ORGANOMETALLICS

Synthesis, Reactivity, and Catalytic Application of a Nickel Pincer Hydride Complex

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Supporting Information

ABSTRACT: The nickel(II) hydride complex $[(^{Me}N_2N)Ni-H]$ (2) was synthesized by the reaction of $[(^{Me}N_2N)Ni-OMe]$ (6) with Ph_2SiH_2 and was characterized by NMR and IR spectroscopy as well as X-ray crystallography. 2 was unstable in solution, and it decomposed via two reaction pathways. The first pathway was intramolecular N–H reductive elimination to give $^{Me}N_2NH$ and nickel particles. The second pathway was intermolecular, with H_2 , nickel particles, and a five-coordinate Ni(II) complex $[(^{Me}N_2N)_2Ni]$ (8) as the products. 2 reacted with acetone and ethylene, forming $[(^{Me}N_2N)Ni-O'Pr]$ (9) and $[(^{Me}N_2N)Ni-Et]$ (10), respectively. 2 also reacted with alkyl halides, yielding nickel



halide complexes and alkanes. The reduction of alkyl halides was rendered catalytically, using $[({}^{Me}N_2N)Ni-Cl]$ (1) as catalyst, NaO'Pr or NaOMe as base, and Ph₂SiH₂ or Me(EtO)₂SiH as the hydride source. The catalysis appears to operate via a radical mechanism.

INTRODUCTION

Transition-metal complexes of pincer ligands are heavily pursued as catalysts or precatalysts, thanks to their enhanced stability and their demonstrated ability to mediate unusual chemical transformations.¹⁻⁴ Within this context, many nickel pincer complexes have been prepared,⁵⁻¹⁹ and some of them are shown to be catalysts for C-C and C-S cross-coupling, double-bond functionalization, and CO₂ reduction reactions. Guan et al. reported that a well-defined nickel PCP pincer hydride complex was an efficient catalyst for hydrosilylation of aldehydes and ketones as well as the reduction of CO_2 with a borane.^{5,6,20} These reports provided some of the few examples in which isolated nickel hydride species were catalytically competent.²¹⁻²³ In general, nickel hydride species are highly reactive and their roles in catalysis are largely hypothesized. The isolation, reactivity, and catalytic application of nickel hydride complexes are thus interesting.

Our group recently developed the pincer bis(amino)amide ligand ^{Me}N₂N.^{24,25} The nickel chloride complex $[({}^{Me}N_2N)Ni-$ Cl] (1) is an excellent catalyst for cross-coupling of nonactivated alkyl halides and direct C–H alkylation (Scheme 1).^{26–32} It was shown that β -H elimination was kinetically viable but thermodynamically uphill for the corresponding nickel alkyl species.³³ This was thought to be one of the key factors for efficient alkyl–alkyl coupling. The metal-containing product of β -H elimination was the hydride complex $[({}^{Me}N_2N)Ni-H]$ (2), which was also proposed as an intermediate for the isomerization of $[({}^{Me}N_2N)Ni-Pr]$ (3) to $[({}^{Me}N_2N)Ni-Pr]$ (4).³³ Preciously 2 was only observed in situ. Herein we report the preparation and isolation of 2, its structure and reactivity, and its involvement in the catalytic hydrodehalogenation of alkyl halides. Like some other nickel hydride complexes, 2 is unstable and we are able to identify two interesting decomposition pathways.

RESULTS AND DISCUSSION

Synthesis and Characterization of [(^{Me}N₂N)Ni-H] (2) and [(MeN2N)Ni-D] (2D). Two general methods are known for the synthesis of Ni(II) hydride complexes: (1) N-H oxidative addition of HNL₂ ligands with $Ni(0)^{8,11}$ and (2) reaction of nickel halide complexes with a hydride donor such as LiAlH₄ or LiEt₃BH.¹⁵ These two methods were attempted for the synthesis of $[(^{Me}N_2N)Ni-H]$ (2). No reaction occurred when ^{Me}N₂NH (5) was treated with Ni(COD)₂; thus, the oxidative addition route was unsuccessful. The hydride transfer reactions were then examined. $\left[\binom{Me}{N_2N}Ni-Cl\right](1)$ did not react with NaBH₄. It reacted with LiAlH₄, only leading to unidentifiable products. As communicated earlier,³³ reaction of 1 with LiEt₃BH produced $\left[\binom{Me}{N_2N}Ni-H\right]$ (2), but only in solution. The identity of 2 was confirmed by a diagnostic singlet at -22.81ppm in the ¹H NMR spectrum in C_6D_6 . In solution, 2 decomposed within 1 h at room temperature to give a black and metallic precipitate. The decomposition was faster if the solvent was removed in vacuo. As a result, it was not possible to isolate 2 in the solid form.

Silanes are sometimes used as hydride sources. No reaction occurred between 1 and Ph₂SiH₂. However, when NaOMe was added to a solution of 1 and Ph₂SiH₂ in C₆D₆, the solution changed from brown to purple and then to red. A hydride signal was observed in the ¹H NMR spectrum of the red reaction mixture. The purple color was indicative of $[(^{Me}N_2N)Ni-OMe]$ (6),²⁵ suggesting that this species reacted with Ph₂SiH₂

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to produce the hydride complex. Indeed, reaction of preisolated 6 with Ph_2SiH_2 proceeded smoothly to give 2. Due to the instability of 2, isolation by solvent evaporation at room temperature was unsuccessful, leading again to a black precipitate.

