primary or secondary amines and phenols, this transformation provides access to a wide range of valuable anilines in good yields. Mechanistic experiments support a keto–enol tautomerization of phenol as the key step, facilitated by η6-coordination of the aryl ring by the rhodium complex.