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Article

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Efficient *Z*-Selective Semi-Hydrogenation of Internal Alkynes Catalyzed by Cationic Iron(II) Hydride Complexes

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ABSTRACT: The bench-stable cationic bis(σ-B-H) aminoborane complex [Fe(PNP^{NMe}-*i*Pr)(H)(η^2-H_2B=NMe$_2$)]$^+$ (**2**) efficiently catalyzes the semi-hydrogenation of internal alkynes, 1,3-diynes and 1,3-enynes. Moreover, selective incorporation of deuterium was achieved in the case of 1,3-diynes and 1,3-enynes. The catalytic reaction takes place under mild conditions (25°C, 4-5 bar H_2 or D_2) in 1 h and alkenes were obtained with high *Z*-selectivity for a broad scope of substrates. Mechanistic insight into the catalytic reaction, explaining also the stereo- and chemoselectivity, is provided by means of DFT calculations. Intermediates featuring a bis-dihydrogen moiety [Fe(PNP^{NMe}-*i*Pr)(η^2-H_2)$_2$]$^+$ are found to play a key role. Experimental support for such species was unequivocally provided by the fact that [Fe(PNP^{NMe}-*i*Pr)(H)(η^2-H_2)$_2$]$^+$ (**3**) exhibited the same catalytic activity than **2**. The novel cationic bis-dihydrogen complex **3** was obtained by protonolysis of [Fe(PNP^{NMe}-*i*Pr)(H)(η^2-AlH_4)]$_2$ (**1**) with an excess of nonafluoro-*tert*-butyl alcohol.

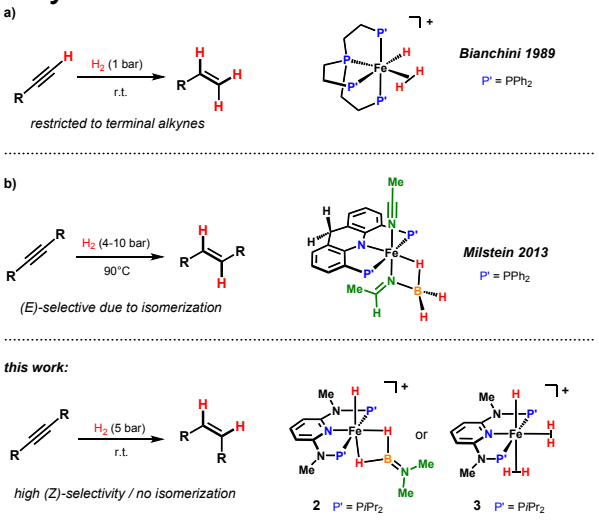
INTRODUCTION

The semi-hydrogenation of alkynes to alkenes is an important transformation for the industrial manufacture of bulk and fine chemicals.[1] Since the reduction of C≡C triple bonds to alkenes may potentially lead to the formation of (*E*)- or (*Z*)-alkenes as well as saturated hydrocarbons, it remains a challenging task to control the chemo- and stereoselectivity of this reaction.[2] For example, (*Z*)-olefins are traditionally obtained by heterogenous hydrogenation with the Lindlar catalyst being the most prominent example.[3] However, these systems require a careful control of the reaction conditions in order to avoid isomerization or overreduction of the products.

Although significant progress could be achieved in the field of heterogeneous catalysis and homogeneous transfer hydrogenations, the number of molecular defined catalysts that operate under an atmosphere of H_2 is surprisingly low.[4-6] Concerning the stereoselectivity of the reaction, recent examples were shown to deliver (*E*)-alkenes which, except in some cases,[7] are formed due to secondary isomerization processes.[8] Consequently, the development of new and selective homogeneous semi-hydrogenation catalysts that are able to produce (*Z*)-alkenes without isomerization or overreduction would still be of great advantage.[9]

Within this context, homogeneous catalysts based on first row transition metals attracted particular interest. Apart from obvious advantages such as their low price and high abundance, it is their intrinsic properties that may provide new opportunities paving the way to unprecedented reactivities and selectivities in catalytic transformations.[10] Iron may be considered as a particularly promising candidate in this respect.[11] For example, much progress could be achieved in the field of iron catalyzed hydrogenations of olefins.[12] Concerning the selective reduction of alkynes, some iron complexes could successfully be applied that operate via hydrofunctionalization or transfer hydrogenation procedures.[13] However, only two examples are currently known that can promote this transformation using hydrogen gas as the reductant (Scheme 1).[8a,14]