The decomposition was avoided by conducting the reaction and isolation at -70 °C (Scheme 2). Higher yields were



obtained when ambient light was excluded. In a typical procedure, Ph_2SiH_2 was added to a concentrated solution of **6** in toluene to give **2** in solution. Addition of precooled pentane to this solution produced **2** as an orange precipitate, which could be isolated in a yield of 67%. Solid samples of **2** can be stored at -28 °C in the dark. When it was exposed to light or warmed to room temperature, **2** gradually turned black.

The characteristic hydride signal was found at -22.8 ppm in the ¹H NMR spectrum of **2** in C₆D₆. This signal is shifted upfield compared to those for the analogous [(POCOP)Ni-H] (-8 ppm),⁵ [(PCP)Ni-H] (-10 ppm),¹⁵ and [(PNP)Ni-H] (-18 ppm)¹¹ complexes, probably indicating a more electron rich nickel center. The IR spectrum of **2** in C₆H₆ shows a Ni–H vibrational band at 1768 cm⁻¹. The solid-state molecular structure of **2** was established by a single-crystal X-ray diffraction study (Figure 1). The nickel center is in a square-planar ligand



Figure 1. X-ray structure of complex **2**. There are two molecules in the asymmetric unit; only one is shown. The thermal ellipsoids are displayed at 50% probability; two toluene solvent molecules and all hydrogen atoms except the hydride ligand are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–N1, 1.936(2); Ni1–N2, 1.881(2); Ni1–N3, 1.935(2); Ni1–H1A, 1.50(2); N1–Ni1–N3, 174.53(8); N2–Ni1–H1A, 177.8(10).

environment. The average Ni–H distance is 1.505(20) Å, comparable to that of [(PCP)Ni-H] (Ni–H = 1.42(3) Å).¹⁵

The $[({}^{Me}N_2N)Ni-D]$ complex (2D) was synthesized similarly, starting from 6 and Ph₂SiD₂. A deuteride signal was observed at -22.8 ppm in the ²H NMR spectrum of 2D.

Decomposition of [($^{Me}N_2N$)Ni-H] (2) and [($^{Me}N_2N$)Ni-D] (2D). When it was freshly prepared in solution at room temperature, 2 decomposed readily to give the protonated ligand $^{Me}N_2NH$ (5) and a black metallic precipitate (Scheme 3). We suspected that the decomposition was due to N–H reductive

Scheme 3. N-H Elimination from Complex 2



elimination. The isolated and purified sample of 2 decomposes in the same way when dissolved in solution at room temperature, but the decomposition rate is slower. To ascertain if the N–H hydrogen in $^{Me}N_2NH$ originated from the hydride ligand of 2, we examined the decomposition of the deuteride complex 2D.

An independent sample of ${}^{Me}N_2ND$ (**5D**) was prepared by reaction of the Li complex $[{}^{Me}N_2NLi]_2$ (7)²⁴ with D₂O. **5D** shows a ²H NMR signal at δ 7.41 ppm for the anilino hydrogen. The decomposition of **2D** was then followed by ²H NMR. A signal at δ 7.4 ppm became visible within 24 h, indicating the formation of **5D**. This result confirms that **2** and **2D** decompose via N–H/D reductive elimination. It is interesting to note that analogous [(PNP)Ni-H] complexes are stable against N–H elimination.¹¹

Examination of the NMR spectrum of the product mixture from the decomposition of **2** revealed that a paramagnetic species (**8**) and H_2 were also formed. A second decomposition pathway appears to exist. We initially hypothesized that the paramagnetic species was a Ni(I) species, produced by a combination reaction of two molecules of **2** to give H_2 . We then attempted to prepare the Ni(I) species independently. Reaction of **1** with a chemical reductant such as Na/naphthalene yielded a paramagnetic nickel species whose NMR spectrum is identical with that of **8** (Scheme 4). The molecular structure

Scheme 4. Formation of Complex 8 from Reduction of Complex 1



of 8 was determined by a single-crystal X-ray diffraction study (Figure 2). Surprisingly, it is not a Ni(I) species, but a Ni(II) complex coordinated to two ^{Me}N₂N ligands ([(^{Me}NN₂)₂Ni]). The nickel ion is in a five-coordinate, distorted-trigonal-bipyramidal coordination environment. One of the pincer ligands is bidentate, with a noncoordinating NMe₂ donor (Ni–N > 3.7 Å). The formation of 8 from 1 likely occurred via a Ni(I) intermediate that was produced by reduction of 1. The Ni(I) species was not stable, and it underwent a disproportionation reaction to form 8 and nickel particles.

A few experiments were carried out to probe how 8 may be formed from 2. First, reaction of 5 with 2 did not lead to 8 and H_2 . Second, 2 did not react with a base such as NEt₃ to give H_2 , which suggested that deprotonation of 2 with the anilide moiety of a second molecule of 2 was not a likely reaction pathway. Third, we found that the decomposition of 2 was significantly slower in dilute solutions. In addition, in dilute solutions, decomposition occurred only via N–H reductive elimination.



Figure 2. X-ray structure of complex 8. The thermal ellipsoids are displayed at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ni1–N1, 2.150(6); Ni1–N2, 1.991(5); Ni1–N3, 2.204(5); Ni1–N5, 2.023(6); Ni1–N6, 2.109(5); N1–Ni1–N3, 142.0(2); N3–Ni1–N6, 111.6(2); N1–Ni1–N6, 101.6(2); N2–Ni1–N5, 177.8(2).

