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Cluster Compounds

Catalytic Hydrogen/Deuterium Exchange of Unactivated Carbon–Hydrogen Bonds by a Pentanuclear Electron-Deficient Nickel Hydride Cluster**

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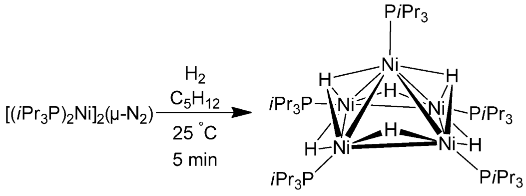
The activation and catalytic functionalization of C–H bonds has gained importance as both a green and economical synthetic approach.[1] A modern goal is the use of less expensive first-row metals, such as nickel, in lieu of the expensive second- and third-row metals currently used for most catalytic C–H functionalization processes. Although there are examples of catalytic C–H bond functionalization using nickel, which include unprecedented reactions such as C–H bond stannylation,[2] these transformations are typically limited to activated substrates like fluorinated aromatics.[3] An alternative approach is to use cooperative bond activation[4] by dinuclear or polynuclear complexes in unusual oxidation states; for example, dinuclear Ni^{I} complexes have been reported to mediate the rearrangement of activated C–H bonds.[5] Polynuclear clusters of the first-row transition metals may have an advantage over their heavier congeners in catalytic reactivity, because of the smaller HOMO–LUMO gap and weaker metal–metal bonds that render these complexes more reactive (HOMO/LUMO = highest occupied/lowest unoccupied molecular orbital).[6]

The reaction of $[(i\text{Pr}_3\text{P})_2\text{Ni}]_2(\mu\text{-N}_2)$[7] and dihydrogen with the loss of N_2 according to Scheme 1 provides the pentanuclear cluster $(i\text{Pr}_3\text{P})\text{Ni}(\mu_3\text{-H})_2[(i\text{Pr}_3\text{P})\text{Ni}(\mu_2\text{-H})]_4$ (**1**). Cooling a pentane solution of the product to −34 °C led to the precipitation of dark-brown rhombic crystals of **1** in 26 % yield; the low yield reflects the high solubility of the product. The infrared spectrum confirmed the presence of bridging hydride ligands and the absence of terminal hydrides. A broad band attributed to ν(Ni–H) is found at 1235 cm^{-1}. The solid-state structure of **1** was determined by X-ray diffraction, and two views are given in Figure 1.[8]



$[(i\text{Pr}_3\text{P})\text{Ni}]_5\text{H}_6$
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Scheme 1. Synthesis of pentanuclear complex **1**.

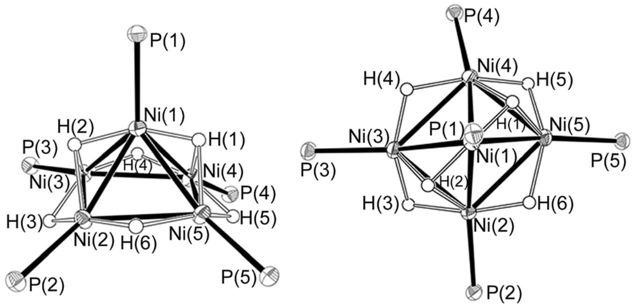

Figure 1. Solid-state molecular structure of $[(i\text{Pr}_3\text{P})\text{Ni}]_5\text{H}_6$ (**1**) as determined by X-ray crystallography, shown with 50% probability ellipsoids. Hydrogen atoms not attached to Ni are omitted for clarity. Selected bond distances [Å] and angles [°]: Ni(1)–Ni(2) 2.3988(4), Ni(1)–Ni(3) 2.4825(4), Ni(1)–Ni(4) 2.4033(4), Ni(1)–Ni(5) 2.4520(4), Ni(2)–Ni(3) 2.4091(4), Ni(2)–Ni(5) 2.6308(4), Ni(3)–Ni(4) 2.6041(4), Ni(4)–Ni(5) 2.3888(4), Ni(1)–P(1) 2.1749(6), Ni(2)–P(2) 2.1652(6), Ni(3)–P(3) 2.1906(6), Ni(4)–P(4) 2.1500(6), Ni(5)–P(5) 2.1719(6).

