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ARTICLE

Development of Silica-Supported Frustrated Lewis Pairs: Highly Active Transition Metal-Free Catalysts for the Z-Selective Reduction of Alkynes

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A supported Lewis acid/base systems based on a triphenyl phosphine fragment and Piers' reagent (HB(C₆F₅)₂) or BARF have been prepared and characterized. Both materials show unprecedented catalytic activity in Z-selective hydrogenation of 3-hexyne to Z-3-hexene with a selectivity up to 87%. Other alkynes can also be hydrogenated Z-selectively, albeit with moderate yields. The activity of the supported phosphine/HB(C₆F₅)₂ adduct is similar to the only homogeneous example reported thus far based on bridged B/N frustrated Lewis pairs under high pressure of hydrogen. Importantly, this transition metal-free supported catalyst was recycled five times in the challenging selective hydrogenation of a non-polar unactivated alkyne.

Introduction

Z-alkenes are very important starting materials for a large number of natural and industrially relevant compounds.¹⁻⁵ Yet, methods to selectively access Z-alkenes are less established than those yielding the E-isomers due to thermodynamic control favoring E-alkenes. A wide variety of methods are amenable to Z-alkenes synthesis (albeit not always general methods), including ubiquitous reactions in organic synthesis such as Wittig olefination, cross-coupling, olefin metathesis and partial hydrogenation of alkynes.^{5,6} Among the mentioned approaches, the most reliable method to obtain Z-alkene selectively is the partial hydrogenation of the corresponding alkynes.

Different homogeneous and heterogeneous alkyne hydrogenation catalysts have been reported.⁷⁻¹⁰ The earliest selective heterogeneous catalyst was developed by Lindlar and consists in Pd supported on CaCO₃.¹¹ Later on, Brown and Ahuja reported an alternative catalyst based on nickel in the presence of ethylenediamine.¹² Homogeneous partial hydrogenation of alkyne can obviously be catalyzed by

organometallic Pd and Ni complexes as well as early transition metals (Ti, Nb).^{13,14} The main issue for transition metal-based catalysis, despite its high activity, is the possible contamination of the final product by trace metals. For some products, especially in fine chemistry and pharmaceutical industry, even trace amounts of toxic or undesired metal must be avoided. Hence, replacing the transition metal center by a metal-free active phase while maintaining the catalytic property unchanged is of high interest.¹⁵ Only recently were highly selective metal-free catalysts for alkyne hydrogenation reported.^{6,16-20} These catalysts are composed of equimolar quantities of sterically hindered Lewis acids-bases, a.k.a. frustrated Lewis pairs (FLP), as introduced by Stephan.²¹ FLP comprise Lewis acidic sites (mainly based on boron) close to Lewis bases (commonly amines or phosphines) without creating Lewis adducts. The reactivity of FLP is reported for the activation or fixation of small molecules²² such as CO₂,²³ CO,²⁴ SO₂,²⁵ NO,²⁶ N₂O,²⁷ and H₂.^{28,29} In particular, the activation of H₂ has attracted attention to hydrogenation reactions of imines, carbonyls, nitriles,^{19,28,30-33} and far more challenging substrates such as alkenes, polyaromatics and alkynes.^{16,19,20,34} In the latter case, FLP yield the Z-isomer of the corresponding alkenes.^{16,19,20} Moreover, H₂ activation was also achieved by several Lewis acids or bases, for example alanes,³⁵⁻³⁸ borenium cations,³⁹⁻⁴¹ pyridines,⁴² amines,⁴³⁻⁴⁶ and carbenes.⁴⁷⁻⁴⁹ However, most FLP-catalyzed hydrogenations employ amines or phosphines as Lewis bases in combination with boranes such as B(C₆F₅)₃ as Lewis acids.