The formation of **8** was not observed. This result suggests that the formation of **8** proceeds through an intermolecular process, which is much slower than N-H elimination in dilute solutions. The latter also suggests that N-H elimination is intramolecular. On the basis of the aforementioned observations and reasoning, we propose that **8** was produced by a bimolecular combination of **2** to form H₂ and Ni(I) species (Scheme 5). The latter was unstable and underwent a disproportionation reaction to give **8** and nickel particles.

This hypothesis is further supported by inhibition and isotopic exchange tests. When the decomposition of **2** was examined under 7 bar of H₂, the formation of **8** was no longer observed, even in concentrated solutions. Only N–H elimination was found. When the decomposition of **2** was followed under D₂, [(^{Me}N₂N)Ni-D] (**2D**) and ^{Me}N₂ND (**5D**) were observed by ²H NMR. These results suggest that the bimolecular combination of **2** is reversible, and the equilibrium can be shifted by hydrogen pressure (Scheme 5).

Despite many attempts, our efforts to trap the Ni(I) species using additional donor ligands such as CO and phosphine were fruitless.

Reactivity of $[(^{Me}N_2N)Ni-H]$ (2). Nickel hydride complexes are known to insert into double bonds (C=C and C=O). These reactions are key steps in Ni-catalyzed hydrosilylation and hydrogenation reactions.³⁴ The reactions of 2 with acetone and ethylene were studied in order to examine its possible utility in reduction catalysis (Scheme 6).

The reaction of **2** with acetone was sluggish. The reaction took 12 h to complete; the expected insertion product, $[({}^{Me}N_2N)Ni-O^{i}Pr]$ (9), was formed in ca. 50% yield. 9 was independently prepared by reaction of $[({}^{Me}NN_2)Ni-Cl]$ (1) with NaOⁱPr in 76% yield.

The reaction of **2** with ethylene was faster. When a solution of **2** in C₆D₆ was treated with ethylene (6 bar), $[({}^{Me}N_2N)-Ni-Et]$ (**10**) was formed in minutes. **10** was prepared earlier by reaction of **1** with EtMgCl.²⁴ After the reaction, **2** was no longer observed, consistent with the earlier conclusion that β -H elimination is thermodynamically uphill and the equilibrium lies largely on the side of nickel alkyl complexes. The rapid reaction of **2** with an olefin to form a nickel alkyl complex also provides

Scheme 5. Second Decomposition Pathway of Complex 2 That Led to H₂, Nickel Particles, and Complex 8



Scheme 6. Reactivity of Complex 2 with Acetone, Ethylene, and Alkyl Halides



evidence that 2 is an intermediate in the isomerization of $[({}^{Me}N_2N)Ni^{-i}Pr]$ (3) to $[({}^{Me}N_2N)Ni^{-n}Pr]$.

The reactions of 2 with alkyl halides were instantaneous. In these reactions, alkyl halides were reduced to the corresponding alkanes, and nickel halide complexes were formed as the metal-containing species (Scheme 6). Alkyl iodides, bromides, and chlorides, but not fluorides, were reduced. The reaction rates followed the order alkyl iodides > bromides > chlorides.

Catalytic Hydrodehalogenation of Alkyl Halides. Hydrodehalogenation is an important reaction in organic synthesis.³⁵ Tin-based reduction methods are selective and efficient. However, the toxicity associated with tin reagents has prompted the developments of alternative methods, such as transition-metal-catalyzed reduction using organic silanes.^{35,36} The formation and reactivity of 2 constitute a stoichiometric reaction cycle for the reduction of alkyl halides by silane (Figure 3). We reasoned that the Ni–Cl complex 1 could be



Figure 3. Proposed catalytic cycle for hydrodehalogenation reactions of organic halides. X = halide.

used as a catalyst. 1 could react with an alkoxide to from a nickel alkoxide complex (e.g., 9), which could then react with a silane to form the Ni–H complex 2. The latter could react with an alkyl halide to give the reduction product and regenerate the catalyst.

The catalytic reduction of tetradecyl chloride was used as the test reaction. Table 1 summarizes the influence of various reaction parameters. With toluene as solvent, NaOⁱPr as base, and Ph₂SiH₂ as hydride source, the reduction gave a quantitative yield of tetradecane (entry 1, Table 1). Two equivalents of silane and base were required for full conversion. Reduction in other solvents such as THP (tetrahydropyran), THF, DMA, or dioxane gave lower yields (entries 2-5, Table 1). No reduction was observed using Et₃SiH (entries 6-8, Table 1). Reduction using PHMS or PhSiH₃ as the hydride source was less efficient (entries 9–12, Table 1). Me(EtO)₂SiH could be a good hydride source, but only in conjunction with NaOMe as base and THP as solvent (entries 13 and 14, Table 1). Under these conditions, tetradecane was also formed quantitatively (entry 14, Table 1). Even with the best systems, the loading of catalyst is in the range of 8–10% (entries 1 and 14, Table 1). A reaction time of 5–6 h was sufficient.

The scope of the hydrodehalogenation was explored using the $Ph_2SiH_2/NaO^iPr/toluene$ protocol (Table 2). Not only primary alkyl halides but also secondary and tertiary alkyl halides could be reduced (entries 1–7, Table 2). The minimum catalyst loading for a high yield decreased in the order Cl > Br > I (e.g. compare entries 1–3, Table 2). The order correlates with the bond strength. The yields were between 73% and 99%. Aryl halides could also be reduced, but only with 39–57% yields (entries 8–10, Table 2). For the reduction of aryl halides, THP was used as the solvent and Me(EtO)₂SiH was used as the hydride source. These changes were made to ensure that benzene did not originate from Ph_2SiH_2 or toluene.

