Cyclic (Alkyl) (Amino) Carbene (CAACs)-Mercury(II) Adducts and their Role as Catalysts in Intermolecular Hydroamination Reactions

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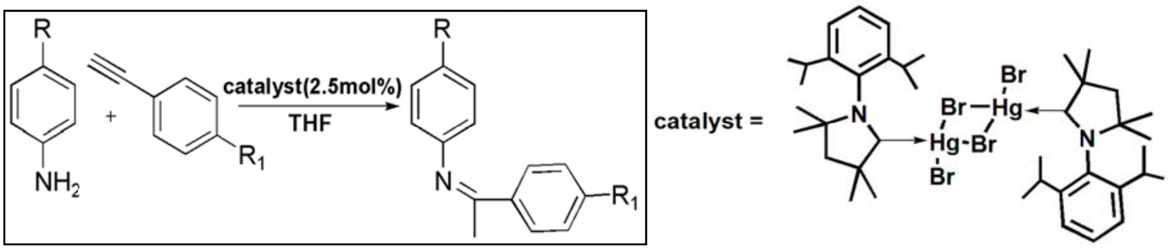
Abstract:

Since the discovery of bottle-able carbenes (NHCs, CAACs etc.) there has been a resurgence of interest in the organometallic chemistry involving complexes of carbenes with various metal ions. The unprecedented low valent metal compounds, highly active catalysts are the outcome of the stabilization offered by the appended carbenes to the metal center. The present work deals with the syntheses of adducts of Cyclic (Alkyl) (Amino) Carbene (CAACs) with HgX_2 salts as $[CAAC{\cdot}HgCl(\mu\text{-}Cl)]_2$ **(1)**, $[CAAC{\cdot}HgBr(\mu\text{-}Br)]_2$ **(2),** $[CAAC{\cdot}HgI(\mu\text{-}I)]_2$ **(3)**.

In an attempt to substitute the halide with a different weakly coordinating anion, a cationic mercury species, $[(CAAC)_2Hg]^{2+}[NO_3]^{2-}$ **(4)**. This product was isolated by reacting $AgNO_3$ with $[CAAC{\cdot}HgBr(\mu\text{-}Br)]_2$ **(2)**. Similarly, when $Hg(OAc)_2$ was reacted with $[CAACH]^+[Cl]^-$ the ionic complex, $[CAACH]^+[HgCl_3]^-$ **(5)** was isolated. After the successful synthesis of some of these adducts, their application has been explored in the hydroamination reactions between aromatic amines and terminal alkynes as shown in the Scheme below. The catalytic ability of $[CAAC{\cdot}HgBr(\mu\text{-}Br)]_2$ **(2)** in intermolecular hydroamination has been explored in detail.



Scheme: Intermolecular hydroamination catalyzed by the $[CAAC{\cdot}HgBr(\mu\text{-}Br)]_2$ adduct.

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