Well-Defined #-Diketiminatocobalt(II) Complexes For Alkene Cyclohydroamination of Primary Amines

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Well-Defined β-Diketiminatocobalt(II) Complexes For Alkene Cyclohydroamination of Primary Amines

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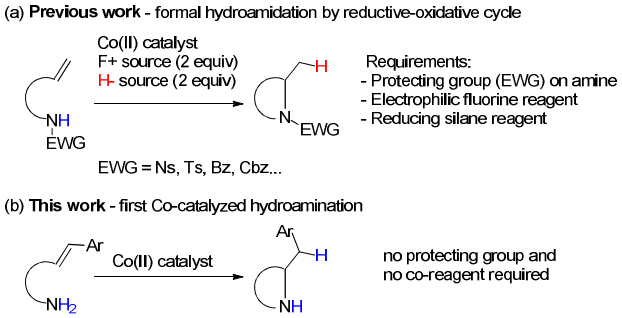
hydroamination, cobalt, primary amines, alkenes, mechanistic studies, DFT calculations.

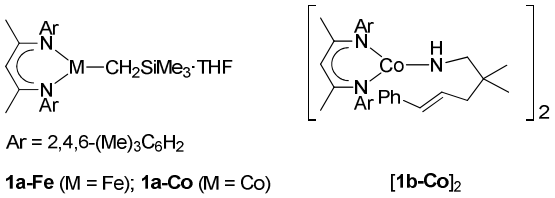
ABSTRACT: A well-defined low-coordinate β-diketiminatocobalt(II) alkyl complex is reported as an active precatalyst for the selective alkene cyclohydroamination of unprotected primary amines under mild conditions (rt-90 °C). The reaction mechanism has been investigated by deuterium-labelling, kinetics and stoichiometric experiments and in-depth computational DFT studies. On the basis of these studies, we propose a stepwise non-insertive mechanism that features a rate-determining nucleophilic attack of the amido group of a monomeric cobalt(II) amidoalkene-aminoalkene adduct intermediate to the non-coordinated pendant alkene followed by a rapid proton transfer from the coordinated aminoalkene to the cyclized adduct.

Over the years, the catalytic alkene hydroamination – the direct addition of an amine across a carbon-carbon double bond – has received considerable interest among the scientific community as an appealing route to valuable nitrogen-containing compounds from ubiquitous amines and olefins.[1] The general concern for sustainable metal catalysis has recently stimulated the exploration of earth-abundant, first-row late transition metals for the development of eco-compatible hydroamination catalysts with a wide applicability.[1c] Although still in its infancy, this exploration has already led to outstanding advances with Zn,[2] Cu[3] or Fe[4] metal relying on either a classical[2,3a-b,4a-b] or a formal hydroamination approach such as metal-hydride mediated umpolung electrophilic amination[3c,4c] or hydrogen atom[4d] transfer. However, although these reports by formal hydroamination have advanced the state of the art, they are far from the concept of atom and step economy of the original hydroamination reaction, and so progress in the direction of "truly" hydroamination systems from earth abundant transition metal is still in high demand. In this context, there is, to our knowledge, no report on the cobalt-catalyzed hydroamination of unactivated alkenes. Only a single but interesting report by Shigehisa *et al*. has disclosed a Co-catalyzed intramolecular C-N bond formation by a closely related formal hydroamidation reaction of protected amines bearing electron-withdrawing groups (EWG) and requiring a substoichiometric amount of oxidizing electrophilic fluorine agent and reducing silane agent (Scheme 1 (a)).[5] Herein, we report the first example of cobalt-catalyzed alkene hydroamination of unprotected primary amines under co-reagent-free conditions using well-defined low-coordinate β-diketiminatocobalt(II) complexes (Scheme 1 (b)).



Scheme 1. (a) Seminal Work on Related Co-catalysed N-H Addition on Unactivated Alkenes; (b) This Work

Some of us have recently reported that structurally defined β-diketiminatoiron(II)-alkyl or -amido complexes, such as **1a-Fe** (Scheme 2), have the ability to catalytically promote the highly selective cyclohydroamination of primary aliphatic alkenylamines at mild temperatures, as the first example of iron-catalyzed hydroamination of such electronically unbiased amines.[4a] With our concern in base metal catalysis, we have explored the reactivity of analogue complexes derived from cobalt in alkene hydroamination.