As reduction of alkyl halides by 2 appears to be faster than reactions of 2 with alkene or ketone, we thought this reduction method might tolerate unsaturated functional groups. Indeed, a C-C double bond was tolerated, with a 64% yield in reduction (entry 11, Table 2). The reaction was accompanied by a small degree of isomerization (~5% trans to cis). Alkyl bromides with ether and amide groups were selectively reduced in modest yields (entries 12 and 13, Table 2). Unfortunately, ketone and ester groups were not tolerated (entries 14 and 15, Table 2). Overall the group tolerance is modest, probably because the reactions were run under basic conditions.

Mechanism of Catalytic Hydrodehalogenation. The overall catalytic cycle should be similar to that shown in Figure 3. All the nickel-containing species, i.e., the nickel chloride, hydride, and alkoxide complexes, have been isolated and characterized. Their reactivity is consistent with the proposed catalytic cycle. The byproduct of hydride formation, $Ph_2SiHO'Pr$, was identified by GC-MS. The catalytic reduction of tertiary alkyl halides such as adamantyl chloride and bromide suggests that the reduction does not occur via a $S_N 2$ type mechanism. The reaction is more likely to go through radical or carbenium intermediates. To differentiate these two possibilities, reduction with radical- and carbenium-probe substrates was examined (Scheme 7).

Article

			/	Cat. 1 Silane Solvent	f >12		
entry	silane	base	solvent	cat. loading (mol %)	time (h)	amt of silane (equiv)	conversion/yield (%) ^b
1	Ph ₂ SiH ₂	NaO ⁱ Pr	toluene	8	6	2	100/99
2	Ph_2SiH_2	NaO ⁱ Pr	THP	10	5	2	77/18
3	Ph ₂ SiH ₂	NaO ⁱ Pr	THF	9	6	2	100/23
4	Ph ₂ SiH ₂	NaO ⁱ Pr	DMA	10	6	2	100/53
5	Ph ₂ SiH ₂	NaO ⁱ Pr	dioxane	8	6	2	51/12
6	Et ₃ SiH	NaO ⁱ Pr	toluene	6	6	1	0/0
7	Et ₃ SiH	NaOMe	THP	10	5	2	1/1
8	Et ₃ SiH	NaO ⁱ Pr	THP	10	5	2	1/1
9	PMHS	NaO ⁱ Pr	THP	10	5	2	33/32
10	PhSiH ₃	NaO ⁱ Pr	toluene	6	6	1	35/20
11	PhSiH ₃	NaOMe	THP	10	5	2	29/27
12	PhSiH ₃	NaO ⁱ Pr	THP	10	5	2	82/25
13	Me(EtO) ₂ SiH	NaO ⁱ Pr	toluene	10	6	3	30/30
14	Me(EtO) ₂ SiH	NaOMe	THP	10	5	2	100/100
'See the H	Experimental Section	n for condition	s. ^b GC yields.				

First, we examined the catalytic reduction of cycloheptyl bromide (Scheme 7). If a carbenium intermediate is involved, skeletal rearrangement should take place, leading to methyl-cyclohexane. This was observed for hydrodehalogenation using $AlCl_3/Et_3SiH$.³⁷ In the current case, only cycloheptane was produced, ruling out the involvement of a carbenium intermediate.

Next, we examined the reduction of 6-bromohex-1-ene and 2-iodohept-1-ene (Scheme 7). Only methyl- and 1,2-dimethylcyclopentane were formed. In principle, two reaction pathways can lead to the formation of these compounds. The first involves the insertion of the Ni-H bond into the terminal olefin, followed by an intramolecular substitution of the halide. However, insertion of 2 into an olefin is slow compared to reduction. This reaction pathway can thus be excluded. The second reaction pathway involves a single-electron transfer (SET) from 2 to the organic halide to generate an alkyl radical, which undergoes a fast ring-closing addition to the double bond, before receiving a hydrogen radical.³⁸ The SET likely occurs through a Cl-bridged, inner-sphere process, as the reduction potentials of alkyl halides are in the range of -1 V vs SCE³⁹ and the oxidation potential of (^{Me}N₂N)Ni complexes are in the range of 0.3 V vs SCE.²⁵ We currently favor this reaction pathway. Alternatively, the reactions might proceed through a σ -bond metathesis type transition state involving Ni-H and R-X. It would be interesting to probe this possibility by computational methods.

Stoichiometric reactions of **2** with cycloheptyl bromide and 6-bromohex-1-ene were also examined, and the results were similar to those for the catalytic reductions.

Hydroalkylation of Olefin. Pincer complex 1 was shown earlier to be a catalyst for cross-coupling of alkyl halides with alkyl Grignard reagents.²⁶ This type of cross-coupling is challenging because metal alkyl intermediates tend to undergo unproductive β -H elimination.^{30,40–42} The proposed reaction sequence for the alkyl–alkyl coupling is shown in Figure 4 (left). A nickel halide complex first reacts with a Grignard reagent to form a nickel alkyl complex, which reacts with an alkyl halide to give the coupling product and regenerate the nickel halide complex.³⁰ We thought that if a nickel alkyl complex could be generated from a nickel halide complex using a reagent other than an alkyl Grignard reagent, alternative alkyl–alkyl coupling

reactions might be developed. One possibility is to produce a nickel hydride complex from the nickel halide complex through a hydride transfer reaction, and the hydride complex may react with an olefin to form a nickel alkyl complex. The latter could react with an alkyl halide to complete a catalytic cycle for hydroalkylation of olefin (Figure 4 (right)).

