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Phosphine-free cobalt pincer complex catalyzed Z-selective semihydrogenation of unbiased alkynes^{\dagger}

Received 00th January 20xx, Accepted 00th January 20xx Vinod G. Landge,^a Jayaraman Pitchaimani,^b Siba P. Midya,^a Murugan Subaramanian,^a Vedichi Madhu,^{b,*} and Ekambaram Balaraman^{a,*}

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Here, we report a new, molecularly defined NNN-type cobalt pincer complex catalyzed transfer semi-hydrogenation of unbiased alkynes to Z-selective alkenes. This unified process is highly stereo-, and chemo-selective and exhibits a broad scope as well as wide functional group tolerance. Ammonia-borane (AB), a benchstable substrate with high gravimetric hydrogen capacity was used as a safe and practical transfer hydrogenating source.

Catalytic hydrogenation of unsaturated compounds is a fundamental synthetic transformation, finding application in the agrochemical, pharmaceutical, and commodity chemical industries.¹⁻² The hydrogenation of alkyne, in general, bears the dual challenge of product- (E/Z-isomerisation and overreduction) and stereo-selectivity. Thus, a stereoselective semihydrogenation of alkynes under mild conditions is a grand challenge.^{2a} The majority of the efficient homogeneous catalytic (transfer)hydrogenation reactions depend on the precious and less abundant 4d and 5d transition-metals.² Indeed, one of the major goals in transition-metal catalysis is the replacement of expensive precious metals by cheap, lowtoxic, and abundant base metals for similar or better reactivity.³⁻⁴

In recent times, notable progress has been made employing well-defined soluble cobalt complexes in various (de)hydrogenation reactions.⁴⁻⁷ In particular, cobalt catalysts have been reported in the hydrogenation reactions of olefins, ^{4,5a-e,5o} ketones, ^{5a,5f} imines, ^{5a} nitriles, ^{5n-o} esters, ^{5k-1,5u} carboxylic acids, ^{5l} CO₂, ^{5b,5e,5m,5t} and *N*-heterocycles. ^{5s} Importantly, it should be noted that the molecularly-defined cobalt catalysts mainly used in the (de)hydrogenation reactions have possessed (electron-rich)phosphine ligands.

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^b Department of Chemistry, Karunya University, Coimbatore - 641 114, INDIA. †Electronic Supplementary Information (ESI) available: [details of experimental Despite the tremendous success of phosphine ligands in homogeneous catalysis, they have encountered common drawbacks. This includes their preparation often with far from trivial methods, multi-step syntheses, handling under an inert atmosphere, etc., As a consequence, the phosphine ligands are expensive and potentially challenging to make on a large scale.⁸

Very recently, transfer semihydrogenation of alkynes to Z- and E-alkenes catalyzed by PNP and NNP-Co(II) pincer complexes, respectively derived from an electron-rich phosphine ligand was reported by the research group of Liu and Luo.⁹ Subsequently, Fout and co-workers developed an elegant (^{Mes}CCC)Co-(H₂)(PPh₃) cobalt(II) complex, for the semihydrogenation of internal alkynes with E-selectivity using molecular H₂ as the hydrogen source.¹⁰ Based on this report, Zhang and Dong reported cobalt-catalyzed (in situ generated from Co(II) salt, NaBH₄, and ethylenediamine) Z-selective semihydrogenation of internal alkynes under 3 bar of H₂ pressure.¹¹ In all the above approaches, only internal alkvne was employed for hydrogenation reactions. However, hydrogenation of terminal alkynes and olefins has not been investigated. Here, we have now prepared air-stable, easy to synthesize, NNN-cobalt(II) pincer complexes I-III (Figure 1a). Remarkably, these phosphine-free Co(II)-complexes efficiently catalyze the transfer semihydrogenation of unbiased internal alkynes to Z-alkenes using ammonia-borane as a transfer hydrogenating source. These reactions operate under mild, neutral, additive and/or base-free conditions,¹² as well as without the need of any special high-pressure equipment.

Our interest in catalytic hydrogenation began with the discovery of new, bench-stable, phosphine-free cobalt pincer complexes. The reaction of the tridentate ligand, Py-NNN with CoBr₂ in MeOH at room temperature results in the corresponding Py-NNN cobalt(II)-pincer complexes in excellent yields.¹³ Complexes I-III were characterized by HRMS, IR, and UV analysis. NMR analysis of I showed peaks at δ = 84 (s), 44.4 (br.s), 24.0 (s), and -29.9 (br.s) and strongly indicates the paramagnetic nature. The structure of I was confirmed by a single-crystal X-ray diffraction study (Figure 1b).

