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# Nickel Hydrides Supported by a Non-Innocent Diphosphine Arene Pincer: Mechanistic Studies of Nickel−Arene H-Migration and Partial Arene Hydrogenation

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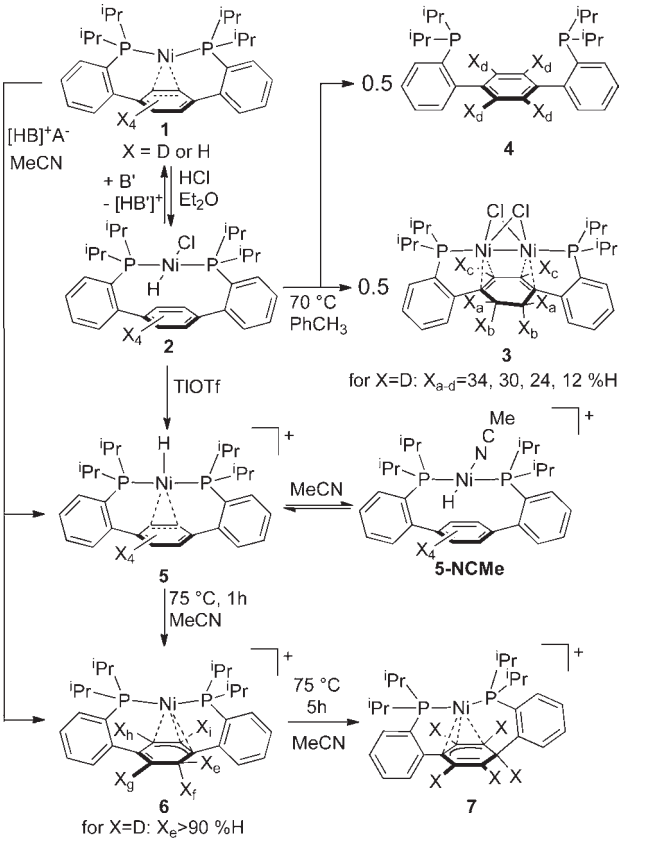
Supporting Information

**ABSTRACT:** Nickel hydrides supported by a terphenyl diphosphine were synthesized and found to undergo nickel-to-arene H-transfers. Some of the resulting complexes also undergo the reverse (C-to-Ni) H-migration, indicating the potential for storing H-equivalents in this type of pincer ligand. NMR spectroscopy, single crystal X-ray diffraction, and isotopic labeling studies investigating the mechanism of these processes are discussed.

Metal hydrides are intermediates in a wide variety of catalytic transformations. Improved understanding of the parameters that affect hydride reactivity is of interest in developing effective catalysts for proton reduction, $CO_2$ reduction, hydrosilylation, hydroboration, heterocycle activation, arene reduction, and olefin hydrogenation and isomerization.[1−18] Furthermore, molecular designs for shuttling of hydrogen equivalents are of importance in biological transformations such as dioxygen activation and reduction. A diphosphine−arene pincer ligand was recently reported to support mononuclear and dinuclear nickel complexes that exhibit strong nickel−arene interactions.[19,20] These complexes provide access to a new class of nickel hydrides supported by arene $\pi$-interactions. We report on the reactivity of these species and a series of H-migration processes relevant to arene hydrogenation and to potential storage of H-equivalents in the ligand backbone.