In the current study, we demonstrated the production of the nickel hydride complex 2 from the nickel chloride complex 1 and the reaction of ethylene with 2 to form the corresponding nickel ethyl complex. The stoichiometric reaction cycle for the hydroalkylation of olefin was thus in place. We then tried to turn the reaction catalytic, using 10 mol % 1 as catalyst, NaOMe as base, Me(EtO)₂SiH as hydride source, decene as olefin, and dodecyl iodide as electrophile. To suppress the competing reduction of alkyl halide, the silane was added slowly as the limiting reagent. The catalysis was not efficient, with a yield of about 10% for hydroalkylation. The reduction product, dodecane, was produced in a yield of about 5%. The majority of the starting materials, i.e., decene and dodecyl iodide, remained unreacted. The inefficiency of the catalysis might originate from the instability of the nickel hydride complex 2, as described above.

CONCLUSION

In summary, we developed a clean synthetic route to the nickel hydride complex $\left[\binom{Me}{N_2N}Ni-H\right](2)$ and determined its crystal structure. 2 decomposed in solution via two pathways, including intramolecular N-H reductive elimination and a bimolecular combination reaction. The former reaction led to the protonated ligand and nickel particles, while the latter reaction produced the five-coordinate Ni(II) species $\left[\binom{Me}{N_2N_2N_1}(8), H_2, \frac{1}{N_2N_2}\right]$ and nickel particles. The bimolecular combination reaction was suppressed in the presence of H₂. Complex 8 was independently synthesized by reduction of $[({}^{Me}N_2N)Ni-Cl]$ (1) and was characterized by X-ray crystallography. 2 inserted into ethylene and acetone to form the corresponding nickel alkyl and alkoxy complexes. 2 rapidly reduced alkyl halides to form alkanes. On the basis of the reactivity of 2, a catalytic hydrodehalogenation method was developed. A large number of organic halides could be reduced by silane using 1 as the catalyst. The reduction of alkyl halide was found to proceed via a radical

Table 2. Scope of Catalytic Hydrodehalogenation of Organic Halides a

Cat 1

	R-X —	Silane Solvent = I, Br, Cl	► R-H		
	. Instants	Ca	at. loading	time	Conversion
entry	substrate		(mol%)	(h)	/yield (%) ^b
1	~~~~~~	CI	7	6	100/98
2	\sim	∕~~ ^{Br}	5	6	100/>99
3	\sim	\searrow	4	6	100/>99
4	~~~~~	Br	6	6	100/>99
5			6	6	100/75
6	-CI		8	6	93/75
7	Br		7	6	73/70
8	CI-CI		9	6	40/39
9	Br		8	6	94/56
10			8	6	99/57
11	$\bigcirc \frown \frown \frown \frown \frown$	Br	12	5	99/64
12		Br	10	5	99/41
13	Br		7	5	98/68
14	O Br		10	6	100/0
15	° , , , , ,		10	6	100/0

^{*a*}For alkyl halides, the Ph_2SiH_2/NaO^iPr /toluene combination was applied; for aryl halides, the Me(EtO)₂SiH/NaOMe/THP combination was applied. See the Experimental Section for details. ^{*b*}GC yields.

Scheme 7. Reduction of Radical- and Carbenium-Probe Substrates



mechanism. The nickel hydride complex 2 belongs to a small group of isolated and defined nickel hydride species that are catalytically active. Its decomposition pathways and reactivity could serve as useful references when considering the roles of nickel hydrides in catalytic transformations.

EXPERIMENTAL SECTION

Chemicals and Reagents. All manipulations were carried out under an inert $N_2(g)$ atmosphere using standard Schlenk or glovebox techniques. Solvents were purified using a two-column solid-state purification system (Innovative Technology, Amesbury, MA, USA) and transferred to the glovebox without exposure to air. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and were degassed and stored over activated 3 Å molecular sieves. Unless otherwise noted, all other reagents and starting materials were purchased from commercial sources and used without further purification. Liquid compounds were degassed by standard freeze–pump–thaw procedures prior to use. The complexes $[(^{Me}N_2N)-Ni-Cl]$ (1), $[(^{Me}N_2N)Ni-OMe]$ (6), and $[^{Me}N_2NLi]_2$ (7) were prepared as previously reported.^{24,25}

Physical Methods. The ¹H and ¹³C{¹H} NMR spectra were recorded at 293 K on a Bruker Avance 400 spectrometer. ¹H, ²H, and ¹³C{¹H} NMR chemical shifts were referenced to residual solvents as determined relative to Me₄Si (δ 0 ppm). GC-MS measurements were conducted on a Perkin-Elmer Clarus 600 GC equipped with a Clarus 600T MS. GC measurement was conducted on a Perkin-Elmer Clarus 400 GC with an FID detector. Elemental analyses were performed on a Carlo Erba EA 1110 CHN instrument at EPFL. The temperature of reactions below room temperature was regulated by a Julabo FT-902 chiller. X-ray diffraction studies were carried out at the EPFL Crystallography Facility. The data collections for both crystal structures were performed at low temperature (100(2) K) using Mo K α radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The data were reduced by EvalCCD⁴³ and then corrected for absorption.44 The solution and refinement was performed by SHELX.45 The structure was refined using full-matrix least squares based on F^2 with all non-hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

Synthesis of [(^{Me}N₂N)Ni-H] (2). In the dark, to a purple solution of 6 (138 mg, 0.401 mmol) in 2 mL of toluene was added at -70 °C a solution of Ph₂SiH₂ (74 mg, 0.40 mmol) in 0.5 mL of toluene. The solution turned dark red and was stirred for 30 min before a precooled solution of pentane (-70 °C, \sim 5 mL) was added. A fine orange precipitate formed. The solution was removed by syringe, and the precipitate was washed with 4 × 5 mL of precooled pentane (-70 °C). After drying in vacuo at -30 °C for 12 h, 2 was obtained as a solid (84 mg, 0.27 mmol, 67% yield). Single crystals suitable for X-ray analysis were obtained 1 day after layering a toluene solution of 2 with pentane at -70 °C.

