Air-Stable #-Diimine Nickel Precatalysts for the Hydrogenation of Hindered, Unactivated Alkenes

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Air-Stable α-Diimine Nickel Precatalysts for the Hydrogenation of Hindered, Unactivated Alkenes

Nadia G. Léonard and Paul J. Chirik*

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ABSTRACT: Treatment of a mixture of air-stable nickel(II) bis(octanoate), $Ni(O_2CC_7H_{15})_2$ and α-diimine ligand, ^{iPr}DI or ^{Cy}ADI (^{iPr}DI = $[2,6^{-i}Pr_2-C_6H_3N=C(CH_3)]_2$, $^{Cy}ADI = [C_6H_{11}N=C(CH_3)]_2$) with pinacolborane (HBPin) generated a highly active catalyst for the hydrogenation of hindered, essentially unfunctionalized alkenes. A range of tri- and tetrasubstituted alkenes was hydrogenated and a bench top procedure for the hydrogenation of 1-phenyl-1-cyclohexene on a multigram scale was demonstrated and represents an advance in catalyst activity and scope for the nickel-catalyzed hydrogenation of this challenging class of alkenes. Deuteration of 1,2-dimethylindene with the in situ-generated nickel catalyst with ^{iPr}DI exclusively furnished the 1,2-*syn*-d_2-dimethylindane. With cyclic trisubstituted alkenes, such as 1-methyl-indene and methylcyclohexene, deuteration with the in situ generated nickel catalyst under 4 atm of D_2 produced multiple deuterated isotopologues of the alkanes, signaling chain running processes that are competitive with productive hydrogenation. Stoichiometric studies, titration and deuterium labeling experiments identified that the borane reagent served the dual role of reducing nickel(II) bis(carboxylate) to the previously reported nickel hydride dimer $[(^{iPr}DI)NiH]_2$ and increasing the observed hydrogenation activity. Performing the catalyst activation procedure with D_2 gas and HBPin generated both HD and DBPin, establishing that the borane is involved in H_2 activation as judged by ^1H and ^{11}B NMR spectroscopies.

Introduction.

Alkene hydrogenation promoted by transition metal catalysts is one of the most widely used chemical transformations in synthesis, both on commodity and fine chemical scale.[1] Catalysts based on precious metals, principally rhodium, iridium, and ruthenium, are routinely employed owing to their high activity, commercial availability, and ease of use.[2] The discovery of a cationic iridium complex by Crabtree[3] (Scheme 1A) for the hydrogenation of unactivated tri- and tetrasubstituted alkenes represented a major advance for the hydrogenation of this challenging class of substrates.[4] State-of-the-art catalysts now include group 4 metallocenes,[5] as well as more recently reported chiral variants of cationic iridium compounds (Scheme 1A).[6]

The increasing emphasis on sustainable and economically viable catalysts has renewed interest in mid- to late first row transition metals for hydrogenation.[7] Among these, cobalt and iron complexes have proven remarkably active for hydrogenation of alkenes.[8] Bis(arylimidazol-2-ylidene) pyridine iron bis(dinitrogen)[9] (Scheme 1B) and cobalt alkyl and hydride complexes[10] have proved to be among the most active first-row transition metal catalysts for the hydrogenation of hindered, unactivated tri- and tetrasubstituted alkenes. The multistep ligand synthesis and extreme air-sensitivity characteristic of these complexes, particularly the iron example, has inspired the search for more easily prepared and handled alternatives. The recent discovery of air-stable, readily prepared α-diimine cobalt and nickel bis(carboxylates) for alkene hydrosilylation[11] and $C(sp^3)$-H borylation[12] suggested that this class of compounds may also prove effective in alkene hydrogenation chemistry.[13]

A. State-of-the-art precatalysts for hindered alkene hydrogenation
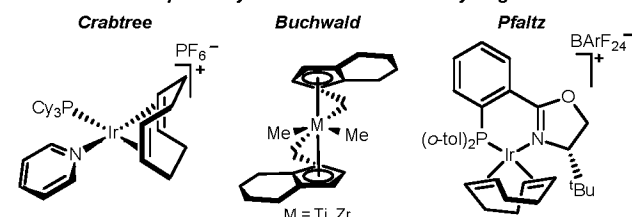
B. Prior work: iron precatalyst for hydrogenation of unactivated alkenes
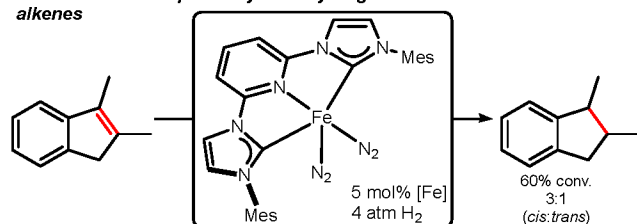
C. This work: easily accessible nickel precatalyst
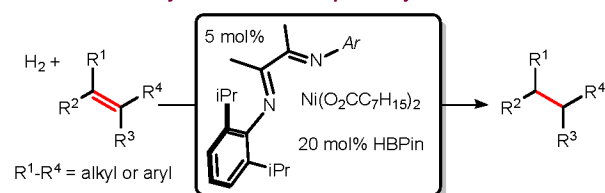
Scheme 1. Catalysts for hydrogenation of unfunctionalized, essentially unactivated alkenes.