Treatment of Ni(0) diphosphine **1** with one equivalent of $HCl/Et_2O$ (Scheme 1) generates a new species that displays a triplet at −29.0 ppm ($J_{PH}$ = 79 Hz) in the $^1H$ NMR spectrum and a doublet in the $^{31}P$ NMR spectrum, consistent with formation of a nickel hydride complex with two equivalent phosphines.[5,8,11,21−24] Two singlets are observed in the $^1H$ NMR spectrum corresponding to the central ring, supporting a $C_s$-symmetric structure (**2**). In THF, compound **2** is 22% deprotonated by one equivalent of dimethylbenzylamine (DMBA) to reform **1**, indicating that **2** is slightly less acidic than [DMBA]-$H^+$ ($pK_a$ approximately 16.79 in MeCN[25,26]). This result also indicates that protonation of **1** is a reversible process. The single-crystal X-ray diffraction (XRD) difference map of **2** shows, in addition to a chloride and two phosphines, a smaller electron density peak in proximity to nickel ($r$ = 1.33(2) Å). This peak was assigned as a hydride ligand to complete a square planar coordination environment around the metal center. Consistent with this geometry, the Ni−C(arene) distances are long (>2.5 Å), indicating weak interaction between the metal and the $\pi$-system of the arene. Further, only a slight variation in the C−C bond lengths of the central arene is observed, with the difference between the longest and the shortest bonds of less than 0.02 Å (**2**, Figure 1). In contrast, the Ni−C bond lengths of **1** are about 1.99 Å, and the C−C bonds show differences of up to 0.07 Å.

**Scheme 1. Synthesis and Reactivity of Nickel Hydrides and Isotopic Labeling Studies**[a]




[a] [HB]$^+$A$^-$ = [H(OEt$_2$)$_2$][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] or [H$_3$NC$_6$H$_4$CN]-[OTf]; B′ = dimethylbenzylamine.

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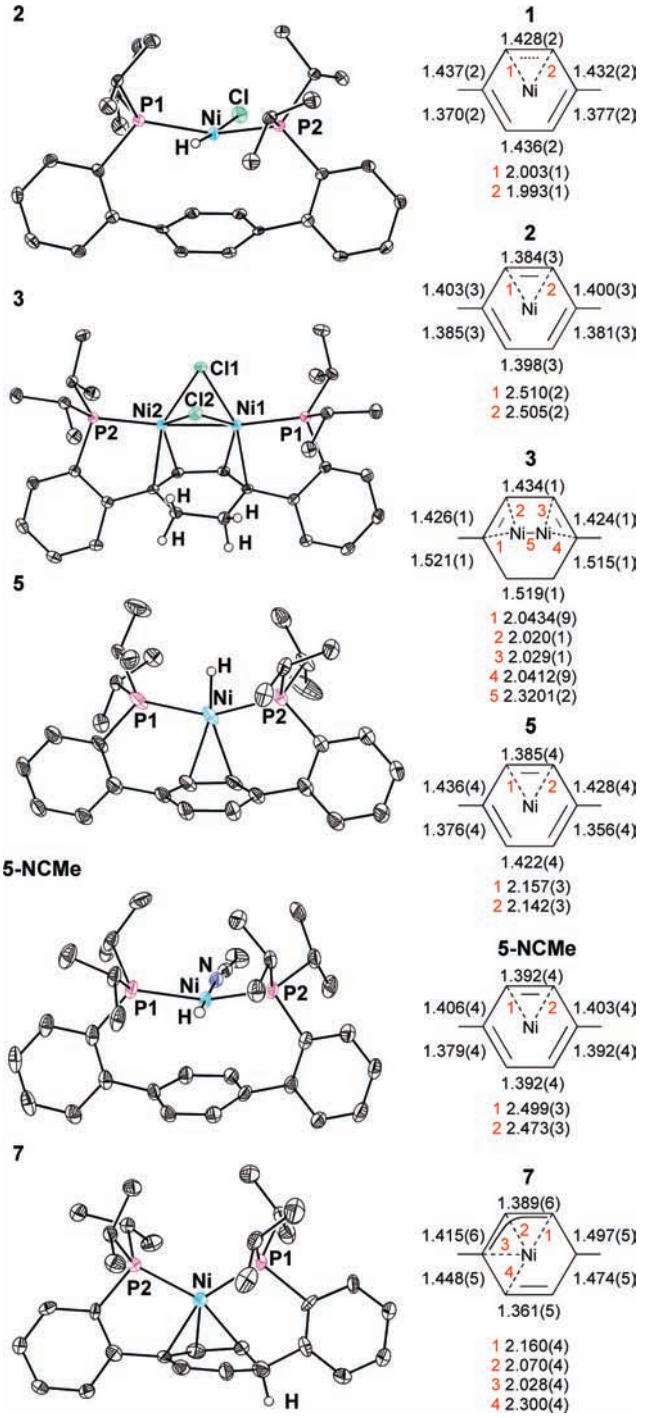


**Figure 1.** Solid-state structures of **2**, **3**, **5-OTf**, **5-NCMe-OTf**, **7-BAr$_{F24}$** (left) and selected C−C and Ni−C distances, including **1** (right). Solvent molecules, anions, and select hydrogen atoms have been cropped for clarity.