¹H NMR (400 MHz, C₆D₆): δ 7.53 (d, J = 8.2 Hz, 2H,CH_{aryl}), 7.08 (t, J = 7.6 Hz, 2H, CH_{aryl}), 6.48 (dt, J = 14.8, 7.5 Hz, 4H, CH_{aryl}), 2.71 (s, 12H, N(CH₃)₂), -22.81 ppm (s, 1H, Ni–H). ¹³C{¹H} NMR (101 MHz, C₆D₆): δ 148.24 (C_{aryl}), 147.69 (C_{aryl}), 128.49 (C_{aryl}), 119.84 (C_{aryl}), 114.36 (C_{aryl}), 114.23 (C_{aryl}), 52.88 ppm (CH₃). Anal. Calcd for **2** and 0.075 toluene (C₁₆H₂₀N₃Ni): C, 61.39; H, 6.44; N, 13.42. Found: C, 61.44; H, 6.44; N, 12.35. The discrepancy in the nitrogen content is probably due to the decomposition of **2**. IR (in C₆D₆): 1768 cm⁻¹ for Ni–H.

Synthesis of $[(^{Me}N_2N)Ni-D]$ (2D). The synthesis was the same as for 2, except that Ph_2SiD_2 was used as the silane. Yield: 60%.

¹H NMR (400 MHz, C₆D₆): δ 7.53 (d, J = 8.2 Hz, 2H, CH_{aryl}), 7.08 (t, J = 7.6 Hz, 2H, CH_{aryl}), 6.48 (dt, J = 14.8, 7.5 Hz, 4H, CH_{aryl}), 2.71 ppm (s, 12H, N(CH₃)₂). ¹³C{¹H} NMR (101 MHz, C₆D₆): δ 148.24 (C_{aryl}), 147.69 (C_{aryl}), 128.49 (C_{aryl}), 119.84 (C_{aryl}), 114.36 (C_{aryl}), 114.23 (C_{aryl}), 52.88 ppm (CH₃). ²H NMR (61 MHz, C₆H₆): δ -22.82 ppm (s, 1H, Ni-D).

Synthesis of $[(MeN_2N)D]$ (5D). To a solution of 7 (10 mg,0.019 mmol) in 1.0 mL of C_6H_6 or C_6D_6 was added 0.2 mL of D_2O . The organic layers were separated and dried over MgSO₄.

¹H NMR (400 MHz, C_6D_6): δ 7.54 (d, J = 7.7 Hz, 2H, CH_{aryl}), 6.98 (dd, J = 14.3, 7.3 Hz, 4H, CH_{aryl}), 6.87 (t, J = 7.4 Hz, 2H, CH_{aryl}), 2.43 ppm (s, 12H, N(CH₃)₂). ²H NMR (61 MHz, C_6H_6): δ 7.41 ppm (N-D).



Figure 4. (left) Proposed reaction sequence for alkyl-alkyl Kumada coupling catalyzed by 1. (right) Hypothetical catalytic cycle for hydroalkylation of olefins. X = halide.

Synthesis of [($^{Me}N_2N$)₂Ni] (8). To a solution of naphthalene (37 mg, 290 mmol) in 5 mL of THF was added Na (7 mg, 304 mmol) at room temperature. The solution turned green and was stirred overnight at room temperature. After filtration, the solution was added to a solution of 1 (100 mg, 287 mmol) in 10 mL of THF. The solution turned dark and was stirred for 2 h. The solvent was removed by vacuum. The solid residue was extracted with 3 × 10 mL of toluene and filtered through Celite. The solvent was reduced to about 0.5 mL, and the red solution was stored at -28 °C overnight. Complex 8 was then obtained as a solid (70 mg, 0.123 mmol, 43% yield). Single crystals suitable for X-ray analysis were obtained from a pentane solution of 8 at -28 °C.

Anal. Calcd for 8 ($C_{32}H_{40}N_6Ni$): C, 67.74; H, 7.11; N, 14.81. Found: C, 68.02; H, 7.27; N, 14.73. Synthesis of [($^{Me}N_2N$)Ni-O'Pr] (9). To a suspension of NaO'Pr

Synthesis of [(^{me}N₂N)Ni-O'Pr] (9). To a suspension of NaO'Pr (59 mg, 0.71 mmol) in 2 mL of THF was added a brown solution of 1 (214 mg, 0.614 mmol) in 2 mL of THF. The solution was stirred for 1 h and turned dark blue. The solvent was removed by vacuum. The solid residue was extracted with 3×20 mL of pentane and filtered through Celite. The solvent was reduced to about 0.5 mL, and the solution was stored at -35 °C overnight to yield a blue crystalline solid. After filtration and washing with pentane (3×3 mL), 9 was obtained as a blue solid. Yield: 76% (163 mg, 0.438 mmol).

