

Nickel Catalysis | *Hot Paper*

Heterogeneous Olefin Hydrogenation Enabled by a Highly-Reduced Nickel(–II) Catalyst Precursor

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Abstract: The hydrogenation of olefins, styrenes, enoates, imines, and sterically hindered tri-substituted olefins was accomplished using the pre-catalyst dilithiumbis(cycloocta-1,5-diene)nickelate(–II) (**1**). The mild conditions tolerate hydroxyl, halide, ester, and lactone functionalities. Mechanistic studies, including reaction progress analyses, poisoning experiments, and multinuclear NMR monitoring, indicate that a heterotopic (nickel nanoparticle) catalyst is in operation.

Olefin hydrogenation is of much industrial and academic importance as a key step in the synthesis of fine chemicals, agrochemicals, fragrances, and food additives.^[1] Precious metal catalysts (Rh, Ir, Pt, Pd, Ru) are most widely applied due to their high activity, selectivity, robustness, and ease of operation.^[2] Nevertheless, economic and environmental concern (in particular the poor crustal abundance and high cost of precious metals) have recently stimulated considerable interest in replacing noble metal catalysts by more abundant 3d metal species^[3] (e.g. with Mn,^[4] Fe,^[5] Co,^[6] and Ni^[7–17]). Over the past decade, major effort has been devoted to the development of iron and cobalt compounds as catalysts for olefin hydrogenation.^[5,6] Especially noteworthy are metal complexes with tridentate pincer ligands.^[5]

Although these developments have been fairly recent, nickel compounds have been applied in technical scale hydrogenations for many decades. Raney nickel was first reported in

1927^[7] and is still industrially used in the hardening of vegetable fats, the manufacture of vitamins, fragrances, and food additives as well as various arene functionalizations.^[8] Nickel boride (obtained from NiX₂ (X=OAc, Cl) and NaBH₄) is an effective catalyst for olefin hydrogenation.^[9] The development of more potent heterogeneous nickel catalysts continues to attract significant interest as shown by the groups of Gómez and Philippot, who reported to use of commercial [Ni(η⁴-cod)₂] (cod=cycloocta-1,5-diene) as a catalyst precursor (see Figure 1, A).^[10,11] Zhao and co-workers demonstrated that Ni⁰ nanoparticles (NPs) in ionic liquids hydrogenate α,β-unsaturated carbonyl compounds at 30 bar H₂.^[12] In addition, well-defined molecular nickel catalysts have been reported recently. The groups of Bouwman and Hanson described the hydrogenation of simple olefins with homogeneous nickel catalysts.^[13] Hazari and Driess prepared heteroleptic carbene/silylene complexes **B** and **C**, which are very active hydrogenation catalysts.^[14,15] Catalyst **D** reported by Chirik and co-workers constitutes the current state of the art in catalytic hydrogenations of sterically hindered tri- and tetra-substituted olefins.^[16] The active catalyst is assembled from the combination of nickel(II) bis(octanoate), pinacol borane, and an α-diimine ligand. Moreover, recent reports on asymmetric hydrogenations of dehy-

