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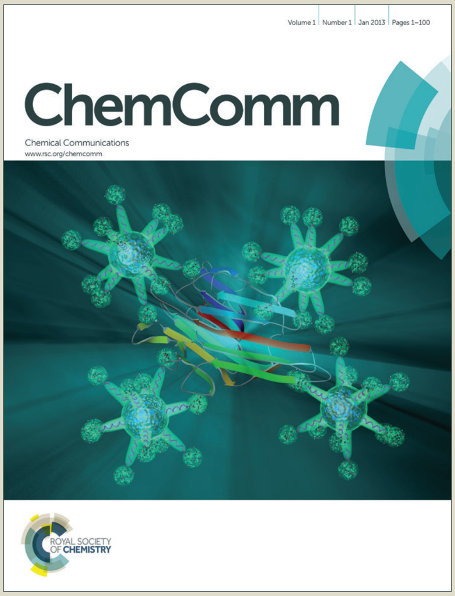

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Boryl-Assisted Hydrogenolysis of a Nickel-Methyl bond

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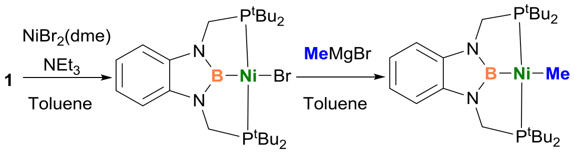
A stable Nickel(II) methyl complex containing a diphosphino-boryl (PBP) pincer ligand is described. Mechanistic studies on the hydrogenolysis of the Ni-Me bond suggest a metal ligand cooperation mechanism that involves the intermediacy of a σ-B–H Ni(0) species that further undergoes B–H oxidative addition to form a Ni(II) hydride complex.

Transition metal complexes containing pincer ligands are used to support catalysts in a large variety of processes due to their potential to promote unusual chemical transformations.[1] In these systems the electronic and steric properties can be easily modulated by varying the ligand architecture. Therefore, correlating their structure and chemical reactivity is crucial in the design of novel catalytic systems. Recently, Nozaki, Yamashita and Hill succeeded in the synthesis of tridentate ligands incorporating boron on the central atom (PBP) and in the coordination of these to transition metals.[2] The interest of this class of ligands lies on their potential to display novel reactivity due to the strong σ-donor ability and high *trans* influence exerted by the boryl moiety.[3] Recently, Peters and co-workers reported the addition of H_2 across a metal-boryl bond mediated by a PBP pincer cobalt complex.[4] The ability of boron to act as 'hydride shuttle' operating in a cooperative manner with the metal, via B-H bond activation, renders the process reversible. Such reactivity has shown to be useful for interesting catalytic applications. In light of these precedents, we became interested in investigating the possible non-innocent character of the boryl-fragment for the development of further catalyst systems that utilize this strategy. Nickel based catalysts represent an excellent alternative for precious metals catalysts and has proven to be versatile in several catalytic transformations.[5] In this contribution we report the synthesis and structural characterization of several PBP pincer nickel complexes.[6] Moreover, we will prove the prominent role of the nickel-boryl moiety in the mechanism of hydrogenolysis of a nickel-methyl bond.

Reaction of hydroborane $C_6H_4\{N(CH_2PP^tBu_2)\}_2BH$ (**1**) with $[NiBr_2(dme)]$ (dme = 1,2- dimethoxyethane) in the presence of NEt_3 allowed the formation of complex **2** as an air and moisture sensitive yellow solid in 65% yield (Scheme 1). The equivalence of both phosphorous nuclei was confirmed by a singlet resonance at 85 ppm in the $^{31}P\{^1H\}$ NMR spectra while, in the ^1H and ^{13}C NMR spectra, the methyl groups of the ^{t}Bu substituents appear as virtual triplets consistent with a square-planar geometry. The $^{11}B\{^1H\}$ spectrum features one broad resonance at 39 ppm assigned to a coordinated σ–boryl ligand.[2]



2 **3**

Scheme 1 Synthesis of complexes **2** and **3**.

