Catalytic hydrogenation of terminal alkenes by a (PPP) pincer-ligated cobalt(II) complex.

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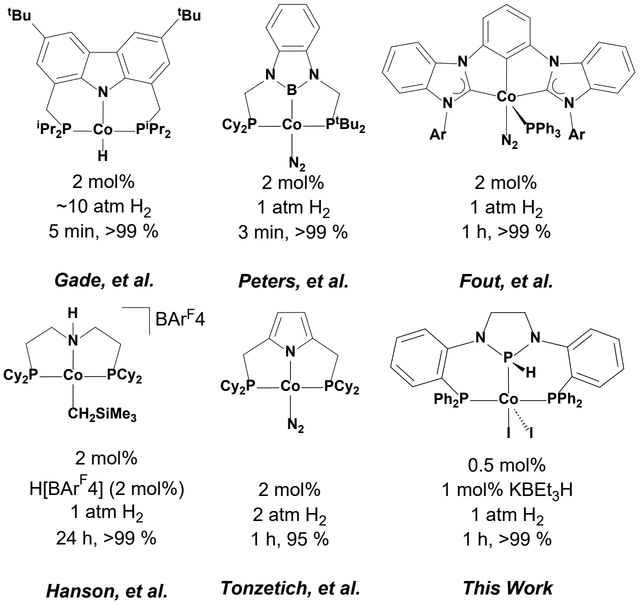
ABSTRACT: A Co(II) complex, $(PP^{H}P)CoI_2$, was synthesized and evaluated as a pre-catalyst for the hydrogenation of terminal alkenes under mild conditions (1 atm H_2, ambient temperature) using $KBEt_3H$ as an activator. This catalytic system was found to be active for terminal alkene substrates, including 1,1'-disubstituted alkenes, and to exhibit modest air and moisture stability. A preliminary investigation into substrate scope and functional group tolerance was performed. Upon the completion of catalytic reactions, the sole metal complex observed was identified as the dimeric species $[(PPP)CoH]_2$ suggesting that the catalytically active species may be a cobalt hydride monomer.

The catalytic hydrogenation of unsaturated C–E (E = C, O, N) bonds by homogeneous transition metal complexes has been extensively studied, predominately using complexes that feature precious transition metals.[1,2] These complexes have been iteratively improved in their catalytic activities and functional group tolerances via detailed structure/activity correlation studies into the influence of different metal centers and ligand environments on catalytic turnover. Within this expansive field, the hydrogenation of terminal olefins has emerged as an important reaction in and of itself and therefore has been extensively studied. Motivated by both economic and environmental considerations, there has been a drive to replicate and expand on the reactivity of precious metal catalysts with Earth-abundant first-row transition metal complexes as catalysts for olefin hydrogenation.[3–11] However, there are a variety of challenges associated with this goal, most notably that there have been fewer detailed investigations of the reactivity and mechanisms of first-row transition metal catalysts.[12] Complexes that feature cobalt(I) or cobalt(II) centers supported by pincer ligands have emerged as an important class of olefin hydrogenation catalysts in their own right (Chart 1).[13,14] In particular, work by Chirik,[4,15–17] Hanson,[18] Lu,[19,20] Jones,[21] Fout,[22] Gade,[23] Tonzetich,[24] Anderson,[25] Huang,[26] and Peters[27,28] has demonstrated the utility of pincer-ligated cobalt complexes to efficiently catalyze olefin hydrogenation at room temperature with low catalyst loading.

In prior work, our group reported facile H_2 activation by the formally Co(I) complex, $(PPP)Co(PMe_3)$;[29] however, attempts to use this complex as a catalyst for olefin hydrogenation were unsuccessful. Instead, we developed a protocol for the *in-situ* activation of a Co(II) complex, $(PP^{Cl}P)CoCl_2$, with $KBEt_3H$ to generate an active catalyst for the room temperature hydroboration of terminal olefins.[30] This catalytic system displayed short reaction times and high selectivity for the anti-Markovnikov hydroboration products. With this catalytic activity demonstrated, we sought to explore olefin hydrogenation reactions using a similar Co(II) pre-catalyst. Herein, we report the synthesis of a pincer-ligated Co(II) complex featuring a central N-heterocyclic phosphine and demonstrate its catalytic activity for the hydrogenation of terminal olefins.

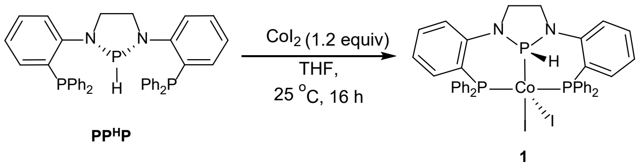
Chart 1. Representative examples of cobalt catalysts for alkene hydrogenation and their catalytic activity for the hydrogenation of styrene at room temperature.