Heating a $C_6H_6$ solution of **2** at 70 °C leads to clean generation of equimolar amounts of a new nickel-containing species (**3**, Scheme 1) and free diphosphine (**4**). The $^1$H NMR spectrum of **3** shows a singlet corresponding to only two hydrogens in the olefinic region. Additionally, two new peaks that integrate to two hydrogens each are present in the aliphatic region. An XRD study reveals that **3** possesses a $Ni_2Cl_2$ core that interacts with four carbons of the central ring (Figure 1). The remaining two central ring carbons are 1.519(1) Å apart, indicative of a single bond. Thus, the present system provides a well-defined architecture to further our understanding of arene hydrogenation and H-migration from metals to arenes.[8] Furthermore, "non-innocent" aromatic ligands that can store H-equivalents by incorporation into a $\pi$-system are of interest and have been recently described in the context of transformations such as water splitting into dioxygen and dihydrogen.[27−31]

To study the H-migration process, a cationic hydride variant was prepared by halide abstraction of **2** with TlOTf. XRD studies of crystals obtained from acetonitrile solution reveal the presence of two cocrystallized cationic species in the solid state. One species (**5**) is a nickel hydride supported by two phosphines and a double bond of the central arene. The Ni−C distances (2.142(3)−2.157(3) Å) are shorter than in **2**, indicating that displacement of the halide to generate a cationic species leads to a stronger interaction of the metal center with the arene (Figure 1). The central arene C−C bond lengths indicate similar dearomatization as in **1** (variation up to 0.06 Å). The second species has acetonitrile coordinated to the site previously occupied by chloride (**5-NCMe**). Similar to **2**, the Ni−C distances are long (>2.4 Å). Peaks in the XRD difference map are assigned to hydrides of **5** and **5-NCMe** and complete pseudo-square-planar coordination environments around the metal centers. On the NMR time scale, a single species is detected in an acetonitrile solution of **5**, with a Ni−*H* signal at −25.1 ppm. In $CD_2Cl_2$, the Ni−*H* peak is at −17.6 ppm. Titration of this solution with acetonitrile leads to a gradual shift of the Ni−*H* peak toward the chemical shift in acetonitrile. This behavior suggests that coordination of acetonitrile to **5** is rapid and reversible in solution. Assuming that in acetonitrile the chemical shift of the hydride corresponds to **5-MeCN**, the equilibrium constant for acetonitrile dissociation from **5-MeCN** was determined to be 1.13 M. In THF, **5** is 26% deprotonated by one equivalent of DMBA, suggesting that it is of comparable acidity to **2**.

Handling of **5** in solvents such as THF or DCM at room temperature leads to the formation of two new species displaying no upfield $^1$H NMR signals indicative of a metal hydride over several days. As determined by various NMR correlation experiments, one species (**6**) possesses three olefinic protons and two methylene protons on its central ring (see Supporting Information [SI]). A pair of doublets ($J_{PP}$ = 10.9 Hz) is observed by $^{31}$P NMR spectroscopy. While reliable crystallographic information has not been obtained for compound **6**, NMR data is consistent with H-migration to the central ring at the position ortho to an aryl−aryl linkage (Scheme 1).

The species (**7**) observed in mixture with **6** possesses two olefinic $^1$H peaks and a pair of $^{31}$P doublets ($J_{PP}$ = 1.4 Hz). XRD characterization of **7** shows that the two arene−arene linkages display different angles, with one being significantly removed from coplanarity with respect to the central ring. The C−C bonds of the central ring adjacent to this aryl−aryl linkage are elongated (>1.47 Å). The nickel center displays close contacts to only three carbons of the central ring (<2.2 Å), reminiscent of a metal−allyl interaction. Consistent with this bonding description, a double bond appears to be localized between the remaining two carbons of the central ring.[32−34] The crystallographic and NMR data are consistent with H-migration to the ipso carbon of the central ring (Scheme 1).