Scheme 1. Iron Catalysts for the Semi-Hydrogenation of Alkynes



In 1989, Bianchini et al. discovered that the non-classical polyhydride $[Fe(PP_3)(H)(\eta^2\text{-}H_2)]^+$ is capable of catalyzing the semi-hydrogenation of terminal alkynes.[14] More recently, the group of Milstein reported on a novel acridine based pincer type complex that bears an imino borohydride co-ligand.[8a] This complex was found to reduce internal alkynes selectively to the respective (*E*)-olefins. The reaction requires several hours and rather high reaction temperatures (90 °C) to achieve high yields and selectivities. Additional studies revealed that the hydrogenation initially affords (*Z*)-alkenes which, however, are isomerized to the respective (*E*)-olefins by the same catalyst.

We describe here the application of the well-defined bench-stable cationic aminoborane complex $[Fe(PNP^{NMe}\text{-}i\text{Pr})(H)(\eta^2\text{-}H_2B{=}NMe_2)]^+$ (**2**) described recently[15] as highly efficient pre-catalysts for the semi-hydrogenation of internal alkynes, 1,3-diynes and 1,3-enynes with molecular hydrogen under mild conditions. We take advantage of the fact that the aminoborane ligand, which is coordinated to the metal center via two weak σ-B-H bonds in η^2-fashion, is substitutionally labile and upon dissociation readily provides two vacant coordination sites to bind dihydrogen and alkynes.

RESULTS AND DISCUSSION

The aminoborane complex $[Fe(PNP^{NMe}\text{-}i\text{Pr})(H)(\eta^2\text{-}H_2B{=}NMe_2)]^+$ (**2**) was tested as pre-catalyst for the hydrogenation of a variety of different alkyne substrates in order to examine the general applicability and functional group tolerance of this novel system. Apart from 1-phenylpropyne, also dialkyl and diphenyl substrates could be reduced to the respective (*Z*)-alkenes (**Table 1, A1-A3**) without isomerization of the products. Neither an increase of the catalyst loading nor higher pressures led to a further reduction of the alkene. Terminal alkynes, however, are further hydrogenated to yield the saturated alkanes. Overreduction could be prevented by the introduction of trimethylsilyl (TMS) moieties as protecting groups which were tolerated throughout without cleavage of the C–Si bond. Even those substrates were quantitatively reduced affording the respective alkenes with excellent (*Z*)-selectivity (except for the TMS-protected phenylacetylene **A4** for which minor amounts of the *trans*-isomer were found in the isolated product). The reaction proceeds well also in case of diynes (**A13**, **A14**) which could successfully by converted to the corresponding (*Z,Z*)-dienes.

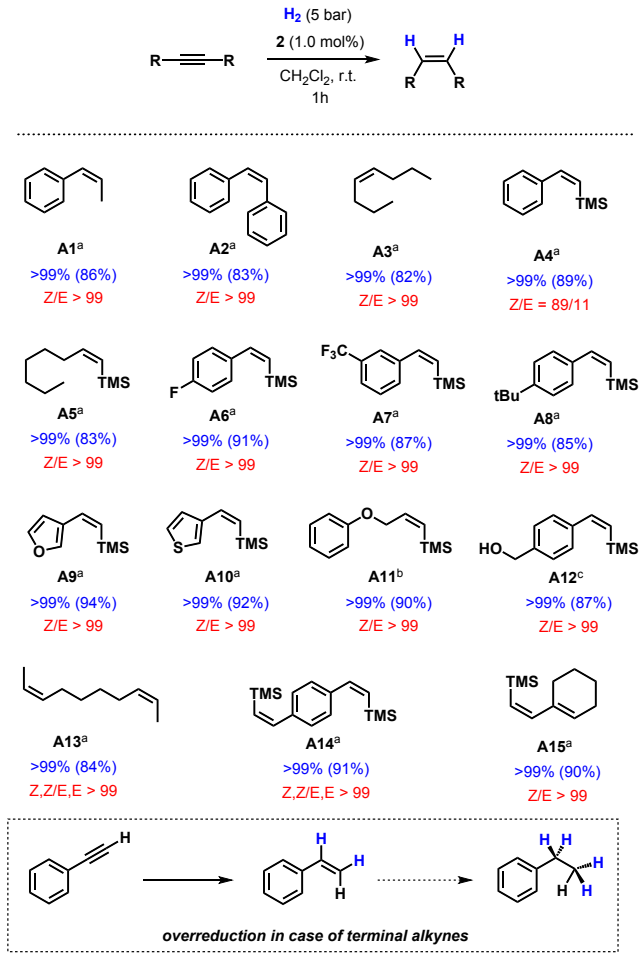
Encouraged by these results, we extended the substrate scope to 1,3-diynes (**A16a**) as well as 1,3-enynes (**A16b**-**A20**). In any case, the respective (*Z,Z*)-butadienes could be obtained with excellent stereoselectivity (Table 2). Functional groups such as esters or amine groups are tolerated whereas the C=C double bond of the enyne substrates remained unaffected.

