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# Mechanism of Heterolysis of $H_2$ by an Unsaturated $d^8$ Nickel Center: via Tetravalent Nickel?

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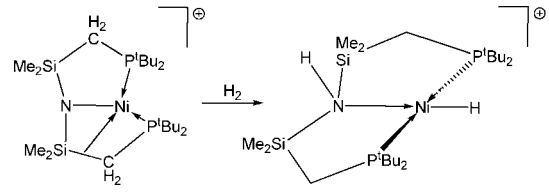
It is reasonable to generalize that the *initial* interaction of $H_2$ with any metal center is to form an $\eta^2$-$H_2$ complex.[1−4] However, the vast majority of isolated examples of this type[5] have the $d^6$ electronic configuration, while we will deal here with a $d^8$ species. When the *overall* observed reaction is the heterolytic splitting of $H_2$, to form $H^+$ and $H^-$, cationic $\eta^2$-$H_2$ complexes are the most Brønsted acidic, thus showing the greatest tendency for such splitting of $H_2$. Generally this heterolysis requires a Brønsted base to receive the $H^+$, and a series of papers on $H_2$ heterolysis by $Ni^{II}$ showed[6−8] that this is greatly facilitated when the base is a component of some ligand, so that the proton transfer is intramolecular; this is also the core of known polar multiple bond hydrogenation catalysis where one ligand is an amide.[9,10]

When the metal electron configuration is $d^8$ in a planar, four-coordinate complex, arriving $H_2$ encounters a filled $d_{z^2}$ orbital along the sterically favored trajectory for $H_2$ approach, so that forming $L_4Ni(H_2)$ is kinetically unfavorable. Consistent with this, we find that (PNP)NiCl, where PNP is $N(SiMe_2CH_2P^tBu_2)_2$, is unchanged after treatment with 1 atm of $H_2$ over 12 h at 25 °C in THF and further unchanged after adding equimolar $NEt_3$, the latter in an attempt to promote heterolysis and loss of HCl. We have reported[11] a "three-coordinate" $(PNP)Ni^+$ species which offers a new mechanistic opportunity, since the T-shaped species has a LUMO in the coordination plane and trans to nitrogen, hence more suited to accept arriving $H_2$. On the other hand, the thermodynamics of $M/H_2$ bonding requires back-donation: $H_2$ does not bind to Lewis acidic $d^0$ metals or to $d^9$ or $d^{10}$ Lewis acids, all because $\sigma_{HH}$ electron density alone is not an adequate donor. The later transition metals, $Ni^{II}$ and especially $Cu^I$, have a high nuclear charge and are thus poor $\pi$-bases, so $H_2$ coordination might be anticipated to be weak; this factor will be accentuated in mono- and (more so) in dicationic species.[12] Note that precisely this point is currently an unsolved puzzle in "Frustrated Lewis Pairs" attacking $H_2$, since the suspected[13−15] adduct of $H_2$ to the Lewis acidic borane has never reached spectroscopically detectable concentrations, apparently due to lack of back-donation leading to unfavorable thermodynamics. This is also why $H_2$ binding to later transition metal ions (divalent Co, Ni, and Cu) in metal−organic frameworks is (desirably, for gas storage purposes)[16−20] weak. Nevertheless, the fact[21] that certain nickel enzymes "split" $H_2$ shows that these negative factors do not fully block hydrogen transformation by nickel in biochemistry.[22−24] We report here a study of the binding of $H_2$ to $(PNP)Ni^+$, which shows some unusual features, which ultimately reflects on the utility of an intramolecular Brønsted base to effect heterolytic splitting of $H_2$.[6−8]

Reaction of $[(PNP)Ni]BAr^F{}_4$ with 1 atm of $H_2$ in $CH_2Cl_2$ at 25 °C was observed (eq 1) to occur at the time of mixing, to form the $BAr^F{}_4$ salt ($Ar^F$ = 3,5-$(CF_3)_2C_6H_3$) of the cation $(PN(H)P)NiH^+$. This cation shows a $^{31}P\{^1H\}$ NMR singlet at 62 ppm and a hydride triplet at −22 ppm and was established by NMR spectroscopies to