Despite the long-standing success of heterogeneous group 10 metals, such as $Pd(C)$ or Raney nickel,[14] nickel catalysts lag behind other transition metals for alkene hydrogenation. In the case of Raney nickel, the highly pyrophoric nature of the catalyst limits its

ease of handling. Nickel(0) nanoparticles derived from $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) are active for hydrogenation of α,β-unsaturated carbonyl compounds, demonstrating that nickel compounds offer considerable promise and potential for catalytic chemistry.[15] Despite these advances, successful demonstration of molecular nickel precursors for reactions of this type remain rare.[16] Seminal studies by Bouwman and coworkers established the high activity of nickel phosphine complexes for the hydrogenation of 1-octene using 50 bar of H_2.[17] More recently, strong donor ligands or sophisticated metalloligands have been used to generate mononuclear and multimetallic nickel complexes that operate at lower (1-4 atm) pressures of H_2 with relatively simple α-olefin or 1,2-disubstituted alkenes as substrates.[18] Driess and coworkers have recently expanded the scope of nickel-catalyzed alkene hydrogenation with the demonstration that a bis(N-heterocyclic silylene)xanthene nickel(0) complex is active for the hydrogenation of a variety of terminal and sterically hindered disubstituted olefins. One example of a challenging tetrasubstituted, unactivated alkene, 2,3-dimethyl-2-butene was reported, reaching 11.5% conversion to alkane over the course of 12 hours at room temperature.[19]
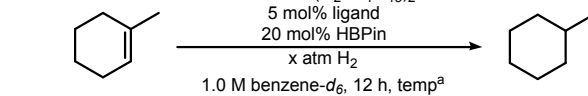
Examples of nickel-catalyzed enantioselective alkene hydrogenation reactions have also recently appeared but are limited to activated substrates bearing functional groups that likely promote interaction between the substrate and catalyst. Asymmetric transfer hydrogenation using combinations of phosphines and nickel(II) carboxylates has been reported by Zhou and coworkers for the preparation of enantioenriched amino acids.[20] Our group has reported the asymmetric hydrogenation of α,β-unsaturated esters in methanol using H_2 as the hydrogen source. A trimetallic (Me-DuPhos)$_3$Ni$_3$(OAc)$_3$I complex was identified as the catalyst resting state and mechanistic studies support heterolytic cleavage of H_2 from the carboxylate ligands.[21] Zhang and coworkers have reported the synthesis of enantioenriched β-amino nitroalkanes using similar phosphine-nickel(II) carboxylate mixtures and have also implicated heterolytic H_2 cleavage; however, the identity of the active species was not elucidated.[22] In these examples, interaction of the carbonyl group on the substrate is likely necessary to promote introduction of the alkene to the nickel.

These studies highlight the need for development of more easily handled nickel-catalyzed alkene hydrogenation methods, especially for sterically hindered substrates lacking coordinating functionality. Ziegler-type catalysts, typically prepared from mixtures of late first-row transition metal salts and trialkyl aluminum reagents, are known to promote the hydrogenation of hindered alkenes. However, the activity and selectivity of these catalysts are strongly influenced by purity of reagents used and catalytic conditions, limiting the generality of their use.[23] Here we describe a robust nickel-catalyzed method for the mild hydrogenation of unactivated tri- and tetrasubtituted alkenes arising from treatment of α-diimine and nickel(II) bis(carboxylate) mixtures with pinacolborane. This catalyst exhibits high activity, is compatible with benchtop set up, and can be applied to multigram scale reactions. Deuterium labeling studies established an unusual catalytic activation mode of H_2 by the added borane and identified chain-walking processes competitive with alkane formation.

Results and Discussion.