Treatment of **2** with MeMgBr generates **3** in 83 % yield. Similarly to **2**, complex **3** proved to be very sensitive and decomposed readily when exposed to air or moisture. In the ^1H NMR spectrum, the most characteristic resonance is a triplet centred at 0.15 ppm ($^3J_{P\text{-}H}$ = 5.9 Hz) assigned to the methyl group and the corresponding carbon signal appears as a triplet at -8.94 ppm ($^2J_{C\text{-}P}$ = 12.9 Hz) in the $^{13}C\{^1H\}$ spectrum. The phosphorous resonance at 97 ppm is shifted downfield relative to **2** in the $^{31}P\{^1H\}$ spectrum. Finally, the $^{11}B\{^1H\}$ spectrum features a broad signal at 46 ppm, consistent with a metal bound boron centre. The solid state structures of **2** and **3** were borne out by X-ray diffraction analysis. Both complexes feature a slightly distorted square-planar geometry at nickel (Figure 1). The Ni–B bond lengths (1.900 (3) and 1.928 (2) Å in **2** and **3** respectively) are close in value to those reported for related nickel-boryl complexes.[7] Likewise, the Ni–Br (2.3700 (3) Å) (**2**) and Ni–C bond lengths (2.059 (2) Å) (**3**) are slightly longer than other reported for analogous tridentate diphosphine aryl pincer derivatives,[8] which can be attributed to the strong trans influence of the boryl ligand. It is worth mentioning that nickel boryl complexes are very rare[7] and complex **3** constitutes the first example to date of a stable nickel species containing both an alkyl and a boryl group. The geometry imposed by the PBP ligand forces the boryl and methyl groups to be mutually *trans* thwarting the reductive elimination of the corresponding methylborane. Accordingly, solutions of **3** can be heated to 70 ºC for long periods of time with no appreciable signs of decomposition as indicated by ^{31}P spectroscopy.[9]

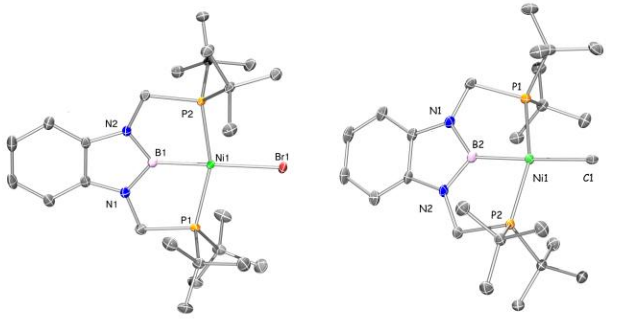
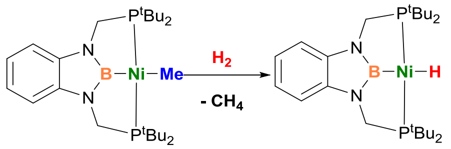


Figure 1. Thermal ellipsoids plots (50%) for **2** (left) and **3** (right). Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni-B = 1.900(3) (**2**), 1.928 (2) (**3**); Ni-Br = 2.370 (3) (**2**); Ni-C = 2.059 (2) (**3**); P-Ni-P = 157.58 (2) (**2**), 155.41 (2) (**3**); B-Ni-Br = 178.35 (8) (**2**); B-Ni-C = 176.88 (7) (**3**).

In order to gain more information about the behaviour of this nickel-boryl species we decided to explore its reactivity toward dihydrogen**,** since examples of homogenous hydrogenation reactions catalysed by nickel complexes are very limited.[10] We were thus intrigued to learn whether, in our case, the heterolytic cleavage of H_2 is facilitated by the presence of the boryl moiety through a mechanism involving metal-ligand cooperation. Thus, exposure of **3** to H_2 (2 bar) at 70 ºC cleanly generates nickel hydride complex **4** and methane (Scheme 2). Complex **4** was characterized by spectroscopic (NMR, IR) and analytical methods. The ^{1}H NMR spectra of **4** (C_6D_6) shows a characteristic triplet hydride resonance at -1.72 ppm ($^{2}J_{P\text{-}H}$ = 33.5 Hz) and the IR spectrum exhibits a Ni-H stretch at 1655 cm^{-1}. In the ^{11}B{^{1}H} spectrum a broad signal at 48 ppm is consistent with a B–Ni bond. Replacement of H_2 with D_2 gives the corresponding isotopologue [(PBP)NiD] and CDH_3 as the only deuterated species.



3 **4**

Scheme 2 Reactivity of **3** towards H_2.

Monitoring the reaction by ^{1}H and ^{31}P NMR spectroscopy, in the range from -50 to 70 ºC, did not provide evidence of intermediates; subsequently the mechanism of this reaction was investigated via computational methods. DFT calculations located a transition state (**TS1**) for dihydrogen splitting at **3** with relative energy $\Delta E^{\ddagger}$ = 22.2 kcal mol^{-1} (zero-point corrected energy in benzene; Figure 2).[11] A minimum for the corresponding η^{2}-H_2 adduct could not be located, however the η^{2} coordination mode of H_2 could be demonstrated for a model system, in which the ^{t}Bu groups on the P atoms were replaced by Me (**3_{Me}·H_2**) (see Figure S25, ESI). The species resulting from H–H cleavage, **5·CH_4**, features a B–H borane group coordinated in a η^{2} fashion to Ni and σ-bonded methane. η^{2} B–H coordination is reflected in the Ni–B and Ni–H distances of 1.99 and 1.81 Å respectively, and in the elongation of the calculated B–H distance from 1.18 Å in the free ligand to 1.25 Å in this intermediate (See Figure S26, ESI). H–H cleavage is not reversible according to the calculated reverse energy barrier ($\Delta E^{\ddagger}$ = 32.8 kcal mol^{-1}), in agreement with the reactivity with D_2 (*vide supra*). After methane loss from **5·CH_4**, B–H oxidative addition at **5** gives the Ni(II)-hydride **4** through a transition state (**TS2**) with a relative energy from **5** of 21.5 kcal mol^{-1}. The calculations also predict that the Ni(II) hydride **4** is more stable than the Ni(0) σ-borane **5** by ca. 10 kcal mol^{-1}.