Scheme 2. Structures of β-diketiminatometal(II) complexes

Firstly, the β-diketiminatocobalt(II) alkyl complex **1a-Co** (Scheme 2) was prepared from 2,4-bis(2,4,6-trimethylphenylimido)pentane, $CoCl_2$ and $LiCH_2SiMe_3$ by a two-step metathesis route (via the formation of chloro ate complex **S1**).[6] Complex **1a-Co** was isolated as a dark-brown air-sensitive crystalline solid that can be stored for weeks at rt without noticeable decomposition. Solid-state analysis of a single crystal reveals that the four-coordinate cobalt atom adopts a pseudotetrahedral geometry with a smaller trigonal pyramidal distortion than that found in **1a-Fe** (τ_{Co}= 0.31 vs τ_{Fe}= 0.55)[6] (Figure 1).[7,8]

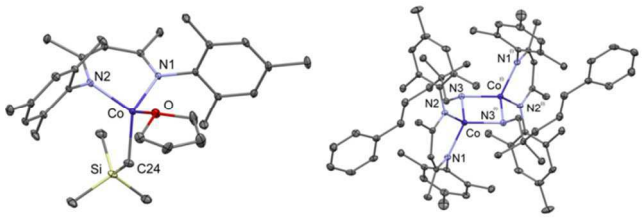
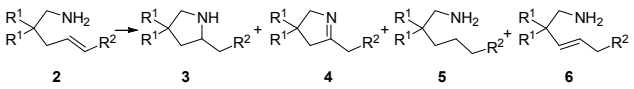
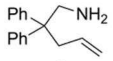
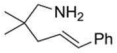


Figure 1. ORTEP drawing of **1a-Co** (left) and [**1b-Co**]$_2$ (right). Thermal ellipsoids are shown at the 30% level. H atoms have been omitted for clarity.

Our initial evaluation of the catalytic efficiency of **1a-Co** focused on the reaction of **2a** as a benchmark reaction under our previously optimized conditions for the iron-catalyzed hydroamination.[4a] To our surprise, heating **2a** in toluene at 90 °C in the presence of 10 mol % of **1a-Co** leads to the formation of **3a**, **4a**, **5a** and **6a** in a 4:9:18:61 ratio respectively after 92% conversion (Table 1, entry 1). This result is in strong contrast with **1a-Fe** which delivers under identical conditions the hydroamination product **3a** in 80% yield with no trace of olefin isomerization product **6a**.[4a] To our delight, introducing a phenyl ring at the terminal position of the C=C bond of the substrate prevents the alkene isomerization to occur.

Table 1. Screening of Substrates and Conditions of the Cyclohydroamination reaction[a]

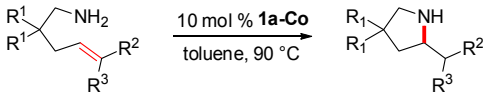


entry	substrate	**2** (%)[b]	**3** (%)[b]	**4** (%)[b]	**5** (%)[b]	**6** (%)[b]
1[c]	 **2a**	8	4	9	18	61
2[d]	 **2b**	5	93	2	0	0
3[e]		25	72	2	0	0
4[f]	[**1b-Co**]$_2$	8	90	1	1	0
5[g]	[**1b-Co**]$_2$	56	0	44	0	0
6[g,h]	[**1b-Co**]$_2$	58	25	17	0	0

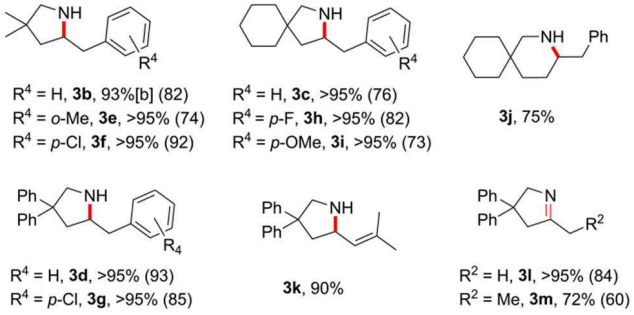
[a]Reaction conditions: [**2**] = 0.96 M, 10 mol % **1a-Co**, toluene, 90 °C, 24 h unless otherwise stated. [b]Determined by GC analysis. [c] 3 h. [d] [**2b**] = 0.81 M. [e][**2b**] = 0.73 M, rt, 47 h. [f]5.55 mol % [**1b-Co**]$_2$ as catalyst. [g][[**1b-Co**]$_2$] = 2.6 mM, toluene, 90 °C, 24 h. [h]With cyclopentylamine (1 equiv per Co).