Addition of the N-heterocyclic phosphine-containing pincer ligand, $PP^{H}P$,[31] to CoI_2 (1.2 equiv) in THF results in the precipitation of a dark yellow solid, $(PP^{H}P)CoI_2$ (**1**) (Scheme 1). Similar to $(PP^{Cl}P)CoCl_2$, the ^1H NMR spectrum of Co^{II} complex **1** contains 10 broad paramagnetically shifted resonances. The solid-state structure of **1** confirms the proposed formulation, wherein a CoI_2 fragment is ligated by the pincer ligand with the

P-H bond of the central NHP-phosphorus atom intact (Figure 1). The coordination geometry of the cobalt center is distorted square pyramidal ($\tau_5 = 0.40$). Although the poor solubility of **1** prevented an Evans' method solution magnetic moment measurement, we posit that the **1** adopts an $S = \frac{1}{2}$ spin state in accordance with the analogous $(PP^{Cl}P)CoCl_2$ compound.[29]

Scheme 1. Synthesis of $(PP^{H}P)CoI_2$ (**1**).



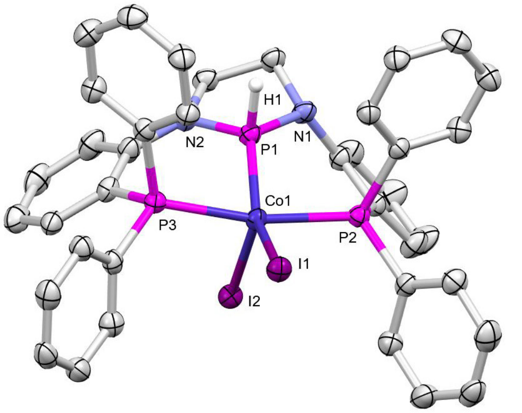


Figure 1. Displacement ellipsoid (50%) representation of **1**. For clarity, all hydrogen atoms except for the P-H moiety, disorder of the amine backbone, and a dichloromethane molecule have been omitted. Relevant interatomic distances (Å): Co1-P1: 2.0842(16), Co1-P2: 2.2177(17), Co1-P3: 2.2283 (17), P1-H1: 1.31(4), P1-N1: 1.680(5), P1-N2: 1.705(5).

With **1** in hand, we sought to explore its utility as a pre-catalyst for the hydrogenation of styrene using $KBEt_3H$ as an activator. In the absence of substrates, **1** reacts with $KBEt_3H$ to produce the previously reported dimeric species $[(PPP)CoH]_2$,[32] which was previously shown to be inactive for hydroboration catalysis and is likewise inactive towards styrene hydrogenation (Table S1 and Figure S17).[30] Thus, it was necessary to prevent the formation of $[(PPP)CoH]_2$ by preventing the reaction between **1** and $KBEt_3H$ prior to the addition of H_2. This was accomplished by combining **1** (2 mol%) and styrene in C_6D_6 in a Schlenk tube under a nitrogen atmosphere, freezing the reaction vessel with liquid N_2, replacing the headspace with 1 atm of H_2, and introducing $KBEt_3H$ (4 mol%) to generate the catalytically active species *in-situ*. The reaction mixture was allowed to warm to room temperature and stirred for 90 minutes; during which time, the color of the solution proceeded from green to a deep red coloration, indicating the formation of the catalytically inactive dimer $[(PPP)CoH]_2$.[32] The reaction mixture was then analyzed by GC-MS and ^1H NMR spectroscopy revealing ethylbenzene as the sole organic product. In the ^1H NMR spectrum, there are resonances at 3.69 and 3.29 ppm and a broad resonance at -8.32 ppm that correspond to the methylene backbone protons of the NHP pincer ligand and the cobalt hydride of $[(PPP)CoH]_2$ (Figure S19).[32] The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture unambiguously confirms that $[(PPP)CoH]_2$ is the sole metal-containing product (Figure S20).