Catalyst Discovery and Optimization. Initial catalyst discovery efforts were motivated by the need for robust and easily handled catalysts devoid of expensive phosphines or other synthetically advanced ligands. Avoiding the use of air-sensitive organometallic components or multistep pre-catalyst syntheses was also taken into consideration. Accordingly, experiments were confined to air-stable nickel precursors and supporting ligands. Because of their availability and low cost, combinations of $Ni(O_2CR)_2$ with α-diimines were examined for the hydrogenation of methylcyclohexene with either 1 or 4 atm of H_2 (Table 1). This substrate was selected for catalyst development studies because unactivated, trisubstituted alkenes remain a relatively challenging class of substrates for many catalyst types. Each catalytic reaction was conducted in the presence of a catalytic amount of HBPin to reduce the nickel(II) bis(carboxylate) and activate the catalyst.[24] Stoichiometric experiments established that addition of four equivalents of HBPin to a 1:1 mixture of $Ni(O_2CC_7H_{15})_2$ and ^{iPr}DI at room temperature generated a blue solution signaling formation of $[(^{iPr}DI)NiH]_2$, a product ultimately confirmed by ^1H NMR spectroscopy. This compound, first reported by Yang and coworkers,[25] has also been generated from treatment of mixtures of ^{iPr}DI and nickel(II) bis(carboxylates) and silanes.[11] In situ activation in the presence of substrate was the chosen mode of activation for catalysis for simplicity and relative ease of handling. However, catalysis can also be initiated from a premixed stock solution of $[(^{iPr}DI)NiH]_2$, generated from nickel carboxylate and HBPin, which is stable in the freezer for 2 months (See SI).

Table 1. Optimization of the hydrogenation of 1-methyl-1-cyclohexene with Ni(II) octanoate-α-diimine mixtures.

| entry	ligand	x (atm)	temp (ºC)	conv. (%)
1	^{iPr}DI	4	50	>98
2	^{iPr}DI	1	50	70
3	^{iPr}DI	4	23	50
4	^{Cy}ADI	4	50	>98
5	^{Cy}ADI	1	50	60
6	^{Cy}ADI	4	23	<5
7	none	4	50	50 (24 h)

[a]Reactions conducted with 1.0 mmol of 1-methyl-1-cyclohexene in 1.0 mL of benzene-d_6 for 12 hours. Conversion determined by ^1H NMR spectroscopy using toluene as the internal standard. See SI for details and full optimization table.

Benzene-d_6 was selected as the solvent for initial catalyst evaluation studies as the progress of each reaction was conveniently monitored by ^1H NMR spectroscopy. Non-deuterated arene and alkane solvents such as toluene, hexane and cyclooctane were also compatible with the nickel-catalyzed hydrogenation procedure (See SI). Reaction conditions were optimized to balance high yield of methylcyclohexene with mild reaction conditions; ultimately, 5 mol% of ^{iPr}DI or ^{Cy}ADI and $Ni(O_2CC_7H_{15})_2$ with 4 atm H_2 at 50 ºC for 12 h (entries 1 and 4) were identified. The reaction also pro-

ceeded at 1 atm of H_2 (entries 2 and 5) or at room temperature (entry 3) albeit with reduced yield after 12 h in both cases. A control experiment in the absence of ligand (entry 7) produced 50% yield of alkane after 24 h, and continued exposure to the reaction conditions did not lead to additional hydrogenation, indicating that catalyst deactivation contibutes to the low yield observed in the absence of ligand.