Indeed, the hydroamination of **2b** catalyzed by 10 mol % of **1a-Co** provides **3b** in 93% yield as almost the sole product without any sign of substrate isomerization (Table 1, entry 2). The reaction can also be run at rt with similar selectivity despite a lower efficiency (Table 1, entry 3). By this methodology, various five- and six-membered nitrogen-heterocycles featuring a phenyl ring attached to the terminal alkene which is either unsubstituted (**3b-d**, **3j**) or substituted by an halogen atom (**3f-h**), an alkyl (**3e**) or a methoxy (**3i**) group were isolated in convenient yields from the corresponding aminoalkenes (Table 2). The *exo*-cyclization also occurs efficiently from primary amines bearing a dimethylsubstituted allene (**2k**) or an alkyne (**2l-m**) functionality. Nevertheless, up to know, the reaction does not proceed with aminoalkenes unbiased towards cyclization or having a trisubstituted olefin.[6]

Table 2. Reaction Scope[a]



2b-m **3b-m**



[a]Reaction conditions: [**2**] = 0.81 M, 10 mol % **1a-Co**, toluene, 90 °C, 24 h. RMN yield determined using an internal standard unless otherwise stated and isolated yield in brackets. [b]Determined by GC analysis.

To investigate the reaction mechanism, kinetic analysis of the cyclohydroamination of **2b** was performed by monitoring the concentration of substrate **2b** over the course of the reaction. Plots of ln[**2b**] vs time are linear to at least 3 half-lives over a 0.51–1.41 M initial concentration range and are consistent with first-order kinetics in [**2b**]. A linear relationship between k_{obs} and [**1a-Co**] over a fourfold concentration range ([**1a-Co**] = 0.041-0.161 M) indicates a first order dependence in catalyst concentration and provides the empirical rate law displayed in eq 1 with k_H (363 K)= 6.6×10^{-4} M^{-1} s^{-1}.

$$-\frac{d[\mathbf{2b}]}{dt} = k_H[\mathbf{1a\_Co}]^1[\mathbf{2b}]^1 \quad (1)$$

This second-order rate law may reflect mono-association of the substrate with a monomeric cobalt species during the rate-limiting step and is consistent with several reported mechanisms such as a proton-assisted concerted C-N/C-H bond-forming mechanism[9a-d] or a stepwise insertive mechanism[9e,4a] with a turnover-limiting aminolysis event. Further measurement of the rate of cyclization of *N*-deutero-amine [D_2]-**2b** with **1a-Co** gives k_D (363 K) = 6.8×10^{-4} M^{-1} s^{-1} and leads to no observation of primary kinetic isotope effect (KIE) (k_H/k_D = 0.97 (90 °C)). Eyring analysis for the cyclization of **2b** over a 353-383 K temperature range afford the following activation parameters: $\Delta H^{\neq}$ = +15.9 kcal mol^{-1}, $\Delta S^{\neq}$ = –29.7 cal mol^{-1} K^{-1}.

To gain a better insight into the nature of the cyclization step, we endeavor to isolate the initial catalyst–substrate intermediate and study its reactivity. The stoichiometric reaction of **1a-Co** and **2b** at rt leads to the isolation of cobalt amido complex [**1b-Co**]$_2$ as a dark green solid in 89% (Scheme 2). X-ray diffraction analysis confirms the solid-state structure of [**1b-Co**]$_2$ as a centrosymmetric amido-bridged dimer (Figure 1). The stoichiometric reactivity of isolated [**1b-Co**]$_2$ was then tested by heating a toluene slurry of the dimer for 24 h at 90 °C. GC analysis reveals the formation of **4b** in 44% yield as the sole insertion product, concomitantly with unreacted **2b** in 56% yield (Table 1, entry 5). It is worth noting that [**1b-Co**]$_2$ is also capable of catalytically mediating the hydroamination of **2b** with similar efficiency as its alkyl precursor (Table 1, entries 4 vs 2) (*vide infra* for more details on the selectivity change). As C-N bond formation clearly occurs directly from [**1b-Co**]$_2$ in the absence of additional proton source, this

stoichiometric experiment militates against a proton-assisted concerted mechanism. The stereochemistry of the cyclization was further elucidated by ^{1}H NMR $^3J_{H,H}$ coupling constant measurements of the tosylated products arising from cyclization of *N*-deutero-amines [D_2]-(*E*)-**3d** and [D_2]-(*Z*)-**3d**. These experiments provide exclusively products with deuterium located at the β-position of the nitrogen atom and with a formal *syn*-addition of the N-D bond across the C=C bond.[6]