(1)

have $C_s$ symmetry, with two inequivalent types of $^t$Bu, SiMe, and $CH_2$ hydrogens. This lack of $C_{2v}$ symmetry is due to the NH proton which differentiates opposite sides of the PNPNi plane. While this heterolytic splitting of $H_2$ (vs oxidative addition) is to be expected on divalent nickel, it gets an assist from the Brønsted basic character of the amide nitrogen. This cation can be deprotonated rapidly by $LiN^iPr_2$ in THF to give the neutral (PNP)NiH.[25]

The rapidity of $H_2$ reacting with $(PNP)Ni^+$ suggests that a low temperature search for intermediates might be informative. While species "$(PNP)NiH_2^+$" are the likely primary products of a bimolecular collision, both of these ($Ni^{IV}$ dihydride or $Ni^{II}$ dihydrogen structures) would seem to have symmetry-equivalent H and thus the follow-up step of migrating one H to nitrogen, with polarizing one H to be $H^+$, is a mechanistically unexplored step. The key step is breaking the symmetry equivalence of the two H, to initiate formation of one positively polarized H.

We have explored possible mechanisms by DFT geometry optimization studies and find (Scheme 1) that optimization starting from a structure (**1**) with the Si−C donation still present but having $H_2$ bonded transoid to N evolves to dissociate that Si−C donation to nickel. The resulting $\eta^2$-$H_2$ complex **2** is a stationary state but is very weakly bound at room temperature ($\Delta G_{298}{}^o \approx 0$). Its structure has the H−H vector (H/H distance 0.80 Å) lying nearly in the plane of atoms P, N, P, and Ni. We found no Ni(IV) dihydride structure as a minimum: such a starting geometry with a Y-shape of $C_{2v}$ symmetry optimizes instead to the above $\eta^2$-$H_2$ structure, but geometry optimization beginning with the H−H vector flanking the Ni−N vector of **1** minimizes directly to the final structure, $(PN(H)P)NiH^+$, **3**, which is more stable than the reagents by 36.0 kcal/mol. This final structure of **3** has a long (2.10 Å) Ni/N distance, consistent with a weak disilyl amine donor, and, curiously, has a Ni−N−H angle compressed to 93.8$^o$ and a Ni/H(N) distance of only 2.40 Å, indicating an interaction between the acidic amine hydrogen and nickel; this we interpret as a weak intramolecular hydrogen bond to the occupied $d_{z^2}$ orbital of $d^8$ nickel, which has its weakening impact on the Ni/N bond, complemented by N dative bond misorientation.

On the experimental side, combining $[(PNP)Ni][BAr^F{}_4]$ with 1 atm of $H_2$ (5-fold excess) in $CD_2Cl_2$ below −78 °C, mixing briefly with avoidance of significant heating, and then recording $^1H$ and $^{31}P$ NMR spectra in 10 °C increments, beginning at −60 °C, show complete conversion to a species with equivalent P nuclei (85 ppm



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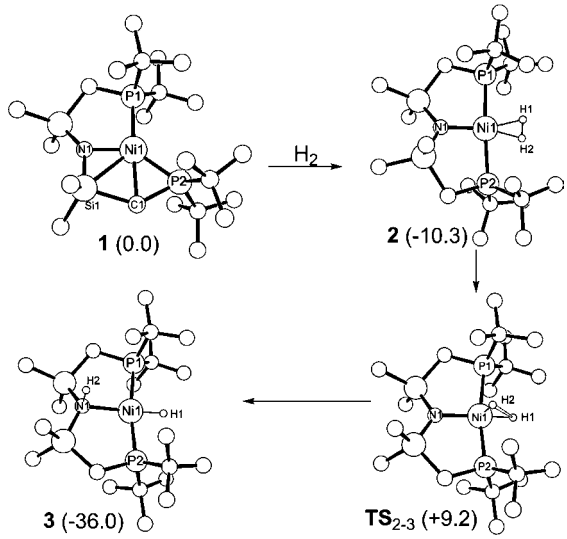
***Scheme 1.*** DFT Structures and Electronic Energies (kcal·mol)




chemical shift) and a broad $^1$H NMR peak at −9 ppm. At −30 °C, the 85 ppm signal is weaker and there is the first appearance of a $^{31}$P{$^1$H} NMR singlet at 62 ppm, accompanied by a well-resolved $^1$H NMR triplet at −22 ppm. At − 20 °C, the peak at 85 ppm has disappeared, leaving a strong singlet at +62 ppm (due to the final (PN(H)P)NiH$^+$ product); the −9 ppm $^1$H NMR signal is now gone and only the −22 ppm hydride signal remains.[26] The reaction run with only equimolar $H_2$ shows only partial conversion of (PNP)Ni$^+$ at −60 °C to the 85 ppm species consistent with the calculated low free energy of adduct formation.