¹H NMR (400 MHz, C₆D₆): δ 7.41 (d, J = 8.1 Hz, 2H, CH_{aryl}), 6.94 (t, J = 7.2 Hz, 2H, CH_{aryl}), 6.59 (d, J = 7.6 Hz, 2H, CH_{aryl}), 6.39 (t, J = 7.3 Hz, 2H, CH_{aryl}), 3.40 (br s, 1H, CH(CH₃)₂), 2.51 (br s, 12H, N(CH₃)₂), 1.44 ppm (br s, 6H, CH(CH₃)₂). ¹H NMR (400 MHz, Tol-d₈, -40 °C): δ 7.33 (d, J = 8.3 Hz, 2H, CH_{aryl}), 6.91 (m, 2H, CH_{aryl}), 6.45 (d, J = 7.9 Hz, 2H, CH_{aryl}), 6.36 (t, J = 7.5 Hz, 2H, CH_{aryl}), 3.41–3.27 (m, 1H, CH(CH₃)₂). ¹³C{¹H} NMR (101 MHz, C₆D₆): δ 148.26 (C_{aryl}), 147.95 (C_{aryl}), 128.19 (C_{aryl}), 120.13 (C_{aryl}), 115.25 (C_{aryl}), 114.34 (C_{aryl}), 63.14 (OC(CH₃)₂), 49.60 (CH₃), 29.44 ppm (OC(CH₃)₂). Anal. Calcd for 7 (C₁₉H₂₇N₃NiO): C, 61.32; H, 7.31; N, 11.29. Found: C, 61.45; H, 7.77; N, 11.97. The nitrogen content is higher than the theoretical value, indicating the presence of a small amount of impurity which is not detectable by NMR.

(1). Monitoring the Decomposition. In situ Generated [$^{Me}N_2N$]Ni-D] (2D) by 2H NMR. A J. Young NMR tube was charged with a solution of 6 (25 mg, 0.073 mmol) in 1 mL of C_6H_6 . Ph₂SiD₂ (14 mg, 0.073 mmol) was added, and the solution immediately turned dark red. 2H NMR spectra were recorded to follow the disappearance of the [Ni]D signal (-22.79 ppm) and the appearance of the ND signal (7.42 ppm).

(2). Isolated [$({}^{Me}N_2N)Ni-D$] (2D) by ²H NMR. A J. Young NMR tube was charged with a red solution of 2D (10 mg, 0.032 mmol) in 0.6 mL of C₆H₆. ²H NMR spectra were recorded to follow the disappearance of the [Ni]D signal (-22.79 ppm) and the appearance of the ND signal (7.42 ppm).

(3). Isolated [$({}^{Me}N_2N)Ni$ -D] (2D) under H_2 Pressure by ¹H NMR. A sapphire NMR tube was charged with 2 (7 mg, 0.02 mmol) in 0.4 mL of C_6D_6 with a sealed capillary containing CDCl₃/TMS as external standard. The NMR tube was pressurized with 6 bar of H_2 . ¹H NMR spectra were recorded. After 12 h, 2 completely decomposed. At no time was the characteristic signal of 8 at 82.41 ppm observed.

Reaction of 2 with Ethylene. A sapphire NMR tube was charged with 2 (7 mg, 0.02 mmol) in 0.4 mL of C_6D_6 with 0.5 μ L of toluene as the internal standard. The red solution was then pressurized with 6 bar of ethylene pressure and shaken for 5 min to dispense ethylene in solution. ¹H NMR spectra were recorded. After about 30 min, 2 was completely consumed. The product **10** was identified by the following NMR signals.

¹H NMR (400 MHz, C₆D₆): δ 7.61 (d, J = 8.1 Hz, 2H, CH_{aryl}), 7.06 (t, J = 7.4 Hz, 2H, CH_{aryl}), 6.63 (d, J = 7.7 Hz, 2H, CH_{aryl}), 6.45 (t, J = 7.4 Hz, 2H, CH_{aryl}), 2.38 (s, 12H, N(CH₃)₂), 0.91 (t, J = 7.7 Hz, 3H, CH₂CH₃), -0.46 ppm (q, J = 7.6 Hz, 2H, CH₂CH₃). The yield was calculated using the signal of toluene as standard (60%). No signals from **2** remained.

Reaction of 2 with Acetone. A J. Young NMR tube was charged with 2 (11 mg, 0.046 mmol) in 0.6 mL of C_6H_6 with a sealed capillary (TMS in CDCl₃) as the external standard. Then acetone (3 μ L, 0.05 mmol) was added. ¹H NMR spectra were recorded. After 12 h, **2** was completely consumed. All volatiles were removed by vacuum, and the residue was dissolved in C_6D_6 . The product **9** was identified by comparing its NMR spectrum with an independently synthesized sample of **9**. The yield was calculated by integration of the N(CH₃)₂ signal of **2** (2.71 ppm) before acetone addition and the N(CH₃)₂ signal of **9** (2.51 ppm), using the signal of TMS as the standard (58%).

Reaction of Cyclohexyl Chloride with 2. A J. Young NMR tube was charged with a solution of 2 (10 mg, 0.032 mmol, 1 equiv.) in 0.3 mL of C_6D_6 and a sealed capillary containing $H_2O/DMSO-d_6$ as internal standard (2.84 ppm). A solution of cyclohexyl chloride (10 mg, 0.085 mmol, 2 equiv) in 0.3 mL of C_6D_6 was added. Then ¹H NMR spectra were recorded periodically every 4 min over a period of 1 h. The disappearance of 2 and $C_6H_{11}Cl$ was observed as the characteristic signals at 2.71, -22.81, and 3.65 ppm diminished. The formation of the products (1 and cyclohexane) was observed as the characteristic signals at 2.57 and 1.40 ppm appeared.