This circumstance was further examined by conducting the hydrogenation in presence of D_2 (Scheme 2). The reaction of 1,3-enyne **A16b** with D_2 catalyzed by **2** resulted in complete and selective deuterium incorporation at the former alkyne carbons, whereas an isotope scrambling into the existing olefin C–H positions was not observed. On the other hand, the respective 1,3-diyne **A16a** gave the fully deuterated butadiene product under the same reaction conditions. Thus, the novel iron hydride complex represents an interesting catalytic system that allows for the selective hydrogen isotope labelling of butadiene derivatives.

Based on the experimental observations, it is likely that the reaction proceeds *via* a classical insertion mechanism. Due to the labile nature of the dihydrogen and bis(σ-B-H) aminoborane ligands, the pre-catalyst gets activated by the addition of the substrate in the presence of dihydrogen. In contrast, dissociation of the aminoborane ligand in **2** under an atmosphere of dihydrogen to form **3** was not be observed.[15]

The hydrogenation of **A1** was conducted at different hydrogen pressures as well as substrate concentrations and the initial turnover frequencies were determined after a reaction time of five minutes. A significant increase of the initial TOFs could be observed at higher hydrogen pressures (see supporting information, Table S1). At 20 bar H_2, after 5 min the product was obtained in >99% yield corresponding to a TOF of 2400 h^{-1}. In contrast, essentially no acceleration took place when the substrate concentration

Table 1. Semi-hydrogenation of Alkynes Catalyzed by 2.

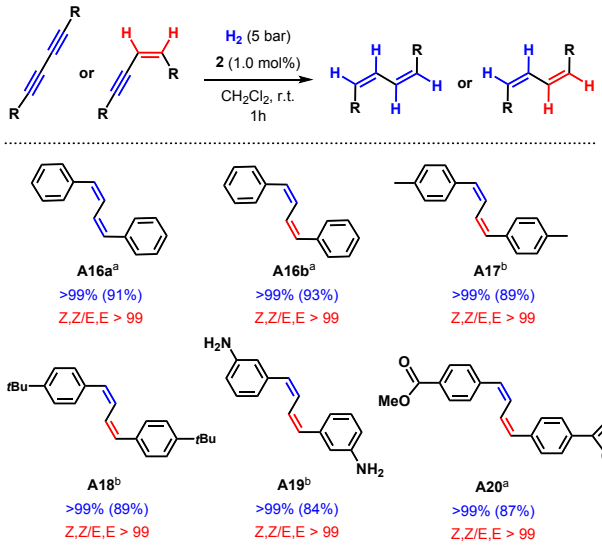


Conditions: (a) alkyne (1.0 mmol), **2** (1.0 mol%), CH_2Cl_2 (1 mL), 25 °C, 1 h, conversion and selectivity determined by ^{1}H NMR, isolated yields given in parenthesis. (b) **3** (2.0 mol%), 2h reaction time. (c) **7** (1.5 mol%), MeOH /CH_2Cl_2 (1:9, 1 mL), 1h.

was raised. These results indicate that the rate determining step of the mechanism should be loss of the aminoborane ligand and formation of the active species being in line with the a very small energy barrier (11 kcal/mol) calculated for the catalytic reaction (*vide infra*).

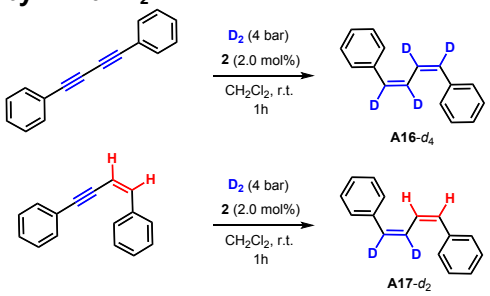
A series of DFT calculations were carried out in order to gain more detailed insight into the catalytic cycle as well as the origin of the observed selectivity.[16] A simplified catalytic cycle for the semi-hydrogenation of internal alkynes is depicted in Scheme 3. The cycle starts with an alkyne dihydrogen complex of the type [Fe(PNP^{NMe}-*i*Pr)(H)(η^2-H_2)(η^2-MeC≡CPh)]$^+$ as the active species. The η^2-coordinated alkyne inserts into the iron hydride bond resulting in a dihydrogen vinyl species (**I**). After coordination of a second equivalent of H_2 (**II**), this intermediate split the H-H bond under release of the alkene product and recovery of the initial hydride dihydrogen complex (**III**).