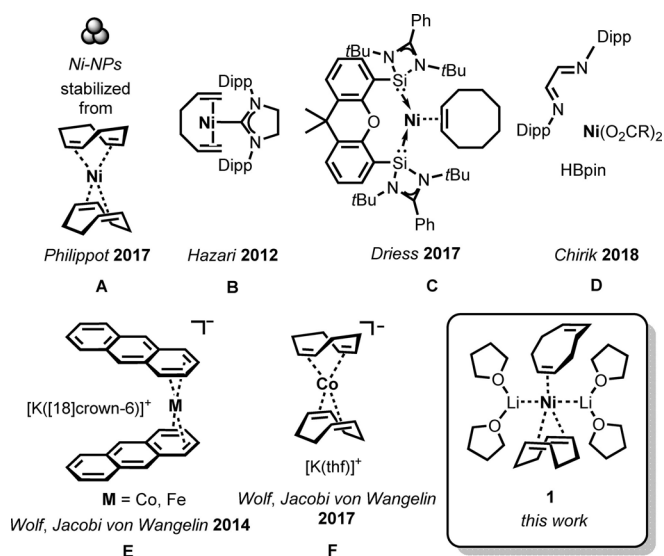


Figure 1. Selected examples of nickel pre-catalysts for the C=C hydrogenation (top). Low-valent anionic transition metal complexes as hydrogenation catalysts by our group (bottom). Dipp = 2,6-diisopropylphenyl.

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<https://doi.org/10.1002/chem.201905537>.

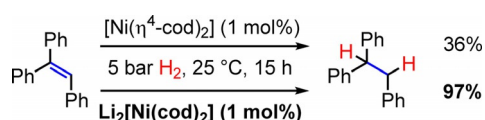
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droamino acids catalyzed by Ni(OAc)₂ and the chiral ligand (*S*)-binapine are noteworthy.^[17]

We previously investigated low-valent ferrate and cobaltate anions [K([18]crown-6)(thf)₂][M(η⁴-anthracene)₂] (M = Fe, Co), and [K(thf)_x][Co(η⁴-cod)₂], first synthesized by the groups of Ellis and Jonas,^[18–20] as catalysts in the hydrogenation of olefins, ketones, and imines.^[6] These “quasi-naked” anionic metal species exhibited high hydrogenation activities for mono/di-substituted C=C bonds but fared poorly for sterically hindered tri/tetra-substituted olefins. Due to the lability of the arene and olefin ligands, both heterogeneous and homogeneous mechanistic pathways are accessible, depending on the nature of the substrate.

Following our recent development of effective olefin hydrogenations with anionic iron and cobalt catalysts,^[6] we were interested to complement these studies with the corresponding nickelate complex [Li₂(thf)₄{Ni(η²-cod)(η⁴-cod)}] (**1**).^[21] This compound was first synthesized by Jonas and co-workers by reduction of [Ni(η⁴-cod)₂] with Li metal. Nickelate **1** was only very recently structurally characterized by Cornella and co-workers, who also reported that **1** effectively catalyzes Kumada-Corriu cross-coupling reactions.^[22] Herein, we show that **1** is a pre-catalyst for the hydrogenation of hindered olefins. We provide solid mechanistic evidence that suggests the in situ formation of highly active Ni particles.

Initial optimization experiments were performed using triphenylethylene as model substrate. Most importantly, the ate-complex **1** showed significantly higher activity in comparison with its oxidized counterpart [Ni(η⁴-cod)₂].^[23] With [Ni(η⁴-cod)₂] only a yield of 36% was achieved within 15 h, whereas full conversion to triphenylethane was observed when using anionic **1** (Scheme 1). The same applies for 1-phenyl-1-cyclohexene.



Scheme 1. Comparison of lithium nickelate **1** and [Ni(η⁴-cod)₂] as pre-catalysts in the hydrogenation of triphenylethylene in DME. Yields were determined by quantitative GC-FID versus internal *n*-pentadecane.

No conversion was observed using [Ni(η⁴-cod)₂], whereas 74% conversion was observed with **1**. The optimized conditions for triphenylethylene use 1 mol% pre-catalyst **1**, a reaction time of 15 h, and 5 bar H₂ at ambient temperature in 1,2-dimethoxyethane (DME) (Table 1, entries 1–3). The reaction was incomplete after 15 h, when the pressure was decreased to 1.9 bar (entry 4).