With optimized conditions in hand, the generality of the hydrogenation method for a variety of substrates, including tri- and tetrasubstituted olefins, was evaluated (Scheme 2). A selection of α-olefins (**1a**, **1b**, **1c**, and **1d**) was readily converted to the corresponding alkane products under the standard conditions. Notably, **1a** reached full conversion in 1.5 hours. The ester and carbonyl containing substrates **1c** and **1f**, yielded >98% and 80% of the desired alkane, respectively, with no observed reduction of the carbonyl groups. Substrate **1e**, 1-phenyl-1-cyclohexene, was readily hydrogenated to alkane product in >98% yield in 3 hours with only 0.4 mol% nickel catalyst, corresponding to a turnover number (TON) of 250.
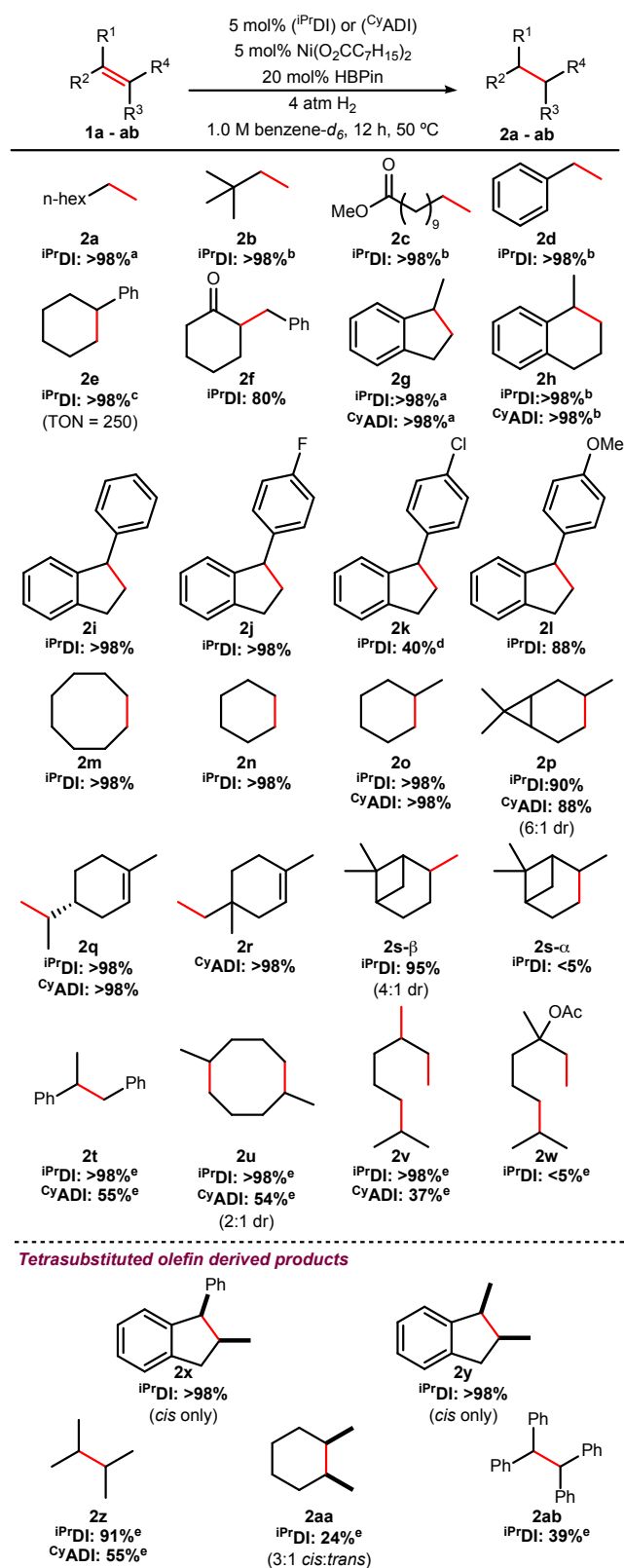
Scheme 2. Catalytic hydrogenation of unfuctionalized alkenes with an in situ activated nickel catalyst. [a]Reaction carried out for 1.5 hours. [b]Reaction carried out for 5 hours. [c]Reaction run with 0.4 mol% Ni(O$_2$CC$_7$H$_{15}$)$_2$ and [iPr]DI, and 0.16 mol% HBPin for 3 hours. [d]Unreacted starting material was recovered. [e]Reaction carried out for 24 hours.

A selection of substituted indenes (**1g**, **1i-l**) and 1-methyldialin (**1h**) underwent hydrogenation, with methylindene reaching complete conversion to **2g** in 1.5 h, highlighting the high activity of the nickel catalyst for hydrogenation of a trisubstituted alkene. Di- (**1m** and **1n**) and trisubstituted (**1o** and **1p**) endocyclic alkenes underwent hydrogenation readily and produced 90-98% yield of the desired alkane product. Interestingly, for 1,4-disubstituted cyclohexene substrates containing multiple sites of unsaturation (**1q** and **1r**), preferential reduction at the less hindered C=C double bond was observed, with no hydrogenation of the endocyclic alkene evident even at longer reaction times. This preference for exocyclic alkene hydrogenation is further demonstrated in the hydrogenation of pinene, where the β-isomer (**1s-β**) is readily hydrogenated, while attempted hydrogenation of the α-isomer (**1s-α**) yielded only trace alkane. The observed absence of reactivity for the endocyclic alkene in 1,4-disubstituted cyclohexenes likely arises from a sterically inaccessible half-chair conformer which is unable to coordinate to the nickel catalyst. In the case of carene (**1p**), the strain of the cyclopropyl ring presumably allows for the substrate to adopt a conformer enabling interaction with the nickel catalyst and results in subsequent hydrogenation.
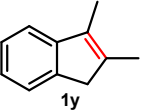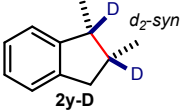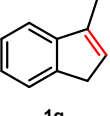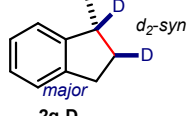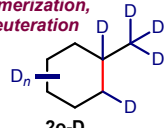
For substrates requiring 24 hours to reach completion, such as **1t**, deactivation of the nickel catalyst was observed when [Cy]ADI was used as the ligand. Formation of the previously reported and catalytically inactive bis(chelate) nickel complex ([Cy]ADI)$_2$Ni[26] was observed as one of the nickel-containing products by ^{1}H NMR spectroscopy following the hydrogenation reaction. This compound was previously identified as a deactivation product in C(sp^3)-H borylation catalysis[12] and therefore, [iPr]DI was the preferred supporting ligand for more challenging substrates that require longer reaction times.