The reaction mechanism for **2b** was also investigated by means of DFT calculations.[10] Among the mechanisms evaluated, the one with the most feasible Gibbs energy profile is shown in Figure 2.[11] The relative stability of doublet and quartet spin states were systematically evaluated obtaining the later as the most stable one.[6] The mechanism can be divided in two parts, one for generating the active species, **III_A3**, and another for the catalytic cycle itself. The generation of the active species, **III_A3** takes place by a proton transfer from the coordinated reactant to the –CH_2SiMe_3 ligand, **I_A1** (Figure 2 and Scheme 3). This step produces intermediate **II_A1**, with a Gibbs energy barrier of 29.2 kcal mol^{-1}, generating an amido group ligand and $SiMe_4$.[12] The formed $SiMe_4$ of **II_A1** is then replaced by a second aminoalkene reactant molecule producing active species **III_A3** at −11.4 kcal mol^{-1}. In turn, intermediate **II_A1** can also form [**1b-Co**]$_2$ that probably corresponds to the resting state of the catalyst once the reactant is consumed (Figure 2 and Scheme 3).[13] Its optimized structure resembles that of X-ray analysis. This species can catalyze the reaction by forming back the monomeric species (Table 1, entry 4).

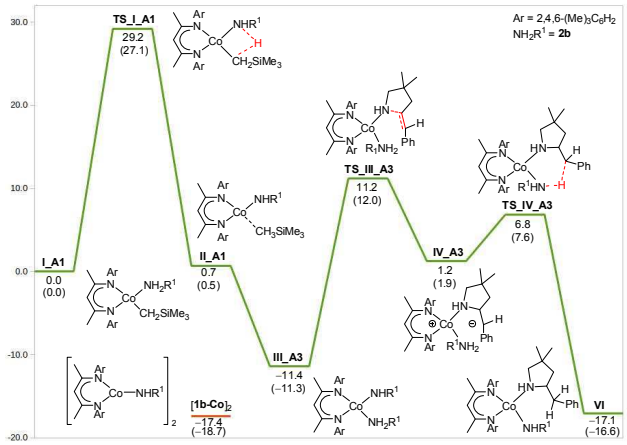


Figure 2. Calculated Gibbs energy profile (T = 298 K (in brackets T = 363K); energies in kcal mol^{-1})

The catalytic cycle contains three steps: (i) intramolecular cyclization by nucleophilic attack of coordinated amido group to the non-coordinated alkene, (ii) proton transfer from a second coordinated aminoalkene to the cyclized amino ligand, and (iii) substitution of the product by a new reactant (Scheme 3). The C-N bond formation step, with a relative barrier of 22.6 kcal mol^{-1}, corresponds to the rate determining cyclization step, and is in very good agreement with $\Delta G^{\neq}$=24.6 kcal mol^{-1} calculated from experimental activation parameters at T = 298.15 K. The large and negative activation entropy determined experimentally also agrees with a step that involves a cyclization process. Intermediate **IV_A3**, which lies at 1.2 kcal mol^{-1}, does not have direct interaction between Co and C_2 (distance of 3.649 Å; Scheme 3 and Figure S11). From this intermediate, there is a proton transfer between the coordinated aminoalkene and the cyclized amino ligand, with an energy barrier of 5.6 kcal mol^{-1}. It generates intermediate **VI**, with a relative Gibbs energy of −17.1 kcal mol^{-1}, that has the hydroamination product coordinated. Replacement of the product by a new aminoalkene molecule closes the catalytic cycle (Scheme 3). This proposed stepwise non-insertive mechanism is the most favorable one among, *inter alia*, the insertive mechanism. All the attempts to find a concerted non-insertive pathway has conducted to this stepwise mechanism. The absence of KIEs is explained by the fact that the proton transfer step (**TS_IV_A3** at 6.8 kcal mol^{-1}) is lower in energy than the cyclization step (**TS_III_A3** at 11.2 kcal mol^{-1}) (Figures 2 and 3).

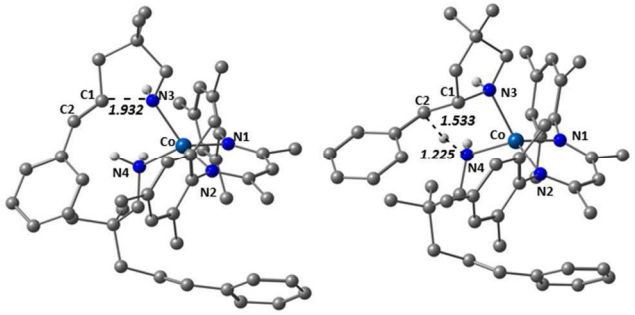
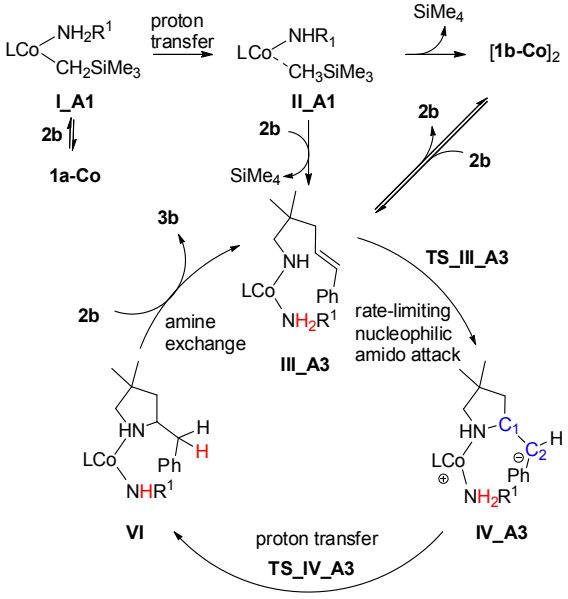