Under these optimized conditions, linear α-olefins (*trans*-4-octene, allylbenzene) and even sterically hindered olefins such as diphenylethylenes, 1-phenyl-1-cyclohexene, and cycloocta-1,5-diene were successfully hydrogenated (Figure 2). Myrcene was converted to 2,6-dimethyloctane after 20 h; α-pinene and (*R*)-limonene were hydrogenated under relatively mild conditions (>80% conversion at 50–60 °C). Cinnamic acid (C=C,

Entry	Catalyst ^[b]	Solvent [mL]	<i>p</i> (H ₂) [bar]	Yield (conversion) [%]
1	1	THF (0.5)	5	81 (82)
2	1	DME (0.5)	5	97 (98)
3	1	DME (0.25)	5	99 (> 99)
4	1	DME (0.25)	1.9	72 (74)
5	1 +exc. Hg ^[c]	DME (0.25)	5	2 (5)
6	1 +dct ^[d]	DME (0.25)	5	92 (> 99)

[a] Standard conditions: substrate (0.2 mmol), 25 °C, 15 h. Yields and conversions were determined by quantitative GC-FID versus internal *n*-pentadecane. [b] 1 mol% catalyst. [c] Large excess of Hg (one drop, 50 mg, 0.25 mmol, 125 equiv). [d] dct (dibenzo[*a,e*]cyclooctatetraene; 0.8 mg 0.004 mmol, 2.0 equiv per [Ni]), 21 h.

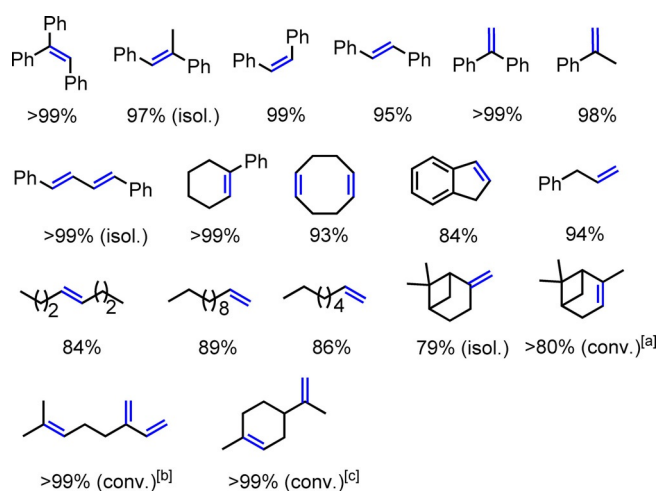


Figure 2. Hydrogenation of olefins with **1** (1 mol%). Standard conditions: 5 bar H₂, 25 °C, 18 h, substrate (0.2 mmol), DME (0.25 mL). Yields and conversions (conv.) were determined by quantitative GC-FID versus internal *n*-pentadecane. Isolated products (isol.) were obtained from reactions performed on a 1.0 mmol scale in 1.25 mL DME. [a] 16 h, 50 °C, 50 bar H₂, DME (0.5 mL). [b] 20 h. [c] 60 °C, 25 bar H₂.

C=O) and benzonitrile (C≡N) remained untouched under the standard conditions. Note that catalytic amounts of benzonitrile (5 equiv per [Ni]) also prevented triphenylethylene hydrogenation (see below and see the Supporting Information, Table S9). Pre-catalyst **1** is not competent for the hydrogenation of polyaromatic substrates, for example, anthracene, naphthalene, and quinolines.

Previous reports on nickel-catalyzed hydrogenation of olefins have barely addressed functional group compatibility.^[7–16] We extended this protocol to olefinic alcohols, which are often found in bioactive molecules (Figure 3). Gratifyingly, olefins with phenolic as well as primary and secondary aliphatic hydroxyl functions were cleanly hydrogenated. Halogen atoms were partially tolerated. The C=C-hydrogenation of α,β-unsaturated lactones (coumarin) and esters (ethyl cinnamate) exhibited high chemoselectivities.