Table 2. Hydrogenation of 1,3-Diynes and 1,3-Enynes Catalyzed by Complex 2.



Conditions: (a) alkyne (1.0 mmol), **2** (1.0 mol%), CH_2Cl_2 (1 mL), r.t., 1 h, conversion and selectivity determined by ^{1}H NMR, isolated yields given in parenthesis. (b) 10 bar H_2.

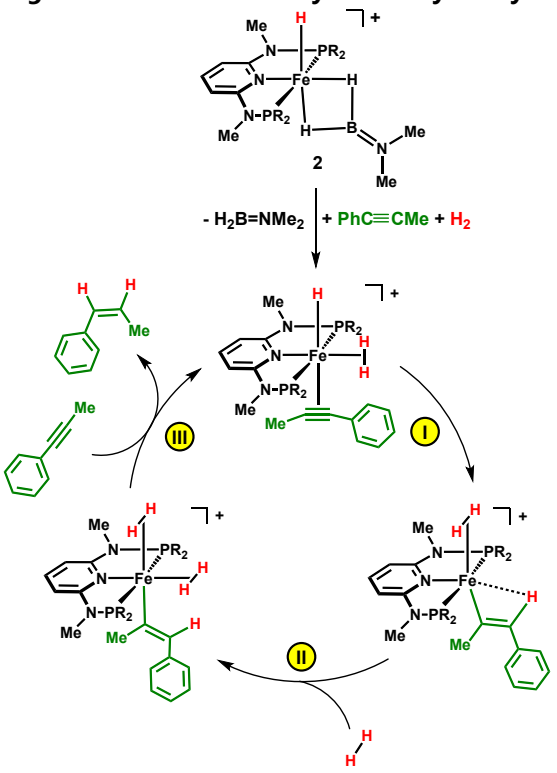
Scheme 2. Selective Deuterium Incorporation through Hydrogenation of 1,3-Diynes and 1,3-Enynes by 2 with D_2



A more detailed picture is provided by the free energy profile in Scheme 4 employing 1-phenylpropyne as the substrate. Insertion of the alkyne into the iron hydride bond proceeds easily with an activation barrier of **1** kcal/mol in an exergonic step (ΔG = –11 kcal/mol). This occurs with a H-shift between two adjacent coordination positions and results in intermediate **1-B** with *trans* dihydrogen and vinyl ligands. Coordination of a H_2 molecule to the resulting iron vinyl complex affords intermediate **1-D** in which there are two dihydrogen ligands parallel to the P-Fe-P axis. **1-D** formation overcomes a barrier of only 3 kcal/mol and that step is exergonic with ΔG = –5 kcal/mol. From **1-D**, a second H-transfer with concomitant re-orientation of the H_2 ligand produces **1-E**, where the recently formed olefin is loosely coordinated as a C–H σ-complex. Requiring 11 kcal/mol, this step represents the highest barrier in the catalytic cycle. The overall free energy balance of the cycle is favorable with ΔG = –22 kcal/mol and closing the cycle with liberation of the olefin and addition of a new alkyne molecule regenerates the initial species (**1-A**) in a slightly exergonic process (ΔG = –3 kcal/mol).

Regarding the chemoselectivity of the reaction, we also considered a second hydrogenation step to the respective alkane in our calculations (right side of the profile in Scheme 4). Here, the loosely bonded olefin in intermediate **1-E** rearranges to η^2-coordinated (in **1-G**). This process occurs in two steps. First there is H-exchange, bringing the H_2 ligand back to its original position, *i.e.*, opposite to the N_{py}-atom, in intermediate **1-F**. Then, a reorientation of the olefin brings it to the η^2-coordination mode present in intermediate **1-G**. These steps have negligible barriers ($\leq$ 1 kcal/mol) and **1-G** is 7 kcal/mol more stable than **1-E**, reflecting the additional stability associated with stronger coordination of the olefin. From **1-G**, there is H-transfer to the inner C-atom of the C=C double bond with formation of an alkyl complex (**1-H**). The process occurs with concomitant H-transfer between the two adjacent coordination sites and, thus, both the H_2 as well as the alkyl ligands occupy two apical positions *trans* to each other, in **1-H**. This step corresponds to a formal olefin insertion in a Fe–H bond and parallels the first step of the entire path (alkyne insertion, over **1-TS$_{AB}$**). This is an endergonic process with ΔG = 6 kcal/mol and the associated barrier (13 kcal/mol) is 2 kcal/mol higher than the one found for alkyne insertion, indicating that the second hydrogenation is less favorable than the first one, in agreement with the experimental results. However, the small difference between the calculated barriers may suggest the possibility of competitive processes. After H_2 coordination (from **1-H** to **1-I**) a final H-transfer from the dihydrogen ligand to the terminal alkyl C-atom produces the final intermediate, **1-J**, with an alkane bonded as a C–H σ-complex. This is a facile process with a barrier of 6 kcal/mol and, also, clearly favorable with ΔG = –27 kcal/mol.

