

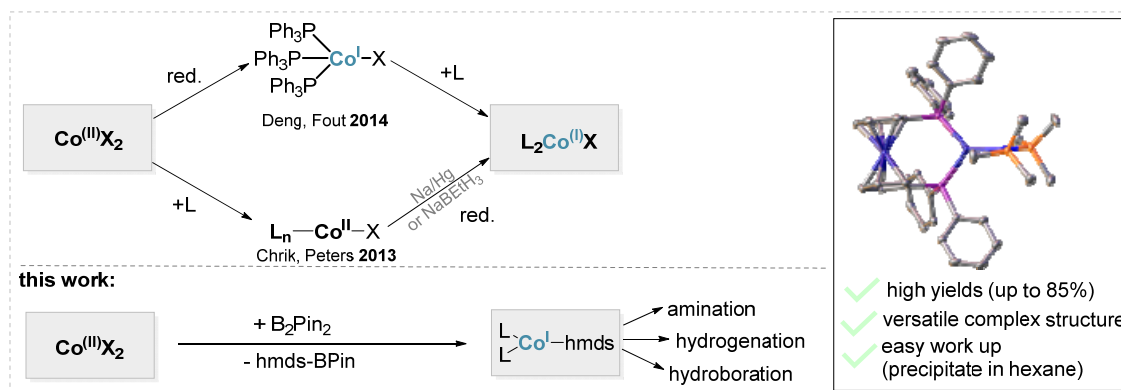
A RAPID AND CONVENIENT SYNTHESIS OF COBALT(I) COMPLEXES

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There is an increasing demand of rapid, robust, and versatile syntheses of base metal complexes for the exploration of catalytic processes. Especially, 3d transition metal catalysts have recently been demonstrated to bear great potential as sustainable alternatives to noble metal catalysts in various reactions such as hydrogenations, hydrofunctionalizations, cross-couplings, (cyclo)isomerizations, aminations, CH activations etc.^[1] Cobalt(I) complexes have matured to a front runner position in the search for efficient, active, inexpensive, and less toxic catalyst species with numerous synthetic applications.^[2] The preparation of ligand-stabilized cobalt(I) has mostly been performed by sequential ligand exchange and reduction steps starting from available cobalt(II) salt precursors.^{[3],[4]} Here, we report a most effective, high-yielding, and highly versatile strategy that utilizes the convenient precursor $\text{Co}[\text{N}(\text{SiMe}_3)_2]_2$, or $\text{Co}(\text{hmds})_2$, and the commercial borane reagent bis(pinacolato)diboron, B_2pin_2 , in the presence of various phosphine ligands. This approach exploits two distinct properties for rapid conversion: *i*) the high driving force of N-B Lewis pairing enables rapid ligand dissociation, and *ii*) the intrinsic reducing power of the B-B bond that effects $\text{Co}(\text{II}) \rightarrow \text{Co}(\text{I})$ reduction. The resultant cobalt(I) phosphine complexes can be obtained with different coordination patterns including monodentate, chelating, and pincer-type phosphines. The amido ligand confers basic reactivity onto the complex that may be utilized in the initial activation of substrates. The activity of these complexes in catalytic applications has been demonstrated.



Scheme 1: Common syntheses of cobalt(I) phosphine complexes (top); new B_2pin_2 -mediated ligand substitution and reduction pathway (bottom). Selected applications of such prepared cobalt(I) complexes in catalytic hydroboration, hydrogenation, and amination (right).

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