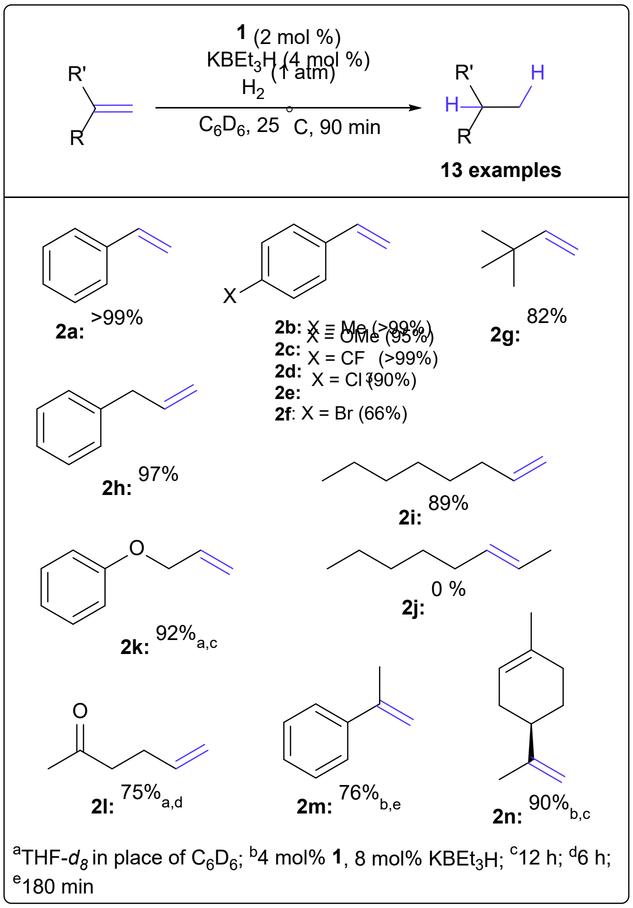
Next, we sought to further probe and optimize the catalytic alkene hydrogenation conditions using styrene (**2a**) as a model substrate (Table S1). Although our initial screening involved careful exclusion of air and moisture, it was quickly discovered that catalysis was not significantly impacted by the deliberate addition of small quantities of air or water, with hydrogenation proceeding to completion in the presence of either. The $(PP^{H}P)CoI_2/KBEt_3H$ system, therefore, exhibits appreciable stability towards adventitious exposure to atmospheric contamination. Indeed, when the hydrogenation reactions were performed under less rigorous conditions using round bottom flasks and rubber septa, 1 atm of H_2 could easily be introduced via balloon with no significant impacts to reaction outcome. Even at very low catalyst loading (ca. 0.1-0.5 mol%), it was possible to achieve yields >90% for the reduction of **2a** to ethylbenzene with prolonged reaction times. However, as our goal was to develop a catalytic system that demonstrated both ease-of-use and widespread application, we decided on a catalyst loading of 2 mol% for our further studies. It was found that this loading offered higher yields across our examined substrate scope without requiring the use of specialized glassware to establish rigorously air and moisture free conditions.

The molecular/homogeneous nature of the *in situ*-generated hydrogenation catalyst was next probed using a series of control reactions (Table S1). In the absence of either **1** or $KBEt_3H$, no catalytic activity was observed (Table S1). Catalysis was not found to be hindered by the addition of metallic mercury, supporting a homogeneous reaction. More convincingly, we found that catalysis was halted entirely by the addition of PMe_3 (Figure S16), which is consistent with previous observations that alkene hydroboration is halted by the formation of the catalytically inactive species $(PP^{H}P)Co(H)(PMe_3)$[29] upon addition of PMe_3 to an in-progress hydroboration reaction using the $(PP^{Cl}P)CoCl_2/KBEt_3H$ system.[30]

With our optimal catalytic conditions in hand, we sought to explore a wider substrate scope (Chart 2) to determine the capabilities and limitations of our catalytic system. Variously 4-substituted styrene derivatives (**2b-2f**) were screened. 4-methylstyrene (**2b**, >99%), 4-methoxystyrene (**2c**, 95%), 4-trifluoromethylstyrene (**2d**, >99%), and 4-chlorostyrene (**2e**, 90%) were all readily reduced under standard conditions in 90 minutes; only 4-bromostyrene (**2f**, 66%) failed to provide the reduced product in high yields, requiring the reaction to be kept cold to achieve modest conversion, which is most likely a result of the more easily activated C-Br bond of **2f**. The terminal alkene of 3,3-dimethylbutene (**2g**), 3-phenylpropene (**2h**), and 1-octene (**2i**), are reduced in high yield to the corresponding alkanes 3,3-dimethylbutane (82%), propylbenzene (97%), and octane (89%), respectively. In the case of substrates that were capable of chain-walking, such as **2h** and **2i**, a small quantity of the internal olefin products of chain-walking were detected. Attempts to hydrogenate internal olefins such as trans-2-octene (**2j**) afforded no reduction products, even at elevated hydrogen pressures (ca. 3 atm). Interestingly, some substrates, such as allylphenylether (**2k**) and 5-hexen-2-one (**2l**) failed to afford the reduction products in satisfactory yield when using C_6D_6. Using