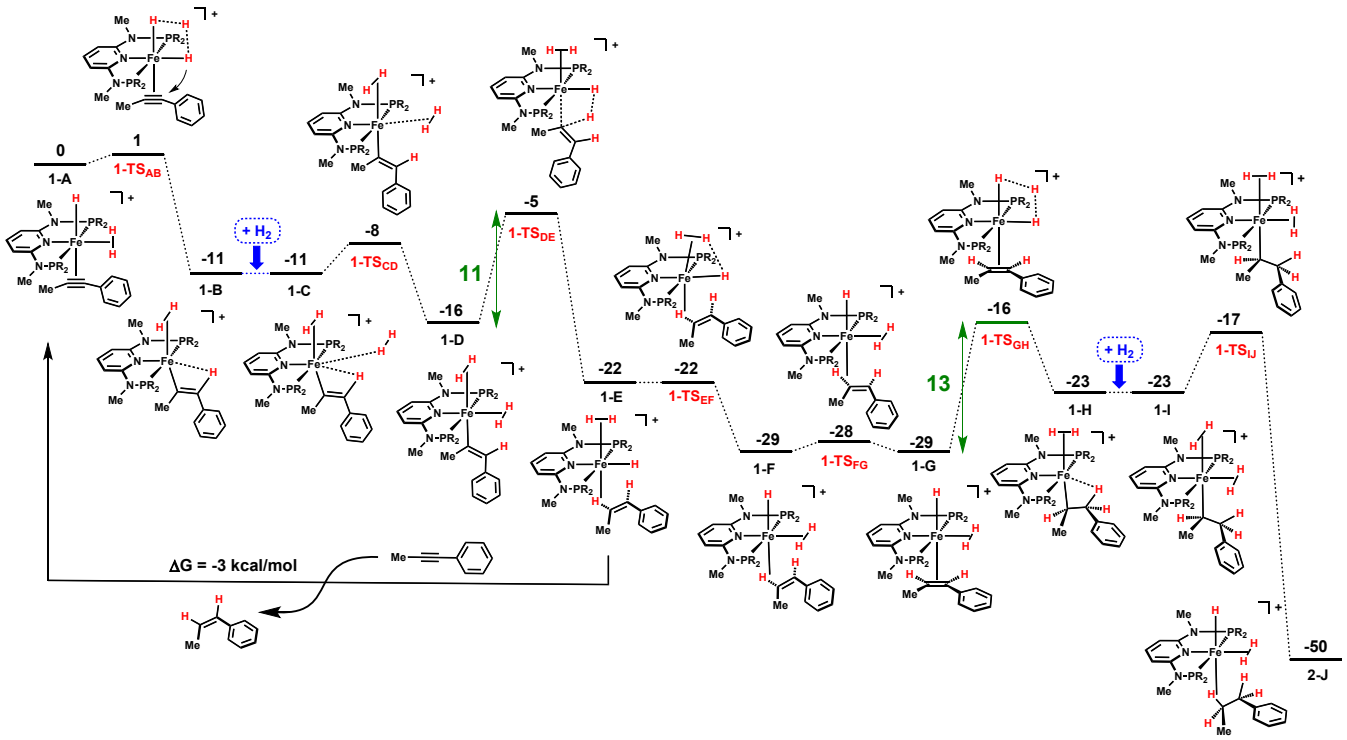
Scheme 3. Simplified Catalytic Cycle for the Semi-hydrogenation of Internal Alkynes Catalyzed by 2.