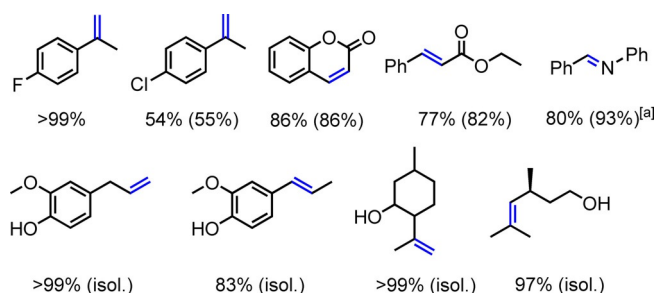


Figure 3. Hydrogenation of functional olefins using **1** (1 mol%). Standard conditions: 5 bar H_2 , 25 °C, 18 h, substrate 0.2 mmol, DME (0.25 mL). Yields were determined by quantitative GC-FID versus internal *n*-pentadecane if not stated otherwise. Conversions are given in parentheses. Isolated products (isol.) were obtained from reactions performed on a 1.0 mmol scale in 1.25 mL DME. [a] 5 mol% **1**.

A brief comparison of the catalytic properties of **1** with related anionic metalate pre-catalysts revealed that bis(η^4 -anthracene)ferrate(–I) and bis(η^4 -anthracene)cobaltate(–I) (**E**, Figure 1) required harsher conditions (60 °C, 2–10 bar H_2 , 24 h) than **1** for the hydrogenation of α -methylstyrene and 2-octene.^[6] Bis(η^4 -cycloocta-1,5-diene)cobaltate(–I) (**F**) exhibited low functional group tolerance. However, it should be noted that the anions **E** and **F** were effective catalysts in the hydrogenation of ketones and imines.^[6]

Pre-catalyst **1** is also comparable to related Ni complexes **C** and **D** developed by Driess and Chirik, respectively (see Figure 1 and additionally Tables S2 and S3 of the Supporting Information).^[14,16] It was reported that catalyst **C** enables the complete hydrogenation of 1-octene using 1 bar H_2 and 1.5 mol% catalyst. In comparison, **1** only gives a slightly poorer yield (86%) under the same conditions. Moreover, a similar turnover number and reaction time was observed for **D** and **1** for the hydrogenation of 1-phenyl-1-cyclohexene with H_2 (4 bar) and 0.4 mol% Ni catalyst at 50 °C (see the Supporting Information for details). Nonetheless, catalyst **D** inarguably is superior in the hydrogenation of highly challenging substrates such as tetra-substituted alkenes.^[16]

To study the nature of the catalytic process, simple reaction-progress analyses of 1-octene, 2-(*E*)-octene, and α -methylstyrene were performed at 1.9 bar H_2 and ambient temperature using catalyst **1** (1 mol%, see the Supporting Information for details). The monitoring experiments revealed significant induction periods and sigmoidal behaviors, which are indicative of slow catalyst formation and nucleation to heterogeneous species (Figure 4).^[6] From these experiments, an approximate turnover frequency (TOF) of 601 h^{-1} can be estimated for 1-octene hydrogenation at low conversion (see the Supporting Information for details), whereas estimated TOFs are expectedly lower for secondary olefins 2-octene (103 h^{-1}) and α -methylstyrene (287 h^{-1}). Note that the reported values are inevitably approximate due to the presence of an induction period.

Poisoning experiments were performed to corroborate the proposed heterotopic nature of the active catalyst.^[24] Addition of excess amounts of mercury led to complete catalyst inhibition in hydrogenations with **1** (Table 1, entry 5). By contrast,

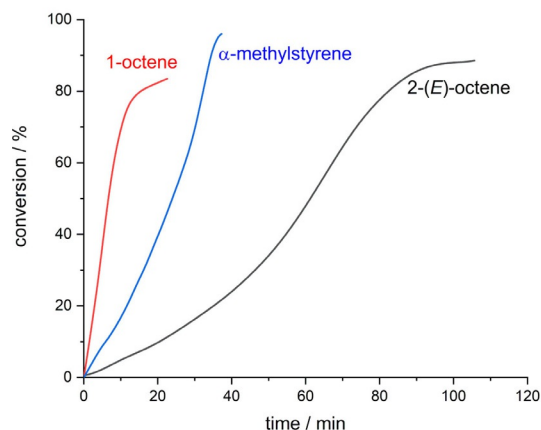
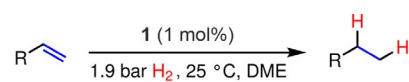