Complex **1** consists of a distorted square pyramid of Ni atoms, with the base atoms exhibiting marked differences in the Ni–Ni distances (2.3891(4)–2.6310(4) Å); the bond lengths and angles associated with these distortions are shown in Figure 2. The electron densities associated with the six hydride ligands were located in a difference map, and the hydride positions were refined. Each basal Ni–Ni edge is spanned by a μ_2-hydride ligand. Hydrogen atoms H(4) and

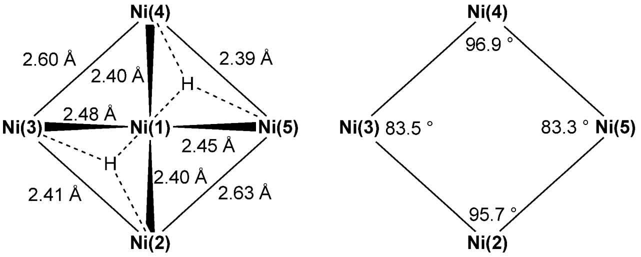

Figure 2. Framework of **1** with selected approximate bond lengths and angles.

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H(6) are above the basal plane and H(3) and H(5) are below the basal plane. Hydrides H(1) and H(2) cap faces of three nickel atoms and are approximately *trans*-disposed. The coordination environment of Ni(1) resembles a square-planar *trans*-$(i\mathrm{Pr_3P})_2\mathrm{Ni^{II}H_2}$ moiety, in which one phosphine donor is removed and the *trans*-$(i\mathrm{Pr_3P})\mathrm{NiH_2}$ moiety caps the $(i\mathrm{Pr_3P})_4\mathrm{Ni_4H_4}$ basal plane. The shorter Ni–Ni distances of the basal plane are bridged by a pair of hydride ligands, reminiscent of the known dinuclear $[\mathrm{L_2Ni}]_2(\mu\text{-H})_2$ complexes of $\mathrm{Ni^I}$, where L is a phosphine donor.[9] A neutron diffraction study would better determine the location of the hydrides, and attempts are currently underway to produce suitably sized crystals for such an experiment.

DFT calculations with model complexes bearing $\mathrm{PMe_3}$ donors deviated in geometry significantly from the experimental results, thus calculations were performed using the entire $i\mathrm{Pr_3P}$-supported complex **1**. These calculations reproduced the gross connectivity and geometry of **1** and also provided support for the positioning of hydride ligands suggested by the X-ray crystallographic data. Other hydrogen locations provided modestly higher-energy local minima, the nickel frameworks of which were not similar to **1**.

Because of reactions with the solvent, which render the NMR spectra of **1** more complicated, NMR spectra of **1** were obtained in nondeuterated benzene. The ^{1}H and ^{31}P{^{1}H} NMR spectra of diamagnetic **1** recorded at 25 °C in benzene are consistent with a rapid fluctional process that exchanges the hydride and phosphine environments. The ^{1}H NMR spectrum has a singlet at $\delta = -26.5$, attributed to the hydrido ligands. The integrals are consistent with the formulation $[(\mathrm{P}i\mathrm{Pr_3})\mathrm{Ni}]_5\mathrm{H_6}$ observed in the solid state. The ^{31}P{^{1}H} NMR spectrum exhibits a singlet at $\delta = 60.6$. Variable-temperature NMR spectra were recorded in toluene. Significant broadening of resonances was not observed until 213 K. Decoalescence was not observed for any resonance as low as 183 K. The ^{31}P{^{1}H} NMR chemical shift of **1** was temperature dependent. The ^{31}P chemical shift versus temperature could be modeled with the presence of a thermally accessible electronic triplet ($S = 1$) state $-2900\ \mathrm{cm^{-1}}$ above the singlet ($S = 0$) ground state. The experimental ^{31}P chemical shift data and the modeled curve are shown in Figure 3. The model predicts that 0.00025 % of the sample is in the triplet state at 298 K. The magnitude of the temperature-dependence observed is only consistent with a paramagnetic isomer. Above room temperature, the ^{31}P{^{1}H} NMR linewidth also increases with increasing temperature, suggestive of a paramagnetic excited state. The ^{1}H NMR hydride chemical shift is only modestly affected by temperature, which suggests a smaller contact shift for the hydride nuclei relative to the ^{31}P nuclei, consistent with related reports of a temperature dependence of hydride resonances in a $\mathrm{Ni^I}$-$\mathrm{Ni^{II}}$-$\mathrm{Ni^I}$ trinuclear hydride.[10] Full details for the model are provided in the Supporting Information.