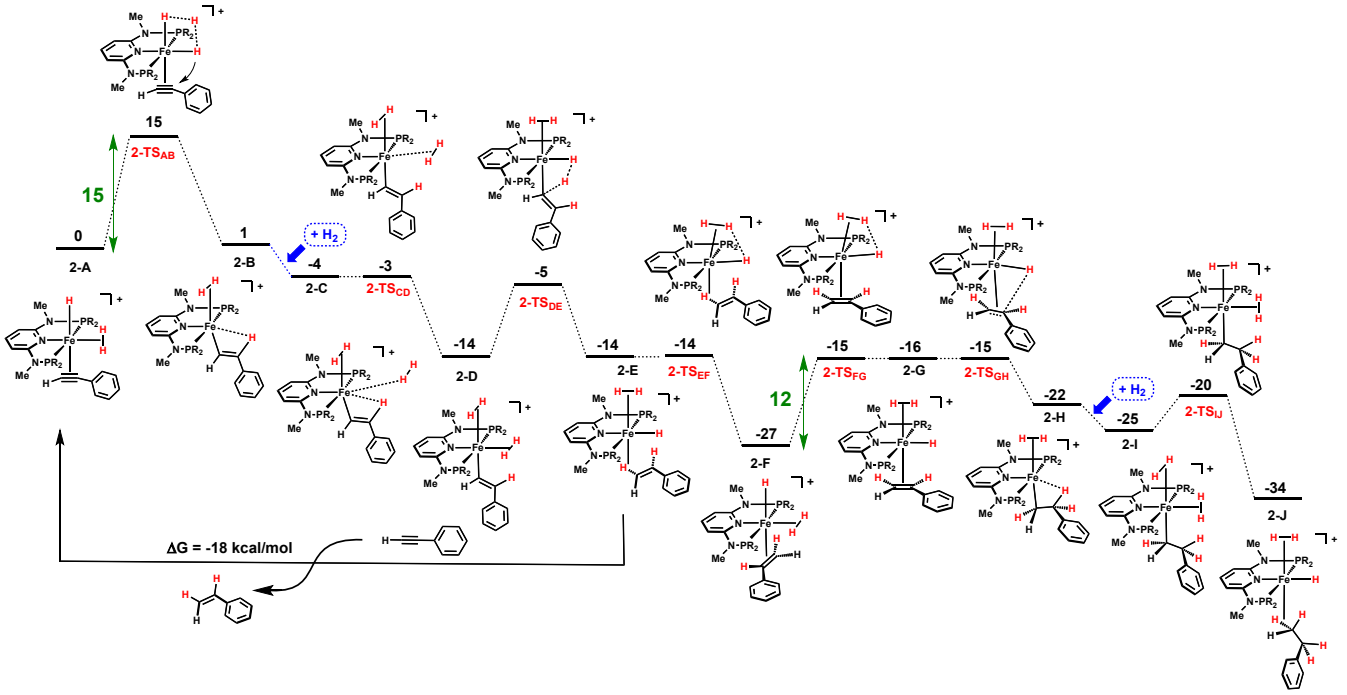
The hydrogenation of phenylacetylene was also considered by means of DFT calculations and the energy profile obtained for the corresponding reaction is depicted in Scheme 5. The mechanism is entirely equivalent to the one discussed above for the hydrogenation of 1-phenylpropyne. Thus, it also comprises two stepwise H-atom additions to CC unsaturated bonds. The first can be viewed as an acetylene insertion into a hydride bond and results in a vinyl complex (**2-B**). Then, there is H_2 coordination followed by another H-transfer producing the olefin (styrene, in this case) and regenerating an hydride ligand (intermediate **2-E**). A repetition of this sequence leads to the hydrogenation of styrene and the formation of the alkane (ethylbenzene) in the final intermediate, **2-K**.

The most important difference between the two paths is the relative value of the highest barrier for each H_2 addition. In the case of the internal alkyne (1-phenylpropyne, Scheme 4) the barrier for the second addition is the higher one, justifying the observed semi-hydrogenation of the substrate. However, in the case of the terminal alkyne (phenylacetylene, Scheme 5) the opposite occurs. That is,

Scheme 4. Free Energy Profile for the Hydrogenation of 1-Phenylpropyne. Free Energies (kcal/mol) refer to Intermediate 1-A.



Scheme 5. Free Energy Profile for the Hydrogenation of Phenylacetylene. Free Energies (kcal/mol) refer to Intermediate 2-A.