THF-d_8 as the reaction solvent, however, enabled the conversion of **2k** to propylphenylether (92%) and **2l** to 2-hexenone (75%) with longer reaction times. Hoping to demonstrate the reduction of a more sterically encumbered 1,1'-alkene, we chose to investigate the hydrogenation of α-methylstyrene (**2m**). Initially, reduction of **2m** resulted in a maximum yield of 37% under our standard protocol in 90 minutes. Allowing the reaction to proceed for a total of 3 hours provided a modest increase in yield (50%). However, increasing the catalyst loading (4 mol% **1**, 8 mol% $KBEt_3H$) and stirring for 3 hours was found to provide the greatest conversion of **2m** (76%). The conversion of **2m** to isopropylbenzene was found to be insensitive to solvent (THF/C_6D_6) or gentle heating (40 °C) over 3 hours. The related 1,1'-substituted alkene substrate, limonene (**2n**), bearing both internal and terminal olefins was noted to react slowly at the terminal olefin, requiring 4 mol% **1** and 12 hours of stirring to afford 1-methyl-4-propan-2-ylcyclohexene (90%).

Chart 2. Substrate scope and general conditions for the hydrogenation (rt, 1 atm H_2) of variously substituted olefins using **1** (2 mol %) in the presence of $KBEt_3H$ (4 mol%) as an activator.



[a]THF-d_8 in place of C_6D_6; [b]4 mol% **1**, 8 mol% $KBEt_3H$; [c]12 h; [d]6 h; [e]180 min

Comparing the catalytic activity of the **1**/$KBEt_3H$ system to previously reported cobalt catalysts for olefin hydrogenation reveals that the low catalyst loading, mild conditions (1 atm H_2, rt), and short reaction times are comparable to the best-known systems (Chart 1). However, the sluggish activity of **1**/$KBEt_3H$ towards 1,2-disubstituted alkenes at room temperature is a notable limitation.[15,17,18,22] It may be possible, however, to devise a more active catalyst for more challenging substrates through modification of the ligand framework and a structure/activity relationship study is therefore underway. Our previous work on the activation of molecular hydrogen across the Co-P bonds in a related (PPP)Co complex suggests that metal-ligand cooperativity may play a role in the activation of H_2, raising questions about the catalytically active species and mechanism for catalytic turnover reported herein.[29] Based on the identification of the inactive dimer, $[(PPP)CoH]_2$, at the end of catalytic reactions, we hypothesize that the catalytically active species is a monomeric Co hydride species. However, further experimental and computational mechanistic studies will be required to further investigate the hydrogenation mechanism and determine the identity of the active catalyst and whether metal-ligand cooperation is involved.

In summary, the Co^{II} pincer complex $(PP^{H}P)CoI_2$ (**1**) effectively catalyzes the hydrogenation of terminal olefins when activated with $KBEt_3H$. Styrene derivatives and a variety of other terminal olefins are hydrogenated with good to excellent yields at a low catalyst loading (2 mol %) and under mild conditions (1 atm H_2, rt, 90 min). Under the optimized conditions, the only metal-containing product that was spectroscopically observed at the end of catalysis was the dimeric species $[(PPP)CoH]_2$, strongly implicating a monomeric cobalt hydride-containing species as the active catalyst. Future studies will seek to gain insight into the mechanism of this catalytic hydrogenation reaction and to leverage this hydrogenation reactivity towards a broader range of substrates.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, NMR spectra, further information about optimization of catalytic conditions, X-ray crystallography details for **1** (PDF)

Accession Codes

CCDC 2173379 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

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Notes

The authors declare no competing financial interests.

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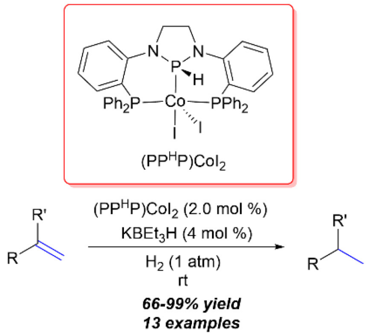
TOC Graphic


N
N
P
H
Ph2P
Co
PPh2
I
I
(PP^HP)CoI2
R'
R
(PP^HP)CoI2 (2.0 mol %)
KBEt3H (4 mol %)
H2 (1 atm)
rt
66-99% yield
13 examples
R'
R