Figure 3. Optimized structures for **TS_III_A3** (left) and **TS_IV_A3** (right) (distances in Å).

The observation of a *syn*-addition of N-D bond across the C=C bond, can be justified by the proposed mechanism if the rotation around C_1-C_2 bond (see **IV_A3** in Scheme 3) is higher in energy than the proton transfer. Then, proton transfer would be fast enough to avoid rotation around C_1-C_2 bond, producing a formal *syn*-addition of the N-H bond across the C=C bond. The relative barrier for the proton transfer is 5.6 kcal mol^{-1}, whereas the rotation is estimated to be 14.4 kcal mol^{-1}, thus explaining the experimental observation of a *syn*-addition. The mechanism is also in agreement with the experimental observation that the reaction of [**1b-Co**]$_2$ in the presence of cyclopentylamine (1 equiv) as an additional proton source generates **3b** (and **4b**) (Table 1, entry 6).



[a]NH_2R^1 = **2b**, L represents β-diketiminate ligand.

Scheme 3. Proposed Reaction Mechanism[a]

In conclusion, we have established that novel well-defined β-diketiminatocobalt(II) alkyl complex **1a-Co** is an efficient precatalyst for the hydroamination of unprotected primary amines tethered to an aryl alkene under mild and co-reagent free conditions. This is the first example of cobalt-catalyzed alkene hydroamina-

tion reaction of unprotected and electronically unbiased primary amines. DFT studies, supported by stoichiometric reactivity experiments, have shown that the reaction operates through a stepwise non-insertive mechanism as original alternative to the classically reported hydroamination mechanisms. This mechanism entails nucleophilic attack of the amido group of monomeric cobalt(II) amidoalkene-aminoalkene adduct intermediate to the non-coordinated pendant alkene as the rate-determining cyclization step associated subsequently to a rapid proton transfer from the coordinated substrate to the resulting cyclized adduct. This proposed mechanism is in agreement with the empirical second-order rate law, no KIE observation, the *syn*-addition of N-D bond across the C=C bond, and the activation parameters determined experimentally. The outcome of this work will help guide the rational design of base metal catalysts with improved reactivity and alternative selectivity patterns. Further studies in this direction are currently ongoing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental procedures, kinetic and isotopic labelling studies, characterization, computational details and copies of NMR spectra (PDF)
Crystallographical data for complex **S1** (CIF)
Crystallographical data for complex **1a-Co** (CIF)
Crystallographical data for complex [**1b-Co**]$_2$ (CIF)

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Notes

The authors declare no competing financial interests.

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(8) DFT optimized structure of **1a-Co** is very similar to that obtained by X-ray analysis and assigns a quartet spin state to this compound as noticed by solution magnetic moment measurement.[6]

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(10) Related DFT analysis of hydroamination reactions: (a) Couce-Rios, A.; Lledós, A.; Ujaque, G. The Origin of Anti-Markovnikov Regioselectivity in Alkene Hydroamination Reactions Catalyzed by [Rh(DPEphos)]$^+$.*Chem. Eur. J.* **2016**, *22*, 9311-9320. (b) Couce-Rios, A.; Kovács, G.; Ujaque, G.; Lledós, A. Hydroamination of C–C Multiple Bonds with Hydrazine Catalyzed by N-Heterocyclic Carbene–Gold(I) Complexes: Substrate and Ligand Effects. *ACS Catal.* **2015**, *5*, 815-829. (c) Kovács, G.; Lledós, A.; Ujaque, G. Hydroamination of Alkynes with Ammonia: Unforeseen Role of the Gold(I) Catalyst. *Angew. Chem. Int. Ed.* **2011**, *50*, 11147-11151. (d) Strom, A. E.; Balcells, D.; Hartwig, J. F. Synthetic and Computational Studies on the Rhodium-Catalyzed Hy-