To further explore the potential of the arene pincer for reversible storage of H-equivalents, the cationic product (**6**) of Ni-to-C H-migration was investigated. Heating of **5** in THF


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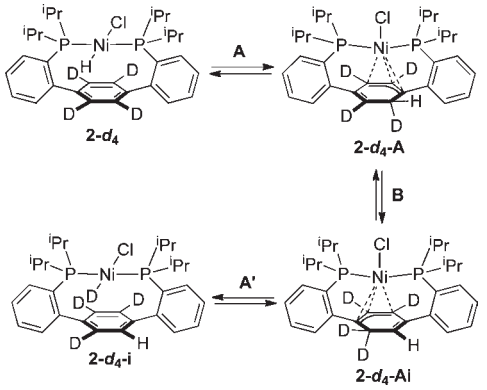
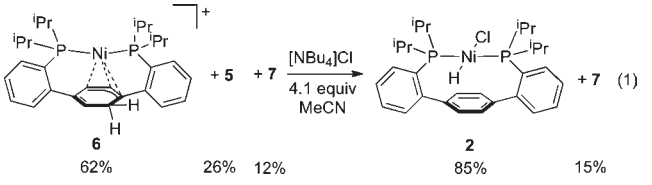
**Scheme 2. Proposed Mechanism for Isotopic Scrambling between the Metal Hydride and the Phosphine Backbone**




was interrupted when a mixture of **6** (62%), **5** (26%), and **7** (12%) was generated (eq 1). Addition of chloride to this mixture leads to the formation of **2** (85%) and **7** (15%) which is consistent with the quantitative conversion of **6** and **5** into **2**. Treatment of the mixture of **6**, **5**, and **7** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) leads to the formation of **1**. While generation of **2** from **5** by coordination of chloride is expected, the generation of **2** from **6** is less mechanistically obvious. In an acid−base mechanism, chloride could act as a base to deprotonate **6**, generating **1** and HCl as intermediates toward **2**. This explanation is inconsistent with the stability of **7** toward chloride and the weak basicity of chloride (predicted $pK_a$(HCl) = 10.30 in MeCN[35]). In an alternate mechanism, chloride could bind to nickel and weaken metal−carbon interactions, leading to more reactive methylene C−H bonds that would be prone to undergo C-to-Ni H-transfer. Intramolecular H-migration between a metal center and a delocalized $\pi$-bound ligand has been proposed previously, for example, for the hydrogenation of arene by cobalt hydrides and for isotopic scrambling in the reductive elimination of alkane from bis(pentamethylcyclopentadienyl)zirconium derivatives.[36,37] However, direct deprotonation of the arenium moiety by added base cannot be ruled out, especially for stronger bases, given that both **6** and **7** are converted to **1** by DBU ($pK_a$([DBU]-H$^+$) = 24.34 in MeCN[26]).




The H-migration processes were studied in detail. Heating of **5** for 1 h at 75 °C in $CD_3CN$ leads initially to formation of **6** with little generation of **7**; further heating converts **6** to **7** (Scheme 1). These observations are consistent with H-migration from the metal center to the less substituted carbon of the central arene, under kinetic control to first generate intermediate **6**. Further H-migration around the ring to the ipso-carbon gives the thermodynamic product **7**. Calculations have suggested that ipso protonation is thermodynamically disfavored vs ortho or para protonation of biphenyl,[38] but the relative stability of **5** might be due to release of terphenyl strain that is present in all other mononuclear complexes of ligand **4** (**1**, **2**, **5**, and **6**). Protonations of **1** with [H(OEt$_2$)][B(C$_6$H$_3$(CF$_3$)$_2$)$_4$] or [H$_3$NC$_6$H$_4$CN]-[OTf] (OTf = triflate) in acetonitrile at room temperature lead to **5** and **6** upon mixing (Scheme 1). The fast formation of **6** suggests that **5** is not an intermediate in this case. Hence, direct intermolecular protonation at the carbon is a viable mechanistic pathway in these systems. Again, formation of **7** is kinetically unfavorable.