Hydrogenation of polyenes (**1u** and **1v**) resulted in the desired complete reduction for both conjugated and nonconjugated alkenes. However, only trace amounts of **2w** were observed following hydrogenation, likely due to substrate-catalyst incompatibility. Most notably, tetrasubstituted alkenes were readily hydrogenated using the standard catalytic conditions. Disubstituted indenes **1x** and **1y** underwent hydrogenation to the *cis*-alkanes in quantitative yield after 12 hours of reaction time. Alkylated tetrasubstituted alkenes **1z** and **1aa** were also hydrogenated using [iPr]DI as the ligand with 91% yield of **2z** and 24% yield of **2aa** after 24 hours. Hydrogenation of **1z** was also achieved with [Cy]ADI as the ligand, albeit with reduced observed yield (55%) due to catalyst deactivation. Finally, the very sterically hindered 1,1,2,2-tetraphenylethylene underwent hydrogenation to the alkane in 39% yield after 24 hours.

Given the observed high activity of the nickel catalyst, the hydrogenation of 1-phenyl-1-cyclohexene was performed on multigram scale using a benchtop procedure and no specialized glassware or reactors. These studies were pursued to make the nickel-catalyzed hydrogenation accessible to a wide range of synthetic chemists. The ligand and nickel carboxylate precursors were exposed to air for three hours prior to catalysis. Following addition of ligand, nickel carboxylate, substrate and solvent, the reaction mixture was purged and placed under an atmosphere of H$_2$ delivered by balloon. HBPin was then added by syringe to activate the catalyst and the reaction mixture was stirred at 50 °C for 12 hours. Standard workup yielded 2.3 g (96%) of the desired alkane, **2e** (See SI for full details of benchtop hydrogenation). These results illustrate that hydrogenation with α-diimine supported nickel is a readily available method for hydrogenation of tri- and tetrasubstituted alkenes

that does not require a glovebox or specialized high vacuum equipment.

Catalytic Deuteration Experiments. Having demonstrated the utility of α-diimine supported nickel catalysts for alkene hydrogenation, a series of experiments was then conducted to gain insight into the mode of substrate-catalyst interaction, particularly, the origin of the *cis*-selectivity observed for the products of hydrogenation of substrates **1x** and **1y**. Deuterium labeling experiments were conducted to explore the possibility of chain running, a pathway frequently observed with α-diimine metal catalysts for alkene polymerization[27] and more recently hydroboration.[28,29] Three representative cyclic alkenes, **1y**, **1g** and **1o** were selected for these studies and the results are presented in Scheme 3.

Entry	Substrate	Product	Isotopic composition
1	**1y**	*No isomerization* d_2-*syn* **2y-D**	>90% single isotopologue (no deuterium in recovered starting material)
2	**1g**	d_2-*syn* *major* **2g-D**	6:3:2 mixture of d_2, d_1, d_3 isotopologues (deuterium in recovered starting material)
3	**1o**	*Isomerization, deuteration* **2o-D**	mixture of isotopologues (deuterium in recovered starting material)

Scheme 3. Catalytic deuteration of selected cyclic alkenes. Deuterations conducted with 1.0 mmol of substrate in 1.0 mL of benzene-d_6. See SI for details.

Exposure of **1y** to 4 atm D$_2$ under standard catalytic conditions provided the deuterated alkane in 76% yield. Analysis by ^{1}H, ^{2}H, and quantitative ^{13}C NMR spectroscopies established exclusive formation of the d_2-isotopologue with deuterium atoms in a *syn* relationship. No deuterium was observed in the recovered alkene starting material. Performing a similar experiment with **1g**, a less sterically hindered alkene, resulted in the complete conversion of the starting alkene to deuterated product. Exclusive *syn*-addition of deuterium was again observed in the alkane product; however, analysis by ^{1}H, ^{2}H, ^{13}C NMR spectroscopies and mass spectrometry revealed formation of a 6:3:2 ratio of the d_2-, d_1-, and d_3-isotopologues. Repeating this procedure where the reaction only reaches partial conversion (~40%) and analysis of the recovered alkene established deuterium incorporation in the starting material, supporting chain walking and β-hydrogen elimination to release alkene that is competitive with substrate hydrogenation. To further probe this chain-walking process, deuteration of the alkyl substituted alkene, **1o** resulted in a complex mixture of isotopologues, with deuterium incorporation observed at the methyl position as well as

at *all* positions on the cyclohexane ring as judged by quantitative ^{13}C NMR spectroscopy.

The results of the deuterium labeling studies provide insight into the role of alkene isomerization during nickel catalyzed alkene hydrogenation, a phenomenon that has been previously observed and implicated in the reaction of nickel complexes with olefins.[30, 17f, 18b,e] With the tetrasubstituted alkene **1y**, the deuteration occurs by nickel insertion into either the 1- or 2-position of the indene (Scheme 4A). The resulting tertiary nickel alkyl does not undergo β-H elimination, migration and reinsertion as evidenced by the observation of exclusive *syn* addition and absence of deuterium in any other position of the alkane or recovered alkene. While insertion at the 1-position would likely be preferred, 1,2 or 2,1 pathways are possible and indistinguishable, and leading to the same exclusive formation of *syn*-**2y-D**. The terms "1,2" and "2,1" insertion used here are based on historical usage with terminal alkenes. The 1-position of the indene ring is designated as 1 and hence "1,2" insertion refers to the case where the nickel is bound to C(1).