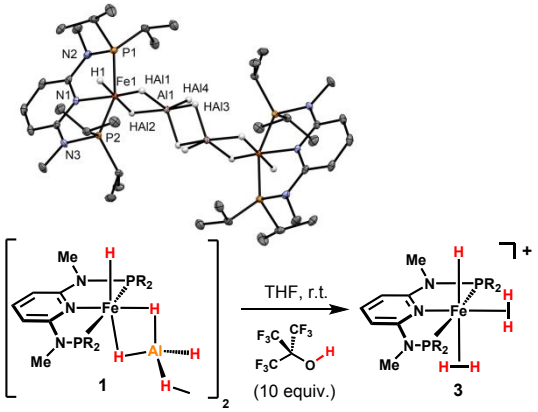
the barrier for olefin hydrogenation (12 kcal/mol, **2-TS$_{FH}$**) is lower than the one calculated for the hydrogenation of the alkyne (15 kcal/mol, **2-TS$_{AB}$**). Both processes correspond to the first H-transfer, from the H_2 ligand to the corresponding CC unsaturation. The results above indicate that in the case of phenylacetylene the reaction is expected to go all the way until the saturated product.

The observed chemoselectivity can also be related to the stability of the η^2-olefin complexes in each case (**1-G** and **2-F**). In fact, those are the initial species in the second H_2 addition, from olefin to alkane. Considering the competition between H_2 and the olefin for the six coordination position (Figure S1, supporting information), it becomes clear that the olefin complex is more stable in the case of the terminal olefin (styrene, in **2-F**), while the opposite happens in the case of the internal olefin (1-phenylpropene, in **1-G**). Therefore, the

existence of the initial species for the second hydrogenation process is favorable in the case of substrates with a terminal C=C double bond, contrarily to what occurs for internal ones.

In order to obtain support for the mechanistic studies from an experimental point of view, in particular the existence of bis-dihydrogen intermediates, we prepared the novel cationic bis-dihydrogen complex $[Fe(PNP^{NMe}\text{-}i\text{Pr})(H)(\eta^2\text{-}H_2)_2]^+$ (**3**). This complex was readily obtained by reacting $[Fe(PNP^{NMe}\text{-}i\text{Pr})(H)(\eta^2\text{-}AlH_4)]_2$ (**1**)[15] with an excess of nonafluoro-*tert*-butyl alcohol (Scheme 6) in THF at room temperature. The coordinated $[AlH_4]^-$ anion is protonated by the acidic alcohol thereby liberating H_2 with concomitant formation of a mixture of several poorly coordinating counterions of the types $[Al(OC(CF_3)_3)_{4-n}H_n]^-$ as detected by $^{19}F\{^1H\}$ NMR spectroscopy and ESI-MS.[16]

Scheme 6. Preparation of a Cationic Non-Classical Fe(II) Polyhydride Complex *via* Protonolysis of 1[a]



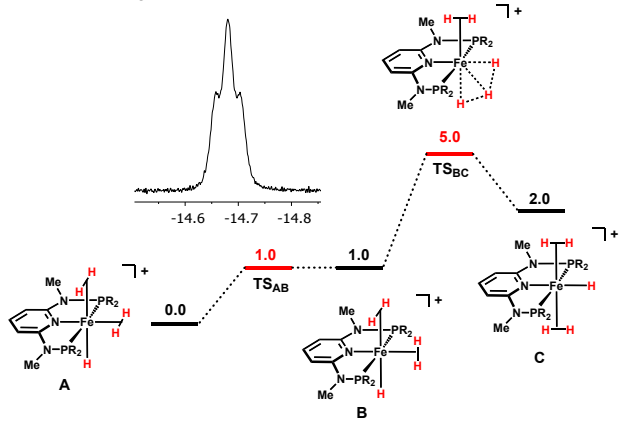
[a] Selected bond distances (Å) and angles (°): Fe1-N1 1.9867(9), Fe1-P2 2.1443(3), Fe1-P1 2.1461(3), Fe1-Al1 2.3507(4), Fe1-H1 1.46(2), Fe1-HAL1 1.48(2), Fe1-HAL2 1.55(2), Al1-HAL1 1.82(2), Al1-HAL2 1.73(2), Al1-HAL3 1.65(2), Al1-HAL4 1.54(2), P2-Fe1-P1 157.22(1).