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procedure, characterization of compounds and copy of NMR data]. See DOI:10.1039/x0xx00000x

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Figure 1. (a) PyNNN-Cobalt(II)-complexes used for the present study. (b) X-ray crystalstructure analysis of I with 50% probability of thermal ellipsoids. Selected bond length $[A^{\circ}]$ and angle $[^{\circ}]$: Co(1)-N(1) 2.529(3), Co(1)-N(2) 2.026(3), Co(1)-N(3) 2.351(3), N(1)-Co(1)-N(2) 73.11(12), N(3)-Co(1)-N(2) 77.11(12) N(1)-Co(1)-N(3) 150.03(11), Br(1)-Co(1)-Br(2) 113.89(3). CCDC no: CCDC 1557308.

In a typical experiment, the reaction of diphenylacetylene (1a), ammonia-borane (AB),¹⁴⁻¹⁶ and a catalytic amount of Py-PNN cobalt complex (I) afforded only the Z-isomer 2a (94% yield) with the complete conversion of 1a (see ESI for optimization). Analogous Co(II)-complexes II and III showed similar activity and stereoselectivity. Gratifyingly, the cobalt complexes have been readily activated in the presence of AB without any additional sensitive additives, and the reaction operates under mild, neutral conditions. It was well-known that borane reagent forms [Co]-H species, an active catalyst in the hydrogenation reactions.^{10,17} With the optimized conditions in hand, we examined the transfer hydrogenation of various internal alkynes (Table 1). The symmetrical alkynes contain fluorine (1b) and methoxy (1c) groups and gave the partialhydrogenated products in 53% and 77% yields, respectively with complete Z-selectivity. Remarkably, a sterically hindered unsymmetrical alkyne (1e) was hydrogenated and gave only the Z-alkene 2e in 69% yield. Interestingly, halogenated (-Cl and -Br) diaryl alkynes are highly compatible with our present catalytic system. Various functional groups such as trifluoromethyl, cyano, nitro, and ester were highly tolerated and offered the corresponding alkenes with the complete Zselectivity (products 1h in 36%, 1i in 35%, 1j in 83%, 1k in 33%, and 11 in 90% yields). Furthermore, substrates featuring pyridyl, and thiophenyl (1m-1n), which are difficult to hydrogenate due to their coordinating ability to the metal center also exhibited good yields with excellent Z-selectivity under regular reaction conditions. Acyclic aliphatic alkynes 10 and 1p smoothly underwent hydrogenation reaction and yielded the corresponding alkenes **2o** in 99% (Z/E : 93:7), and 2p in 91% (complete Z-selectivity) yields, respectively. Significantly, alkynes featuring a hydroxyl group 1q were also formed and gave the Z-alkene in 52% yield. The hydrogenation of 1r led to the desired 2r in 84% with 1:1 of Z/E selectivity. The semihydrogenation of alkyne 1s, which would deliver a Zvinylsilane, is highly important since vinylsilanes are indispensable compounds in organic synthesis.¹⁸ Thus, upon employing trimethylsilyl group (1p and 1s), the reaction proceeded with complete Z-selectivity, and the silvl group remained intact under these conditions, whereas acidic conditions employed in a Pd-catalyzed alkyne reduction¹⁹ resulted in cleavage of the TMS group. Thus, our approach provides an efficient, and stereoselective access to vinylsilane under mild conditions. Notably, unactivated alkynes such as 4octyne (**1t**), and (*R*)-*N*-benzyl-*N*-(1-phenylethyl)but-2-yn-1amine (**1u**) also efficiently proceeded and gave the corresponding alkenes in good yields with excellent *Z*selectivity.

Table 1. Scope of internal alkynes.^a



^{*a*} Reaction conditions: **1** (0.5 mmol), ammonia-borane (AB) (0.6 mmol), and 4.0 mol % **I** in 1 mL of MeOH at 80 °C for 14 h and GC yields of alkenes with *Z/E* ratios are shown. ^{*b*} Isolated yield. ^{*c*} 50 °C for 12 h. ^{*d*} 0.8 mmol of AB was used. ^{*e*} AB (0.5 mmol) and 2 mol% **I** was used. ^{*f*} Complete hydrogenated product (28% in case of **1m** and 16% in case of **1r**) was observed. ^{*g*} reaction time is 30 min.