Removal of a methyl group from the substrate increases the rates of β-H elimination and chain running as a mixture of deuterated isotopologues was observed upon addition of 4 atm of D_2 to **1g** (Scheme 4B). As with **1y**, the major *syn* d_2 isotopologue of **2g-D** likely arises from insertion at the 1-position followed by capture with D_2 gas. A trace amount of Me-d_1-**1g** was recovered in the starting material, indicating that β-H elimination can occur from the 1,2-insertion product and corresponding to trace deuterium incorporation observed at the methyl position in **2g-D**. The formation of recovered 3-d_1-**1g** and the d_3 isotopologue of **2g-D** likely arise from insertion at the 2-position of the indene followed by β-H elimination from the 3-position. Release of the alkene, reinsertion, followed by β-H elimination accounts for 3-d_1-**1g**. Formation of *syn*-1,2,3-d_3-**2g-D** results from the addition of D_2 to 3-d_1-**1g**.
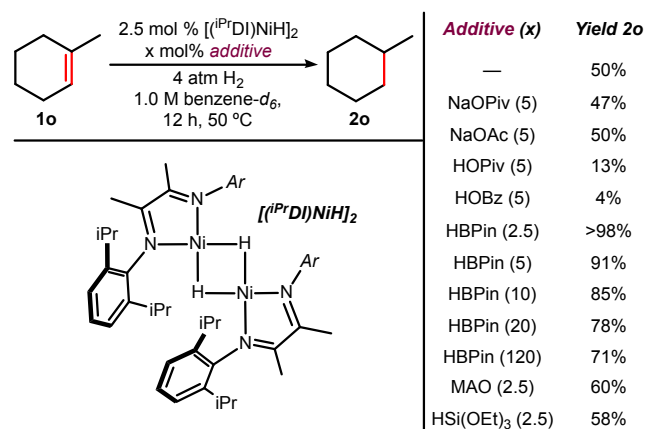
Deuteration of the purely alkyl-substituted alkene, **1o** eliminates potential ambiguity for preferential insertion at benzylic positions (Scheme 4C). The quantitative ^{13}C NMR spectrum of the product is sufficiently complex to prohibit reliable determination of the amount of deuterium incorporated into each position. Deuteration of the methyl group in **2o-D** demonstrates formation of a tertiary nickel-alkyl either from direct insertion into the more hindered position of the alkene followed by migration to the terminal position or by insertion at the less hindered carbon followed by migration. Observation of deuterium in the other positions of the ring demonstrates that migration of the nickel from the alkene positions to the terminal site is not exclusive and that intermediates where the nickel is bound at each site of the six-membered ring are formed during the catalytic hydrogenation reaction (Scheme 4C).
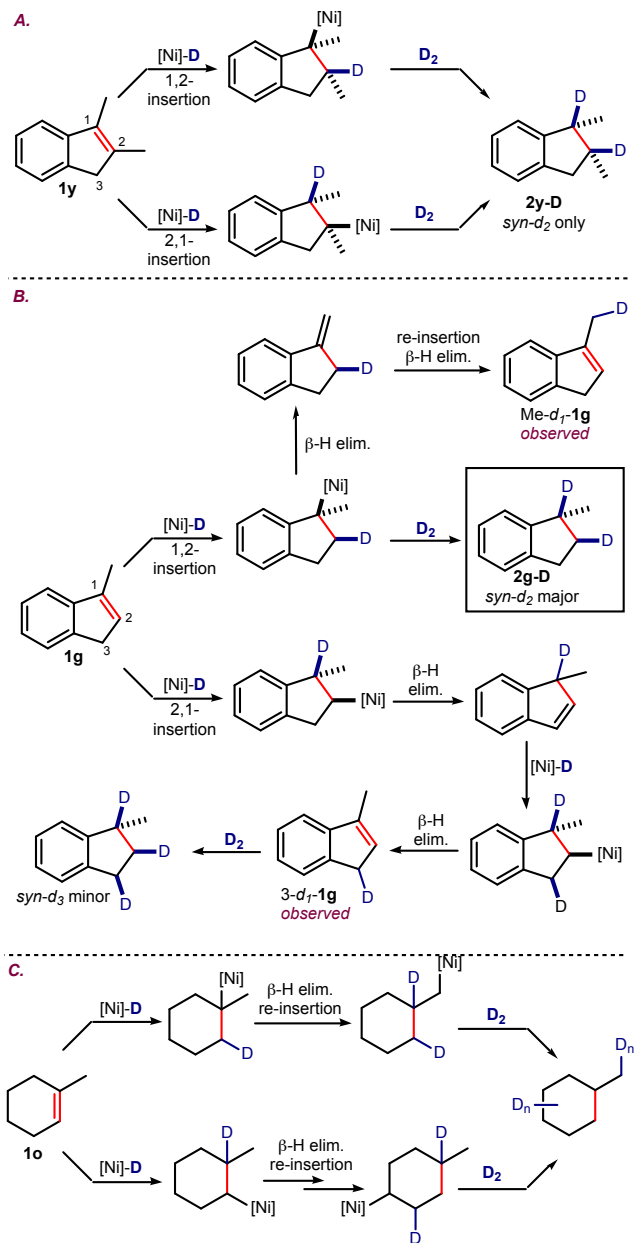
Scheme 4. Proposed alkene insertion and β-H elimination process to account for the observed deuterated alkanes and alkenes.