The ^1H NMR spectrum of **3** in THF-d_8 features a broadened triplet resonance at -14.68 ppm that integrates to five hydrogen atoms, while a singlet at 187.3 ppm could be observed in the $^{31}P\{^1H\}$ NMR spectrum. Owing to fast exchange between classical and non-classical hydrides, it was not possible to determine separate proton resonances for the individual hydride ligands. Even at -100 °C only a slight broadening of the hydride signal was observed. ^1H NMR spectra recorded at variable temperatures revealed an extremely short relaxation time $T_{1(min)}$ of 12 ms (-65 °C, 500 MHz)[17] which is characteristic of coordinated dihydrogen molecules.[18,19]

The experimental observations are further supported by DFT calculations. The *cis*- and *trans*-isomers of the bis(dihydrogen) complex differ merely by 2.0 kcal/mol and their interconversion requires an activation energy of just 5.0 kcal/mol being in line with the experimentally observed fluxional behaviour (Scheme 7).

Complex **3** was also applied as pre-catalyst for the hydrogenation of alkynes. Experiments were conducted in C_6D_6 under an H_2 pressure of 5 bar at 25 °C using 1-phenylpropyne as test substrate. By employing 1 mol% of *in situ* prepared **3** the alkyne could be quantitatively reduced to the corresponding alkyne within 30 min. The product was formed with >99% *Z*-selectivity and no hydrogenation to the respective alkane could be observed even when the reaction time was extended to several hours. Accordingly, complexes **2** and **3** are obviously synthons for the active catalyst which reacts with alkynes in the presence of H_2 to form $[Fe(PNP^{NMe}\text{-}i\text{Pr})(H)(\eta^2\text{-}H_2)(\eta^2\text{-}RC{\equiv}CR')]^+$ thereby initiating the catalytic cycle as shown in Schemes 3-5. It has to be noted that the neutral non-classical iron(II) polyhydride complex $[Fe(PNP)(H)_2(\eta^2\text{-}H_2)]$ did not catalyzed the hydrogenation of alkynes, but the dimerization of alkynes to give 1,3-eneynes with high Z-selectivity. [20]

Scheme 7. Free Energy Profile (kcal/mol) Calculated for the Interconversion of *cis*- and *trans*-Isomers of 3. Inset: ^1H NMR Spectrum of 3 (Hydride Region, 250 MHz, THF-d_8, 20°C).



CONCLUSION

The bench-stable cationic bis(σ-B-H) aminoborane complex $[Fe(PNP^{NMe}\text{-}i\text{Pr})(H)(\eta^2\text{-}H_2B{=}NMe_2)]^+$ (**2**) turned out to be an efficient pre-catalyst for the semi-hydrogenation of internal alkynes, 1,3-diynes and 1,3-enynes. With 1,3-diynes and 1,3-enynes deuterium could be selectively incorporated in the presence of D_2. This was exemplarily shown with 1,4-diphenylbuta-1,3-diyne and (*Z*)-but-1-en-3-yne-1,4-diyldibenzene were the isotopomeres (*Z,Z*-buta-1,3-diene-1,4-diyl-1,2-d_2)dibenzene and (*Z,Z*-buta-1,3-diene-1,4-diyl-d_4)dibenzene, respectively, were obtained. The catalytic reaction takes place under mild conditions (1 h, 25°C, 4-5 bar H_2 or D_2) and all alkenes were obtained with high *Z*-selectivity for a broad scope of substrates. Mechanistic

insight into the catalytic reaction is provided by means of DFT calculations. The stereo- and chemoselectivity was fully explained in agreement with the experimental observations. Intermediates featuring a bis-dihydrogen moiety [Fe(PNP^{NMe}-*i*Pr)(η^2-H_2)$_2$]$^+$ are found to play a key role. Experimental support for such species was provided by the fact that [Fe(PNP^{NMe}-*i*Pr)(H)(η^2-H_2)$_2$]$^+$ (**3**) exhibited the same catalytic activity than **2**. The novel cationic bis-dihydrogen complex **3** was obtained by protonolysis of [Fe(PNP^{NMe}-*i*Pr)(H)(η^2-AlH_4)]$_2$ (**1**) with an excess of nonafluoro-*tert*-butyl alcohol. Thus, complexes **2** and **3** are apparently synthons for the active catalyst [Fe(PNP^{NMe}-*i*Pr)(H)]$^+$ which reacts with alkynes in the presence of H_2 to form [Fe(PNP^{NMe}-*i*Pr)(H)(η^2-H_2)(η^2-RC≡CR')]$^+$ thereby initiating the catalytic cycle.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publications website at DOI: xxxxx

Synthetic procedures, NMR spectra of all compounds, and crystallographic data (PDF)

X-ray crystallographic data for **1** (CCDC entry 1951434) (CIF)

Optimized cartesian coordinates for DFT-optimized structures (XYZ)

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Notes

The authors declare no competing financial interest.

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Table of Contents (TOC)