Importantly, we were able to extend our system further to include terminal alkynes (Table 2). Thus, the hydrogenation of diverse terminal alkynes was tested under optimized conditions. Substituted terminal alkynes such as methoxy, *N*,*N*-dimethylamine, fluoro, and chloro were smoothly underwent transfer hydrogenation and afforded the corresponding alkenes in excellent yields. Aliphatic terminal alkyne **4f** underwent hydrogenated alkene. In most cases, no alkane (or a trace amount) formation was detected. Interestingly, the competitive hydrogenation experiment of alkyne and alkene

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under optimized conditions showed that alkyne reacts much faster than alkene.¹³ This result may suggest that the alkyne favours the insertion reaction with the Co-H complex (see ESI). Table 2. Scope of terminal alkynes.^a



^a Reaction conditions: **4** (0.5 mmol), AB (0.6 mmol), and 2 mol % I in 1 mL of MeOH at 50 °C for 8 h and yields of alkenes are calculated based on GC analysis.

Based on this study, we were able to further extend our system for the step-temperature of switching chemoselectivity in the hydrogenation reactions (Scheme 1).



To our delight, styrenes bearing a range of electron-donating as well as electron-withdrawing substituents were hydrogenated to the corresponding alkanes in excellent yields (up to 99% yield) at the higher reaction temperature (80 °C) and longer reaction time (Table 3). However, disubstituted alkenes fail to give the hydrogenated product under regular conditions.

Table 3. Cobalt-catalyzed hydrogenation of terminal alkenes.^a



^a Reaction conditions: **4** (0.5 mmol), AB (0.6 mmol), and 4 mol % I in 1 mL of MeOH at 80 °C for 14 h and yields of alkanes are calculated based on GC analysis.

Encouraged by high chemoselectivity for this cobalt-catalyzed semihydrogenation of alkynes to alkenes, we believe the removal of alkyne impurities from alkenes is promising for the chemical industry.²⁰ In this context, a mixture of alkyne **1d** and an excess of *cis*-alkene **2a** (**1d/2a**: 1/100) was exposed under optimized reaction conditions. Notably, alkyne was selectively hydrogenated to **2d** with the complete conversion of **1d** (Scheme 2).



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To gain insight into the reaction mechanism, control experiments, and deuterium-labeling studies were performed under standard reaction conditions (Scheme 3).¹³ Initially, the dehydrogenation product of AB was investigated. Under the standard reaction conditions, AB was completely converted to $B(OMe)_3$, which is the only detected boron compound by ¹¹B NMR analysis, along with the generation of semihydrogenated product 2a and H_2 gas (by gas chromatography analysis). Control experiments showed the dehydrogenation of AB (in absence of 1a) delivered B(OMe)₃ and dihydrogen²¹ with the complete conversion AB (by ¹¹B NMR).¹³ However, in the absence of the Co(II) precatalyst, the dehydrogenation of AB is very low. Deuterium-labeling experiments were carried out to verify the hydrogen source of the hydrogenated product. Notably, in absence of AB, no formation of hydrogenated product was observed. This proves that methanol was not the reductant. However, when CD₃OD was used as the solvent, the monodeuterated 2a-[D] was isolated. These results, therefore, demonstrated that methanol mediates the protonation of the alkenyl cobalt intermediate. It is noteworthy that no isomerization of cis-stilbene 2a to trans-stilbene 3a was observed under standard conditions (a trace amount), thereby highlighting the importance of present Py-NNN-Co(II) catalytic system with the NNP-Co(II) system.9 The competitive experiment of electronically diverse alkynes (-F vs -OMe) showed that electron-rich alkynes react faster than electrondeficient alkynes. This result may suggest that the electronrich alkyne favors the alkyne insertion reaction with the intermediate Co-H complex.



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In summary, we have demonstrated the general, efficient stereo-, and chemo-selective semi-hydrogenation of alkynes to produce *Z*-alkenes. These reactions proceed under phosphine-free, additive and/or base-free conditions using a new, well-defined NNN-type cobalt pincer catalyst and ammonia-borane as a practical hydrogen source. This unified process exhibits a broad scope (aliphatic, aromatic and chiral alkynes) as well as wide functional group tolerance, such as halides, alcohol, acetal, amine, ether, nitrile, nitro, ester and heterocyclic motifs. Finaly, the present convenient method was applied for the selective removal of alkyne impurities from alkenes.

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Catalytic partial hydrogenation of alkynes to configurationally defined alkenes is a key transformation in the bulk and fine chemical production. Indeed, it remains a crucial application of industrial synthesis, in part due to the control of selectivity that is viable only through judicious catalyst design. Herein, we report a new, molecularly defined NNN-type cobalt pincer complex catalyzed semi-hydrogenation of unbiased alkynes to Z-selective alkenes. The reaction proceeds readily at a lower temperature (50–80 °C), phosphine ligand-free, and base-free conditions, with no additive being required.