Insights into Catalyst Formation and the Nature of the Active Species. The success of the *in situ* activation protocol for nickel-catalyzed alkene hydrogenation prompted investigation into the activity of the well-defined α-diimine nickel hydride dimer, $[(^{iPr}DI)NiH]_2$. This compound has been previously generated by our group using mixtures of ^{iPr}DI, nickel(II) carboxylates and silanes.[11] Replacement of the silane reductant by HBPin also generated a blue solution that when analyzed by ^1H NMR spectroscopy confirmed formation of $[(^{iPr}DI)NiH]_2$. For catalytic evaluations, $[(^{iPr}DI)NiH]_2$ was prepared by reduction of $(^{iPr}DI)NiBr_2$ with sodium under an H_2 atmosphere to eliminate potential complications on hydrogenation performance arising from the presence of the borylated carboxylate byproducts.[31] Use of pure $[(^{iPr}DI)NiH]_2$ proved much less effective for hydrogenation, yielding only 50% of **2o** after 12 h, representing a marked decrease in activity in comparison to the *in situ* generated catalyst. Addition of exogenous car-

boxylate sources to $[(^{iPr}DI)NiH]_2$ did not increase the catalytic activity (Scheme 5). Additionally, monitoring a mixture of $[(^{iPr}DI)NiH]_2$ and NaOPiv under 1 atm D_2 at room temperature by ^1H NMR spectroscopy did not result in observation of HD, ruling out carboxylate-assisted heterolytic dihydrogen cleavage.[20,21,22]


	Additive (x)	Yield 2o
	—	50%
	NaOPiv (5)	47%
	NaOAc (5)	50%
	HOPiv (5)	13%
	HOBz (5)	4%
	HBPin (2.5)	>98%
	HBPin (5)	91%
	HBPin (10)	85%
	HBPin (20)	78%
	HBPin (120)	71%
	MAO (2.5)	60%
	HSi(OEt)$_3$ (2.5)	58%

Scheme 5. Effect of additives, including HBPin, on the catalytic performance of $[(^{iPr}DI)NiH]_2$. Reactions conducted with 1.0 mmol of substrate in 1.0 mL benzene-d_6. Yields determined by GC-FID or ^1H NMR spectroscopy. See SI for details.

The effect of added HBPin on the hydrogenation of **1o** with isolated $[(^{iPr}DI)NiH]_2$ was also explored to further probe the origin of the superior catalytic performance of the in situ generation method. Addition of 2.5 mol% of HBPin to the catalytic reaction increased the hydrogenation activity (Scheme 5). The performance decreases gradually with additional HBPin and at 20% mol of added borane, significant alkene hydroboration was observed (See SI for full details). Cooperative H_2 activation via boryl-, or other group 13 containing, metalloligands has been previously demonstrated with iron,[32] cobalt,[33] and nickel[18d,e] in the context of olefin hydrogenation. Additionally, oxime-directed catalytic asymmetric hydrogenation of alkenes was recently reported with rhodium catalysts, whereby stoichiometric borane was required for catalyst activity.[34] Under the catalytic conditions reported here, other main group reagents such a HSi(OEt)$_3$ and methylaluminoxane were evaluated for a similar activation effect with isolated $[(^{iPr}DI)NiH]_2$. Addition of 2.5 mol% of either methylaluminoxane (MAO) or HSi(OEt)$_3$ to $[(^{iPr}DI)NiH]_2$ under standard catalytic conditions resulted in 60% and 58% yield of methylcyclohexane, respectively (Scheme 5). These results verify that HBPin is the preferred additive for enhancing hydrogenation performance.