Figure 4. Reaction profiles of the olefin hydrogenations using **1**. Conditions: substrate (0.2 mmol), DME (0.25 mL), 1.9 bar H_2 , 25 °C. Conversion was determined by monitoring H_2 consumption as described in the Supporting Information.

product yield was hardly affected by the presence of two equivalents of dibenzo[*a,e*]cyclooctatetraene (dct) per nickel atom (see Table 1, entry 6).^[25] In addition, benzonitrile (5 equiv per Ni atom) is an efficient catalyst poison, whereas naphthalene only has a very minor inhibiting effect (see the Supporting Information for details). In sum, these results strongly suggest that a heterotopic catalyst is at operation.

The formation of heterogeneous species from the reaction of **1** and 1-phenyl-1-cyclohexene under an H_2 atmosphere was investigated by transmission electron microscopy (TEM, Figure 5). Particles of 10–15 nm diameter were observed alongside a few larger particles.

Further mechanistic experiments were performed with the pre-catalyst **1** under reaction conditions: The rapid color change (orange to black) that was observed when treating a solution of 1-octene in DME with catalytic amounts of **1** under H_2 may indicate nanoparticle formation (Scheme 2a). Isomerization of allylbenzene to 1-propenylbenzene (55%) using **1** (1 mol%) proceeded in the absence of dihydrogen (see the

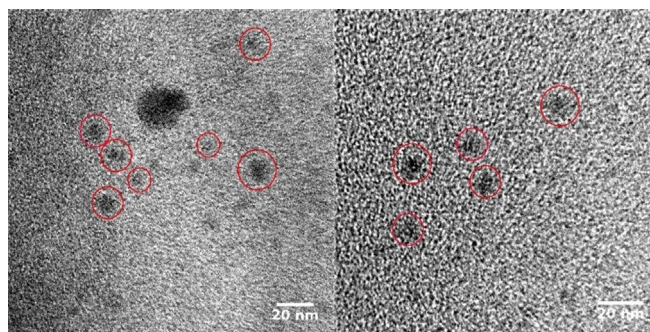
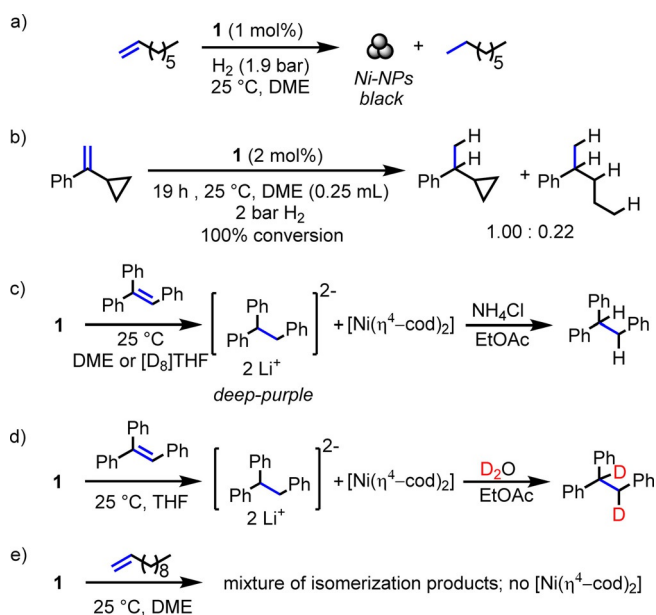


Figure 5. TEM images of particles formed in the hydrogenation of 1-phenyl-1-cyclohexene with **1** (particles highlighted with red circles versus carbon film support).