Optimization of Catalytic Reduction of Alkyl Halides (Table 1). In a flask charged with 2 equiv of base (NaOⁱPr or NaOMe) a solution of 8–10 mol % of 1 in 0.5 mL of solvent, 1 equiv of $C_{14}H_{29}Cl$, and 1 equiv of $C_{12}H_{26}$ (internal standard) were added in sequence. A solution of 1–3 equiv of silane in 0.5 mL of solvent was added by syringe pump over 30 min. After 6 h, the reaction was quenched by addition of 1 mL of water, followed by addition of 3 mL of Et₂O. The organic layer containing the products was separated, and the aqueous layer was further extracted with Et₂O (3 × 3 mL). Conversion was

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Typical Procedure for Catalytic Reduction of Alkyl Halides (Table 2). In a flask charged with NaOⁱPr (25 mg, 0.31 mmol, 2 equiv), a solution of 1 (3.7 mg, 0.011 mmol) in 0.5 mL of toluene, substrate (0.15 mmol, 1 equiv), and internal standard (0.15 mmol, 1 equiv) were added in sequence. A solution of Ph₂SiH₂ in 0.5 mL of toluene was added by syringe pump over 30 min. After 6 h, the reaction was quenched by addition of 1 mL of water, followed by addition of 3 mL of Et₂O. The organic layer containing the products was separated, and the aqueous layer was further extracted with Et₂O (3 × 3 mL). Conversion was determined by GC. The products and yields were determined by GC-MS.

Typical Procedure for Catalytic Reduction of Aryl Halides (Table 2). In a flask charged with NaOMe (30 mg, 0.56 mmol, 3 equiv), a solution of 1 (5.7 mg, 0.016 mmol) in 0.5 mL of THP, substrate (0.19 mmol, 1 equiv), and internal standard (0.13 mmol, 0.7 equiv) were added in sequence. A solution of Me(EtO)₂SiH (52 mg, 0.39 mmol, 2 equiv) in 0.5 mL of THP was added by syringe pump over 30 min. After 6 h, the reaction was quenched by addition of 1 mL of water, followed by addition of 3 mL of Et₂O. The organic layer containing the products was separated, and the aqueous layer was further extracted with Et₂O (3 × 3 mL). Conversion was determined by GC. The products and yields were determined by GC-MS.

Procedure for Hydroalkylation of Decene. In a flask charged with NaOMe (30 mg, 0.56 mmol, 2 equiv), a solution of 1 (10 mg, 0.029 mmol), mesitylene (35 mg, 0.29 mmol, internal standard), dodecyl iodide (85 mg, 0.29 mmol, 1 equiv), and decene (400 mg, 3.81 mmol, 10 equiv) in 0.5 mL of toluene were added. A solution of $Me(EtO)_2SiH$ (80 mg, 0.58 mmol, 2 equiv) in 0.5 mL of toluene was added by syringe pump to the above solution over 30 min. After 4 h, the reaction was quenched by addition of 3 mL of water, followed by addition of 10 mL of Et_2O . The organic layer containing the products was separated, and the aqueous layer was further extracted with Et_2O (2 × 5 mL). Conversion was determined by GC. The products and yields were determined by GC-MS.

Crystallographic Details for 2. A total of 28 696 reflections (-12 < h < 12, -14 < k < 12, -22 < l < 25) were collected at T = 100(2) K in the range $3.06-27.50^{\circ}$, 9325 of which were unique $(R_{\rm int} = 0.0604)$, with Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 0.600 and -0.535 e Å⁻³, respectively. The absorption coefficient was 0.948 mm^{-1} . The least-squares refinement converged normally with residuals of R(F) = 0.0433 and $R_w(F^2) = 0.0996$ and GOF = 1.061 ($I > 2\sigma(I)$). Crystal data for $C_{23}H_{29}N_3$ Ni: $M_w = 406.20$, space group $P\overline{1}$, triclinic, a = 9.9932(12) Å, b = 11.0590(14) Å, c = 19.449(3) Å, $\alpha = 76.138(13)^{\circ}$, $\beta = 83.944(10)^{\circ}$, $\gamma = 85.539(12)^{\circ}$, V = 2072.1(5) Å³, Z = 4, $\rho_{calcd} = 1.302 \text{ Mg/m}^3$.

Crystallographic Details for 8. A total of 6570 reflections (-15 < h < 15, -16 < k < 16, -24 < l < 24) were collected at T = 100(2) K in the range $3.12-27.56^{\circ}$, 6570 of which were unique ($R_{int} = 0.0000$), with Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated idealized positions. The residual peak and hole electron densities were 1.651 and -1.771 e Å⁻³, respectively. The absorption coefficient was 0.709 mm^{-1} . The least-squares refinement converged normally with residuals of R(F) = 0.0855 and $R_w(F^2) = 0.2316$ and GOF = 1.194 ($I > 2\sigma(I)$). Crystal data for $C_{32}H_{40}N_6Ni$: $M_w = 567.41$, space group $P2_1/n$, monoclinic, a = 12.066(3) Å, b = 12.7657(18) Å, c = 18.651(3) Å, $\alpha = 90^{\circ}$, $\beta = 93.517(18)^{\circ}$, $\gamma = 90^{\circ}$, V = 2867.4(9) Å³, Z = 4, $\rho_{calcd} = 1.314$ Mg/m³.

ASSOCIATED CONTENT

Supporting Information

Figures giving NMR spectra of new complexes and reaction mixtures and an IR spectrum of **2** and CIF files giving crystallographic data for **2** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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Biography



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