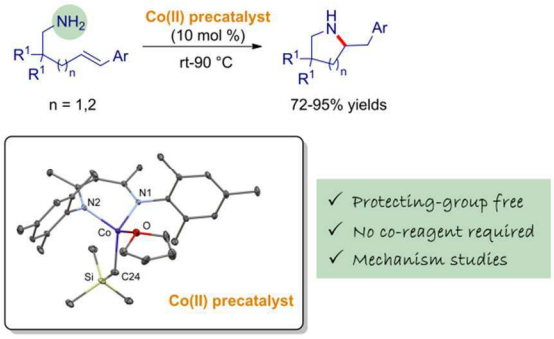
droamination of Aminoalkenes. *ACS Catal*. **2016**, *6*, 5651-5665. (e) Tobisch, S. CuH-catalysed hydroamination of arylalkynes with hydroxylamine esters – a computational scrutiny of rival mechanistic pathways. *Chem. Sci.* **2017**, *8*, 4410-4423.

(11) Optimization geometries and Gibbs energies are computed in toluene at M06 level; for Co the SDD pseudopotential along with its associated basis set, adding f orbitals, and a triple-ς basis set for the rest of atoms was employed.[6]

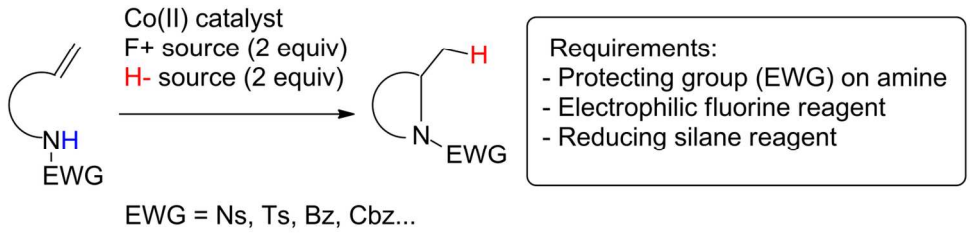
(12) Monitoring the reaction of **1a-Co** (1 equiv) and **2b** (2 equiv) at 90°C by ^{1}H NMR experiments reveals full disappearance of the methyl signals of CH_2SiMe_3 fragment of **1a-Co** in less than 10 minutes. Additionally, no induction period was noticed under catalytic conditions.[6]

(13) This dimer is also generated under stoichiometric reaction conditions.

Insert Table of Contents artwork here

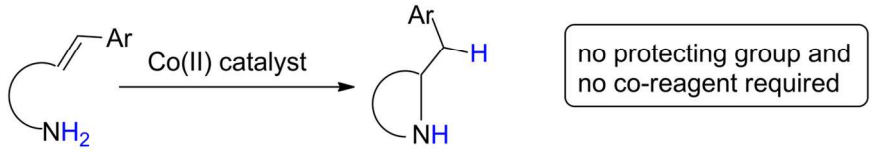


(a) **Previous work** - formal hydroamidation by reductive-oxidative cycle



EWG = Ns, Ts, Bz, Cbz...

(b) **This work** - first Co-catalyzed hydroamination



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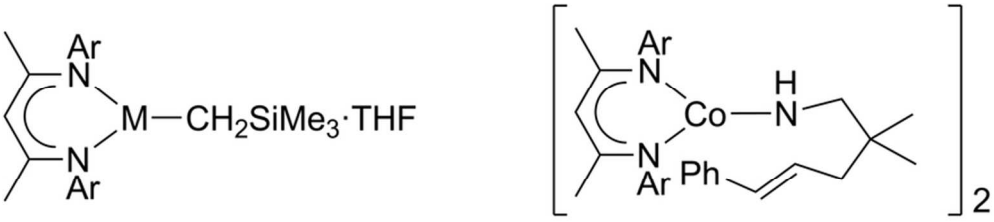

Ar = 2,4,6-$(Me)_3C_6H_2$

1a-Fe (M = Fe); **1a-Co** (M = Co) **[1b-Co]$_2$**

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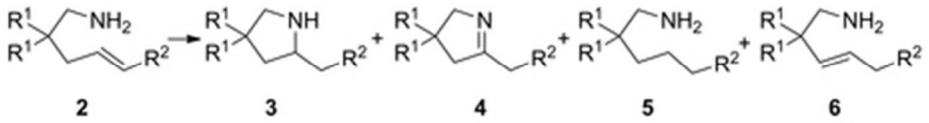