Scheme 2. Mechanistic experiments: a) nanoparticle formation in the hydrogenation of 1-octene; b) ring-opening of radical probe; c) protonation and d) deuteration of dianionic intermediate from electron transfer with triphenylethylene; e) catalytic isomerization of 1-dodecene.

Supporting Information for details). Minor amounts of the ring-opening product (18%) were detected in the hydrogenation of α -cyclopropylstyrene (Scheme 2b).^[26] ^1H NMR spectra of **1** and triphenylethylene in the absence of dihydrogen indicated the operation of rapid two-electron transfer from **1**. The resultant deep-purple solution ($\lambda_{\text{max}} = 511$ nm, see the Supporting Information, Figure S40) showed the characteristic ^1H NMR signals of $[\text{Ni}(\eta^4\text{-cod})_2]$ (Scheme 2c). Aqueous work-up afforded significant amounts of triphenylethane (see the Supporting Information). The cyclic voltammogram of the postulated triphenylethylene-dianion exhibited one irreversible reduction peak at -2.9 V vs. Fc/Fc^+ in THF and DME (see the Supporting Information, Figures S36, S37). This species was already detected in literature.^[27] Surprisingly, the rate of hydrogenation of triphenylethylene by $[\text{Ni}(\eta^4\text{-cod})_2]$ is significantly slower than with **1**. Deuteration experiments were performed to distinguish between H atom transfer (HAT) and possible ionic reaction pathways (Scheme 2c, 2d). Reaction of **1** and triphenylethylene in $[\text{D}_8]\text{THF}$ led to no incorporation of D atoms after aqueous work-up. The same reaction in THF and subsequent work-up with D_2O furnished $[\text{D}_2]$ triphenylethane (GC-MS, ^1H NMR and ^2H NMR). These data strongly support an ionic mechanism. No electron transfer appeared to operate in reactions between **1** and 1-dodecene as no $[\text{Ni}(\eta^4\text{-cod})_2]$ was observed but rather olefin isomerization products (Scheme 2e). In summary, the preliminary mechanistic data may suggest an electron-transfer initiation of the catalytic mechanism with reduction-sensitive substrates. Nonetheless, further mechanistic investigations are required to conclusively clarify the catalyst activation mechanism.

In conclusion, we have shown that dilithiumbis(cyclo-1,5-oc-tadiene)nickelate (**1**) is a promising pre-catalyst for the hydro-

genation of sterically hindered olefins. The catalytic hydrogenation operates under very mild conditions (5 bar H_2 , 25°C , DME as solvent). This work complements earlier studies of catalytic applications of “quasi-naked” base metal anions to olefin hydrogenations. In comparison with related arene metalates (**E** and **F**), the active nickel catalyst generated from **1** operates at lower H_2 pressures and lower temperature, yet it is compatible with several functional groups (OH, esters, halides). Key mechanistic studies including reaction progress analyses, stoichiometric reactions, poisoning experiments, and transmission electron microscopy were conducted. These investigations support the notion of catalytically active nickel nanoparticles being operative under the reaction conditions. The catalyst formation from **1** is substrate-dependent and involves electron-transfer reactions with reducible olefins (e.g. triphenylethylene). This first catalytic application of a stabilized nickelate anion to olefin hydrogenations provides a firm basis for further investigations into the role of highly reduced, anionic metal catalysts in reductive transformations.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie (fellowship to T.M.M.), the Deutsche Forschungsgemeinschaft (JA 1107/6-1 and WO 1496/6-1), and the European Research Council (CoG 683150) is gratefully acknowledged. Dr. Daniel Scott is thanked for valuable comments on the manuscript.

Conflict of interest

The authors declare no conflict of interest.

Keywords: catalysis · hydrogenation · nanoparticles · nickel · olefins

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Manuscript received: December 8, 2019

Revised manuscript received: February 3, 2020

Accepted manuscript online: February 7, 2020

Version of record online: April 24, 2020