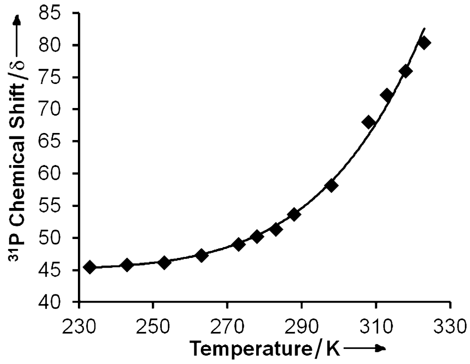
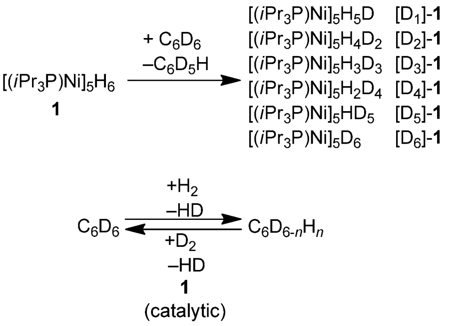


Figure 3. Plot of the ^{31}P{^{1}H} NMR chemical shifts versus temperature for complex **1**. The solid line is a fitted curve based on a model assuming that **1** is a ground-state singlet ($S = 0$) with a triplet state ($S = 1$) that is thermally accessible.

The rapid fluxionality exhibited at all accessible temperatures renders an assignment of the solution structure of **1** in benzene ambiguous; however, in [D$_6$]benzene H/D exchange between the hydride ligands and the solvent allowed for the assignment of the solution structure. By monitoring the ^{31}P{^{1}H} NMR spectrum of **1** in [D$_6$]benzene, a reaction that exchanges the hydride ligands for deuterium produced the isotopologues [D$_1$]-**1**, [D$_2$]-**1**, [D$_3$]-**1**, [D$_4$]-**1**, [D$_5$]-**1**, and [D$_6$]-**1**, as shown in Scheme 2. Under these conditions, deuterium scrambling into the $i\mathrm{Pr_3P}$ ligands was not observed by ^{2}H NMRspectroscopy. The observation of resonances for each isotopologue indicates that the rapid fluctionality observed by NMR spectroscopy cannot involve intramolecular exchange of hydride or phosphine ligands from the $[(\mathrm{P}i\mathrm{Pr_3})\mathrm{Ni}]_5\mathrm{H_6}$ framework on the NMR timescale, or else unique signals for each isotopologue of **1** would not be observed. The presence of seven isotopologues confirms that **1** is a hexahydride of the likely composition $[(\mathrm{P}i\mathrm{Pr_3})\mathrm{Ni}]_5\mathrm{H_6}$, as determined from the solid-state structure. In the presence of added $\mathrm{H_2}$ or $\mathrm{D_2}$ complex **1** can also be used to catalyze H/D exchange, as shown on the bottom of Scheme 2; however, the rate of this reaction at room temperature is currently too slow to be practical for the large-scale deuteration of hydrocarbons using $\mathrm{D_2}$.



Scheme 2. Room-temperature H/D exchange between complex **1** and $\mathrm{C_6D_6}$.