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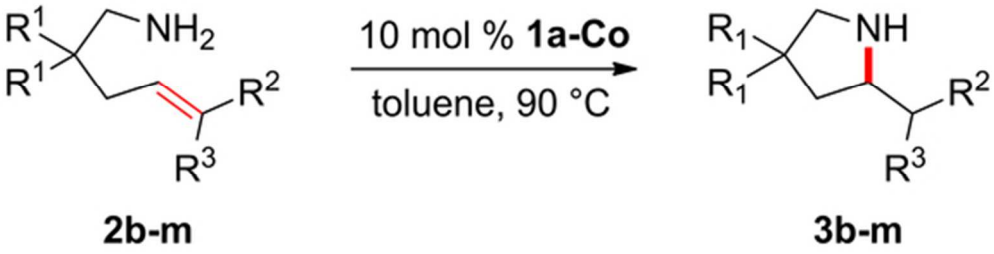

2b-m **3b-m**

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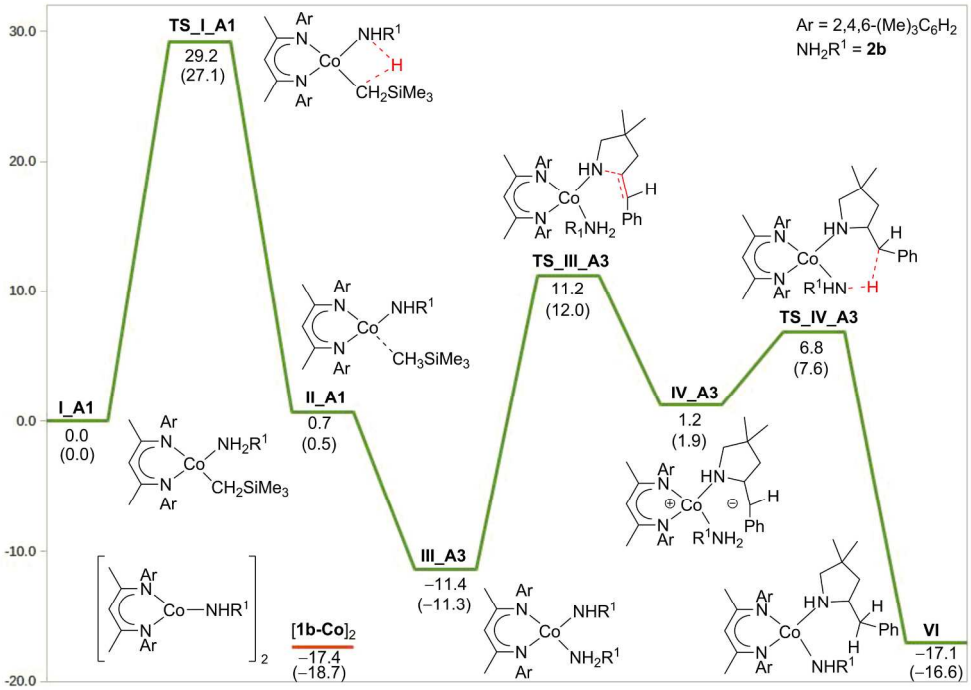