Isotopic labeling studies have provided further mechanistic insight (Scheme 1). Nickel complexes of **4**-$d_4$ ($^2$H-labeled at the central arene) were prepared. Complex **5**-$d_4$ converts to **6**-$d_4$ with $^1$H incorporation primarily at the endo methylene position of the central ring ($X_e$, Scheme 1). No $^1$H incorporation occurs at the olefinic positions ($X_g$, $X_h$, or $X_j$). Unreacted **5**-$d_4$ (during the conversion to **6**-$d_4$) showed no label scrambling. Lack of $^1$H incorporation at the olefinic positions indicates that, after H-transfer from metal to carbon (similar to process A, Scheme 2), 1,2-H shifts (process B) from methylene to methine do not occur on the time scale of the experiment.[39,40] $^1$H incorporation at the endo methylene position suggests an intramolecular mechanism for conversion of **5** to **6**. The rate of formation of **6** from **5** is solvent dependent, indicating that coordination of nitrile to **5** inhibits H-migration. The nickel interaction with the $\pi$-system, which is stronger in the absence of acetonitrile, may be a determining factor for ring activation toward H-transfer.

Upon heating, **2**-$d_4$ leads to significant label distribution to all positions of the ring in **3** (% $^1$H incorporation at aliphatic positions $X_a$ and $X_b$, and olefinic position $X_c$ is respectively 34:30:24, Scheme 1) but also into free phosphine, **4** ($X_d$, 12%). Analysis of unreacted **2**-$d_4$ at 50% conversion shows ~60% of $^1$H scrambled into the aromatic positions. Label scrambling in **2**-$d_4$ suggests a mechanism similar to the conversion of **5** to **6** (process A, Scheme 2), but followed by either 1,2-H-shift from methylene to methine (process B) and then migration of H(D) back to nickel (process A′), or intermolecular H-transfer back to metal to give isotopomer **2**-$d_4$-**i**. This scrambling further attests to the reversible H-shuttling potential of pincer arenes. As with **5** in acetonitrile, compound **2** requires heating for H-migration to occur; this again may be a consequence of a weaker interaction between nickel and the central arene. This proposal is consistent with the difference in the isotopic label scrambling between the cationic and neutral hydrides; a weaker interaction between the halide-coordinated nickel and the $\pi$-system may allow for facile 1,2-H shifts if an arenium moiety is formed. In contrast, assuming that the $\pi$-system of **6** is localized as in **7** (as a strong nickel−allyl-like interaction adjacent to a double bond), 1,2-H shifts are less accessible for the cationic species.

The sequence of steps subsequent to H-migration leading to the dinuclear species **3** and free phosphine **4** are not clear. Nevertheless, isotopic scrambling in **2**-$d_4$ (Scheme 2) explains the incorporation of $^1$H at all positions on the central rings of **3** and **4**; the lower than expected statistical $^1$H content in the resulting free phosphine, however, suggests an isotope effect for subsequent steps that favors $^1$H incorporation into the partially reduced arene of **3**. The driving force for this reaction may be the formation of a Ni$^{I}_2$Cl$_2$ moiety, which has been observed in a few reactions with this ligand. A combination of bridging halides, Ni−Ni bonding, and Ni−arene interactions may render **3** as the thermodynamic product.

In summary, neutral and cationic nickel hydride complexes supported by a terphenyl diphosphine have been synthesized. The neutral nickel hydride has been shown to partially hydrogenate the pincer arene. The H-migration was studied in detail using isotopic labeling and characterization of intermediates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observed with the cationic hydrides. Metal-to-arene H-migration was found to be reversible by isotopic labeling; chloride addition to a nickel-bound arenium species results in H-migration from carbon back to metal. Future studies will focus on exploring applications of the uncovered H-storage capacity of the arene pincer and the effect of the ligand framework on the hydridic character of the Ni−H moiety.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Experimental procedures, characterization data, and crystallographic details for **2**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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