To investigate what role the borane is playing in activating the catalyst a series of deuterium labeling experiments were performed. Mixing a 1:1:4 mixture of ^{iPr}DI, $Ni(O_2CC_7H_{15})_2$, and HBPin at room temperature under 1 atm of D_2 and monitoring by ^1H and ^{11}B NMR spectroscopy resulted in formation of HD and DBPin, demonstrating rapid exchange between hydride ligands, free deuterium and the borane reagent (Scheme 6A). A similar experiment was conducted using isolated $[(^{iPr}DI)NiH]_2$ and DBPin at room temperature under 1 atm H_2 (Scheme 6B). Both HD and HBPin were observed by ^1H and ^{11}B NMR spectroscopies. Formation of HD from the in situ activation procedure using D_2 gas may account for some of the observed isotopologues in the deuteration of **1g** and **1o**. Monitoring $[(^{iPr}DI)NiH]_2$ under an atmosphere of D_2 in the absence of borane did not result in formation of HD (Scheme

6C). A control experiment established that the borane and D_2 did not exchange in the absence of nickel. In an additional stoichiometric experiment, mixing of $[(^{iPr}DI)NiH]_2$ with DBPin in the absence of H_2 produced no evidence for isotopic exchange even upon heating to 50 ^{o}C for 19 hours. The only species observed by ^1H NMR spectroscopy was $[(^{iPr}DI)NiH]_2$ with eventual degradation to free ligand upon prolonged heating (>24 hours). While attempts to isolate or observe nickel boryl or borane complexes have been unsuccessful, these results highlight the important role of the free gas, H_2 or D_2, on the isotopic exchange process and identify the role of the borane in H_2 (or D_2) cleavage, likely accounting for the improved hydrogenation activity over the isolated dimeric nickel hydride.
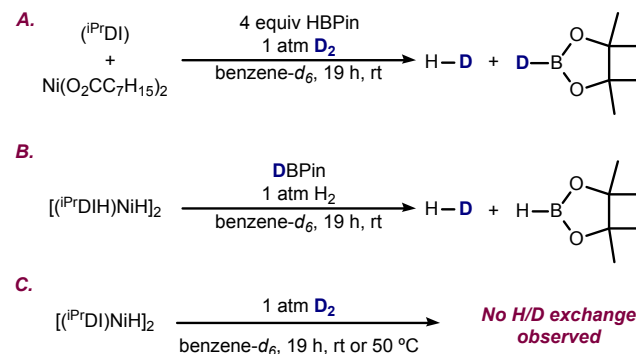
Scheme 6. Hydrogen-deuterium exchange experiments with $[(^{iPr}DI)NiH]_2$

The observed difference in activity between the two procedures also prompted kinetic experiments to establish the relative rates of hydrogenation. Details of these experiments are reported in the Supporting Information. With the in situ generated catalyst, a first order dependence on nickel was observed, suggesting that a nickel hydride, perhaps interacting with the borane, is generated following activation, and is responsible for alkene insertion and ultimately alkane formation. For the isolated nickel hydride dimer, $[(^{iPr}DI)NiH]_2$, a half order dependence on the metal precursor was observed, suggesting dissocation to a monomer is required to generate the active species during turnover. The robustness of the dimeric structure of $[(^{iPr}DI)NiH]_2$ likely accounts for the reduction in activity compared to the in situ activated catalyst or the catalyst generated upon addition of HBPin. With both catalyst generation methods, the formation of heterogeneous or soluble nickel nanoparticles cannot be discounted; we note that the catalytic reactions and the deuterium labeling experiments reported here are highly reproducible, yet "ligand-less" or higher order clusters could possibly account for the observed hydrogenation activity as well. It is possible that the role of HBPin is to activate the surface of a nanocluster to enable hydrogenation. More detailed kinetic analyses and other experiments are in progress to distinguish this possibility.

Concluding Remarks.

Readily accessed α-diimine nickel catalysts generated from air-stable metal and ligand precursors have been discovered that are active for the hydrogenation of hindered, unfunctionalized alkenes, one of the most challenging classes of olefins for hydrogenation. Successful reduction of a host of tri- and tetrasubstituted alkenes, including cyclic compounds, has been demonstrated, representing

one of the most active first row transition metal catalysts discovered to date. The nickel-catalyzed method was scaled and successfully executed with standard laboratory glassware without the need for high-pressure equipment. Deuterium labeling experiments with trisubstituted cyclic alkenes demonstrate that reversible β-hydrogen elimination and alkyl migration is operative during the hydrogenation cycle, resulting in observation of a host of deuterated isotopologues. Investigations into the nature of the active species with both the in situ generated catalyst and the isolated, dimeric precursor demonstrated the role of the borane in the activation of dihydrogen, accounting for the observed enhancement in activity upon addition of HBPin. The modularity of the α-diimine suggests that new catalyst libraries, including asymmetric variants, should be possible and investigations into these catalyst types is currently under study.

ASSOCIATED CONTENT

Supporting Information

Complete experimental details including pre-catalyst optimization studies, and characterization data for deuterated products. This material is available free of charge via the Internet at http://pubs.acs.org.

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