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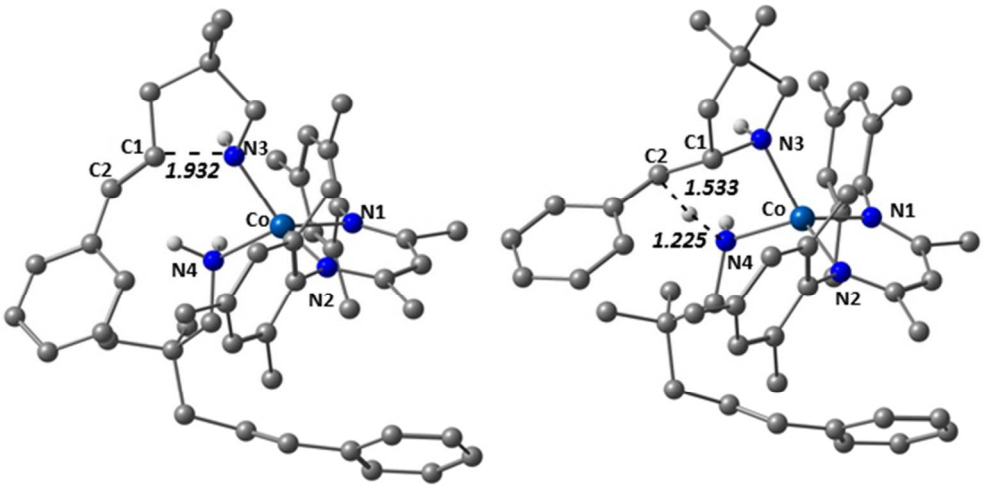
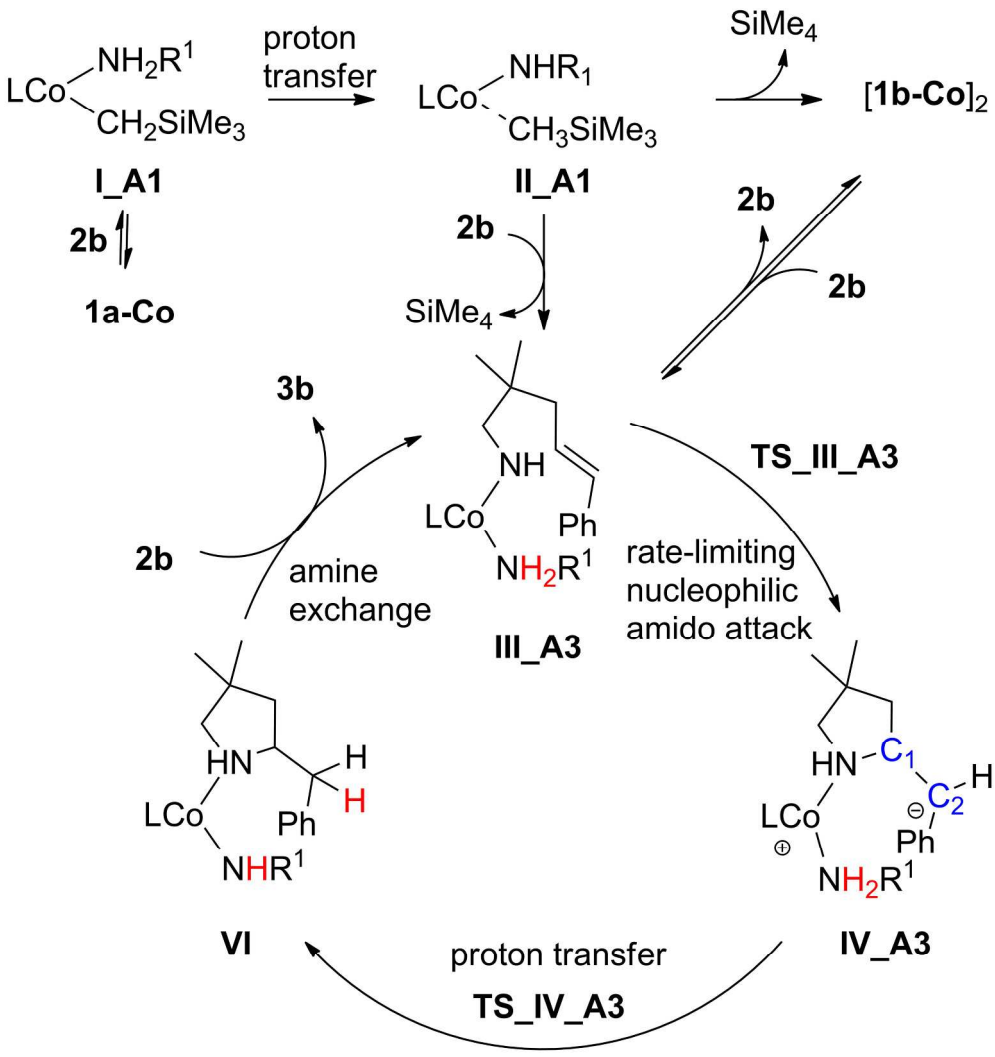


Figure3

174x84mm (96 x 96 DPI)



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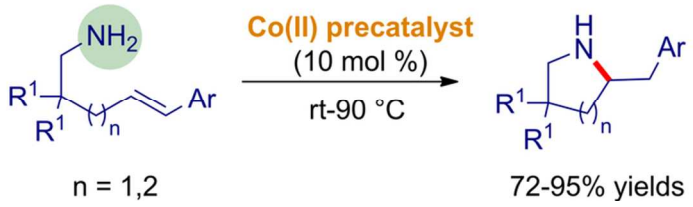
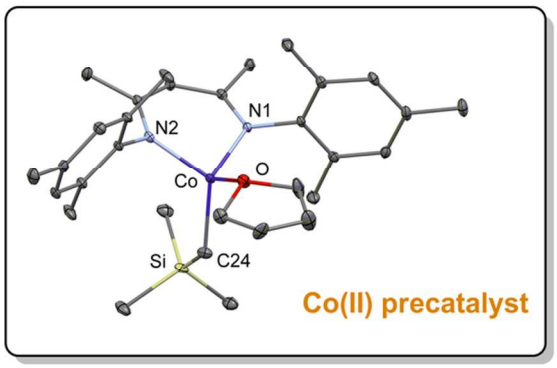


n = 1,2

72-95% yields



- ✓ Protecting-group free
- ✓ No co-reagent required
- ✓ Mechanism studies

TOC

44x27mm (600 x 600 DPI)