We tested the DFT result that the detected intermediate was indeed a dihydrogen complex by measuring the $T_{1\ \mathrm{min}}$ value of the −9 ppm signal of this species. This minimum occurs at −65 °C in $CD_2Cl_2$ at 500 MHz, at a value of 15 ms. This short value is consistent with a dihydrogen ligand with a very short H/H distance (lengthened from the value in free $H_2$ by only 0.06 Å in the DFT calculation, due to minimal back-donation).

We thus view the mechanism as involving an $\eta^2$-$H_2$ complex as the only detected intermediate, but migration of one of these H-atoms to the amide nitrogen would appear to be a long distance (*trans* mutual positioning of N and $H_2$ in **2**). We identified a transition state for this intramolecular migration, $\mathbf{TS_{2-3}}$. This TS for H/H bond splitting (Scheme 1) no longer has an H/H bond (distance 1.76 Å) and has Ni/H distances shorter than that in the $H_2$ complex (hence more characteristic of distances in nickel hydrides), and it has every appearance of full oxidative addition to Ni, hence Ni$^{IV}$. Also consistent with this oxidation state/electron configuration is that it has a square pyramidal structure. It is not a minimum, and hence the mechanism does not involve a tetravalent *intermediate*. The local activation energy from the $H_2$ complex to this TS is +19.5 kcal/mol, which corresponds to a half-life of only minutes at −10 °C, and so has a predicted rate consistent with the experimental observations. A $J_{HD}$ value of 33 Hz for (PNP)Ni(HD)$^+$ independently confirms this conclusion; subsequent formation of **3** shows $k_H/k_D = 2.5$.

Comprehensive studies of divalent nickel with bidentate phosphines incorporating tertiary amine functionality[6,7] have shown that proton transfer participates in $H_2$ heterolysis and even in conversion of $H_2$ fully[8] to two protons with two-electron reduction of Ni$^{II}$. In none of these cases has coordinated $H_2$ been directly detected, due to the facility of intramolecular proton transfer. In one case,[6] detection of two signals at negative chemical shift has been interpreted as a dihydride of Ni$^{IV}$. Our success here in detecting a dihydrogen complex from (PNP)Ni$^+$ may originate from the fact that our amide base is sterically constrained to be far from (i.e., trans to) $H_2$, while the design (i.e., ligand flexibility) of the previous work was intended to *facilitate* proton transfer.

In [NiFe] hydrogenase, $H_2$ is generally thought to react with the Fe−SR unit, and there is never a Ni/H bond formed.[22] Instead, nickel plays the role of a source/sink of electrons in the redox changes; this is consistent with the absence of any isolable or detectable Ni/$H_2$ complex. In a later DFT study,[21] Siegbahn has found that Ni$^{III}$ offers an energetically favorable mechanism. Thus, although active site nickel oxidation states of +1, +2, and +3 have been discussed, there is no issue of possible Ni$^{IV}$, and even direct heterolysis of $H_2$ *on* nickel is not currently thought to be relevant to enzyme activity: by DFT, it is not energetically viable. The absence of a Ni$^{IV}$ dihydride intermediate in the system described here appears reasonable if the goal is to break the symmetry equivalence of the two H-atoms since a dihydride does not accomplish that. Combined with the high Brønsted acidity of $\eta^2$-$H_2$, avoiding a Ni$^{IV}$ dihydride might appear to be most logical. However, the mechanism we report here *does* involve a Ni$^{IV}$ species, but with a high energy characteristic of a TS, not of an energetic minimum, and with inequivalent H-ligands.

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**Supporting Information Available:** Complete synthetic, spectroscopic, and computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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