To measure the kinetics of the hydrogenolysis process, complex **3** was heated with 1 bar of H_2 at different temperatures ranging from 65 to 75°C. On bases of the Eyring equation, the measured activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) values are 14.4 ± 1.2 kcal mol^{-1} and -27.6 ± 0.4 cal mol^{-1} K^{-1}, respectively, which corresponds to a Free Energy of activation ($\Delta G^{\ddagger}$) at 298K of 22.7 ± 1.3 kcal mol^{-1}. These values are in good agreement with those calculated. (See ESI). Use of D_2 resulted in a normal kinetic isotopic effect K_H/K_D of 2.0 at 70 ºC, which indicates that a H−H cleavage process is involved in the rate-determining step.

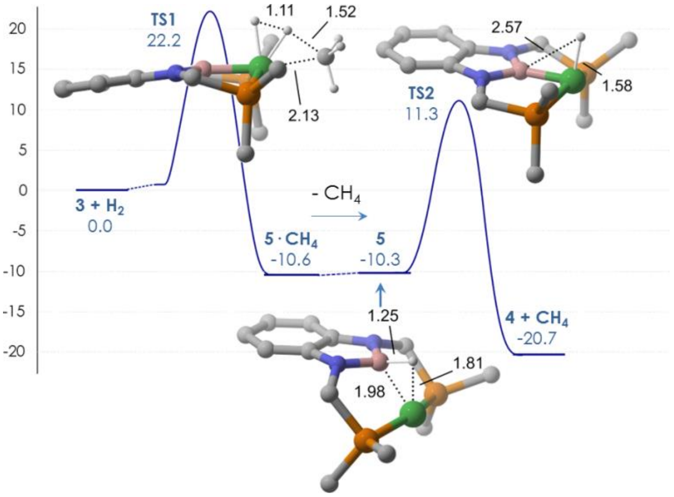
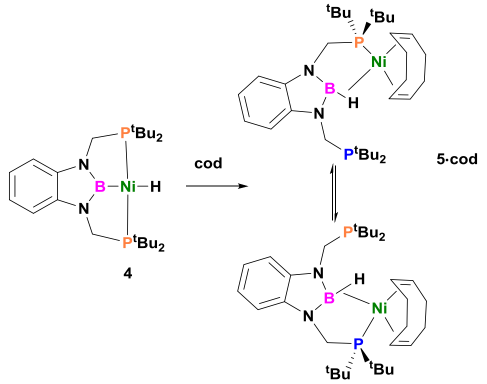


Figure 2. DFT calculated energy profile (kcal mol^{-1}, Zero Point-corrected Energies in benzene) of the hydrogenolysis of the Ni-CH_3 bond of **3**.

Support for our mechanistic proposal was obtained by the characterization by NMR spectroscopy of a [(η^{2}-B–H)Ni(0)] derivative, **5·cod**, from the reaction of **4** with 1,5-cyclooctadiene (cod).[12] Monitoring of the reaction by NMR spectroscopy confirmed the formation of a new species and the presence of the starting material. The $^{31}P\{^1H\}$ spectrum shows three peaks; one of them (δ 123 ppm) corresponds to complex **4**. The other two peaks appear at 10 ppm and 76 ppm suggesting different environments for the two phosphorous nuclei. One of the signals is very close to that observed for the free ligand ($\delta^{31}{}_{P}$ = 16 ppm) while the other appears at significantly lower field, indicative of coordination to the metal atom.[13] The ^1H NMR spectra reveal the presence of coordinated *cod* in the new species and show a broad resonance at -4.7 ppm, which integrates to one proton and sharpens upon ^{11}B decoupling. This resonance is assigned to the H atom of a B–H bond coordinated to nickel.[14] The $^{11}B\{^1H\}$ spectrum exhibits two resonances; one at 48 ppm, that corresponds to complex **4** and a new peak at 31 ppm that we assign to the new species **5·cod**. The methyl protons of the ^tBu groups and the bridging CH_2 protons for new species **5·cod** resonate as two set of doublets at 1.08 and 1.11 ppm, and at 3.38 and 4.42 ppm respectively. These doublets collapse into two singlets upon ^{31}P decoupling. Off-diagonal peaks in 2D NOESY/Exchange Spectroscopy (EXSY) experiments confirmed the exchange between both CH_2 groups and between the aromatic CH protons, suggesting that a fluxional process exchanges both phosphorous atoms (Scheme 3). Overall, these spectroscopic data are consistent with the formation of a [(η^2-B–H)Ni(0)] species **5·cod** from complex **4** in which the hydride ligand has migrated to the boron centre (Scheme 3) [15, 16] Nevertheless, **5·cod** slowly evolves into Ni(cod)$_2$ with the concomitant loss of the free PBP ligand along with formation of several unidentified products (See ESI).