The reaction of **1** with [D$_6$]benzene at 298 K was monitored by ^{31}P{^{1}H} NMR spectroscopy as shown on the left side of Figure 4. With each added deuteride, the isotopologues of **1** have a change in chemical shift of about −0.8 ppm at 298 K. Each spectrum was modeled using the percent conversion of hydride to deuteride as the only fitted

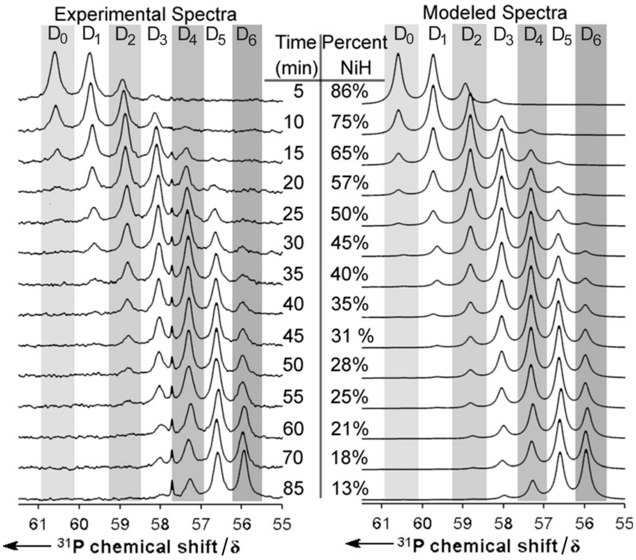


Figure 4. $^{31}P\{^1H\}$ spectra of a solution of **1** in C_6D_6, collected in the time range from 5 to 85 minutes, showing the stepwise conversion from $[D_0]$-**1** to $[D_6]$-**1**. The modelled spectra are shown on the right.

parameter. The modeled spectra shown on the right-hand side of Figure 4 were obtained by assuming a statistical distribution of hydride and deuteride amongst the isotopologues. The conversion of hydride to deuteride follows first-order kinetics under these conditions, with a half-life of 27 minutes, which corresponds to a $\Delta G^{\neq}$ value of activation of 22 kcal mol^{-1}.

The ^{1}H NMR spectrum of the reaction of **1** with C_6D_6 exhibits signals for the six hydride-containing isotopologues, with an upfield shift of about 0.02 ppm from the replacement of each hydride with deuteride. The signal separation is not strongly temperature dependent, and thus a rapid equilibrium between bridging hydride (μ-H) and dihydrogen bonding (η^2-H_2) is unlikely. Consistent with this, the spin–lattice relaxation time constant (T_1) for the hydride signal of **1** at 298 K was 147 ms, which is significantly greater than the T_1 values typically associated with dihydrogen complexes.

In conclusion, we have isolated a distorted-square pyramidal *nido* cluster with a nickel core and six bridging H ligands and five terminal phosphine groups. This complex is electron deficient, with an electron count of 66, rather than the 74 electrons expected for a square-pyramidal *nido* cluster supported by strong-field ligands.[11] The only closely related hydride-rich clusters in the literature is the 68 electron trigonal bipyramidal complex $[Pt(PPh\textit{t}Bu_2)]_5H_8$, the reactivity of which has not been reported.[12] Hydride-rich clusters not stabilized by π-donor or π-acceptor ligands[13] are rare and have been prepared almost exclusively with second- and third-row transition metals such as Pt and Rh,[14] with the exception of some Cu complexes that feature only weak Cu–Cu d^{10}–d^{10} interactions.[15] Complex **1** is highly reactive, with a low-lying thermally accessible triplet state, and provides a rare example of H/D exchange with unactivated substrates catalyzed by nickel; one other example of a trinuclear nickel tetrahydride that facilitates H/D exchange has been reported, but requires longer reaction times (24 h) and higher temperatures (60 °C).[10] Studies are under way to determine the mechanism and scope of H/D exchange using **1** and to determine if the reactivity of this cluster can be used for catalytic applications, such as C–H bond functionalization.

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