Scheme 3 Synthesis of η^2-(B–H)Ni(0) complex **5·cod**.

Details of hydrogen cleavage at **3** were addressed by analysing the centroids of the localized orbitals[17] of the model system $\mathbf{3_{Me}}$ + H_2 at various points along the reaction coordinate, as described by Vidossich and Lledós.[18] According to this study *η*^{2} coordination of H_2 to $\mathbf{3_{Me}}$ does not perturb the electronic structure around Ni, which remains covalently bonded to the methyl ligand and boron atom and through one dative bond (polarized away from Ni) to each phosphorous of the molecule. The presence of four localized orbitals on the nickel atom is consistent with +2 oxidation state. At the transition state **TS1** the symmetry of the H–H bond is broken, as indicated by the displacement of the centroid of the H–H localized orbital towards one of the hydrogen atoms, to give hydride-like (H^-) and proton-like (H^+) atoms (Figure 3); even though the H–H distance is still 1.11 Å. At the same time the centroid of the Ni–B orbital is displaced towards Ni, so that the orbital eventually becomes metal centred. Also, the centroid of the Ni–C orbital is displaced from the line connecting the two atoms towards the H^+. As the molecule further evolves along the intrinsic reaction coordinate (IRC),[19] two new B–H and C–H bonding orbitals form, the former having its origin in the H–H bond and the latter in the Ni–C bond. Thus, it seems reasonable to propose a mechanism in which the boron atom acts as a Lewis-acid accepting H^- whereas the electrophilic Ni(II) does not form a new bond with H^+, at variance with Ni(0) complexes by Peters,[4] instead it acts as an electron sink for the Ni–B bond.[20] Therefore intermediate $\mathbf{5_{Me}\cdot CH_4}$ has five Ni-localized orbitals and forms one dative bond with each phosphorous, as expected for Ni(0).

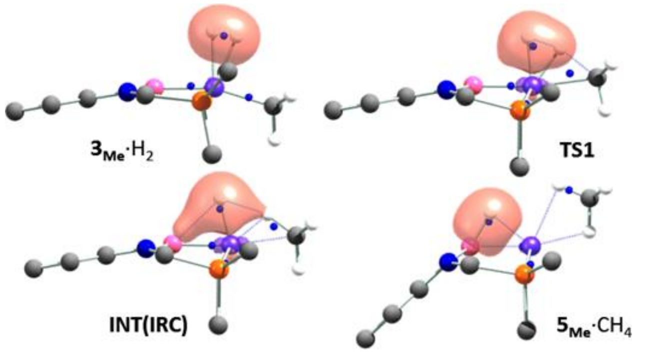


Figure 3. Evolution of the H–H localized orbital along the reaction coordinate. Blue dots represent the centroids of the H–H, Ni–B and N–Me orbitals. The species labelled INT corresponds to a point along the intrinsic reaction coordinate between TS1 and $5_{Me}\cdot CH_4$

In conclusion, the diphosphino-boryl nickel pincer complexes of type [(PBP)NiX] (X = Br (**2**), Me (**3**), H (**4**)) have been described. Theoretical calculations on the hydrogenation reaction of **3** evince a new mechanism for H–H activation that involves a cooperative role for boron and Ni(II). The resulting Ni(0) σ-borane intermediate **5** experiences further oxidative addition of the B–H bond to form the hydride complex **4**. Experimental evidence of intermediate **5** was provided by NMR spectroscopy analysis of the reaction of **4** with 1,5-cyclooctadiene. The implications of this metal-ligand cooperativity in the design of homogeneous nickel hydrogenation catalysts are currently being studied in our research group.

Notes and references

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Electronic supplementary information (ESI) available: Experimental procedures and characterization data for all new compounds described herein along with CIF files for **2** and **3**. CCDC 1011941 and 1011942. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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