Nevertheless, to the best of our knowledge, the concept of FLP is unknown in transition metal-free heterogeneous catalysis with a set of Lewis acid/base pair bearing a suitable anchoring site. Generally, heterogeneous catalysts offer

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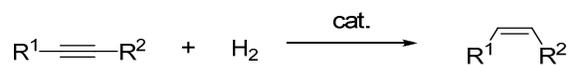
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Electronic Supplementary Information (ESI) available: NMR spectra, IR spectra, reaction scheme, catalytic graphics depicting 3-hexyne conversion and product selectivity, gas chromatograms. See DOI: 10.1039/x0xx00000x

several advantages such as easy separation of the catalyst from the product, catalyst recycling and the possibility to work under continuous flow conditions. In the continuity of our efforts in the preparation of transition metal-free heterogeneous hydrogenation catalysts prepared by surface organometallic chemistry,⁵⁰ we have turned our interest to the heterogenization of FLP based on boranes as Lewis acids and phosphines as Lewis bases. Two strategies can be envisaged: i) grafting of the Lewis acid on a conventional support, such as silica, followed by coordination of phosphine; ii) grafting of the Lewis base, followed by addition of the boron based Lewis acid. Grafting methods of Lewis acids on silica, such as BArF or Piers' reagent (HB(C₆F₅)₂) have already been reported.^{51,52} However, the resulting surface species undergo interactions with nearby siloxane ligands due to their high Lewis acidity. Similar interactions between oxophilic elements or Lewis acids on silica surface have been described in the literature as observed by EXAFS and ¹⁷O NMR.⁵³⁻⁵⁵ Hence, the grafted Lewis acidic center will undergo coordinative competition between surface siloxane moieties and the chosen Lewis base. In addition, no example of FLP based on borate (BHR₃) and borate esters (B(OR)₃) has been reported to be active in catalytic hydrogenation due to continuous redistribution between the B-H and B-OR bonds.⁵⁶ Surface interactions can be avoided by introducing a spacer between the surface and the active center. However, this approach requires the utilization of non-commercial products and thus needs a multi-step synthesis of the spacer incorporating the Lewis acid. The second approach (grafting of phosphine on silica) can be implemented easily by employing bifunctional phosphines. The most common ligand types comprise phosphines bearing alkoxy silane moieties, tri-ethoxysilane being the most popular. However, this methodology suffers from formation of electrostatic bonding to the support through the phosphonium formed, as revealed by classical CP/MAS and HRMAS NMR techniques.⁵⁷ In addition, preparation of the tethered phosphine ligand requires a multi-step procedure. One general strategy to overcome these drawbacks is to treat the surface silanols with a reactive compound to quantitatively consume them and at the same time create sufficiently reactive sites to further react with the spacer. Alkyl aluminum compounds are very attractive to reach this goal, yet to afford selective catalytic systems, this strategy requires a single type of reactive site, which has been difficult to secure in the past.⁵⁸⁻⁶⁵ We have recently developed the synthesis of new and easily accessible organic/inorganic hybrid supports involving first grafting of tri-isobutyl aluminum⁶⁶ on dehydroxylated silica at 700 °C (to consume all silanol groups), followed by reaction with hydroquinone,⁶⁷ to selectively afford the phenolic material [(≡SiO)₂(AlO-C₆H₄-OH)(Et₂O)] in two simple steps. A great advantage with this methodology is that all starting materials are cheap and commercially available. This strategy has previously been used for the grafting of zirconium, molybdenum and tungsten complexes through surface organometallic chemistry.⁶⁷⁻⁶⁹ The catalytic performance of the hybrid material in olefin polymerization and metathesis reactions was compared to those of the previously described

silica-grafted counterpart, and exhibited drastic improvements in terms of activity, stereoselectivity and stability. These combined results validate our strategy toward both reduced surface interactions and improved electrophilic effects at the active center. Our current strategy to access supported FLPs is therefore based on the latter approach, *via* substitution of the hydroquinone ligand by the commercially available (4-hydroxyphenyl)diphenyl phosphine, followed by treatment with B(C₆F₅)₂R (R = C₆F₅: BArF, R=H: Piers' reagent). The resulting Lewis acid/base adducts have been characterized and evaluated in the hydrogenation of disubstituted alkynes (Scheme 1).



Scheme 1. Selective hydrogenation of alkynes to Z-alkenes.

Experimental

General considerations. All experiments were carried out under a controlled atmosphere, using Schlenk and glove box techniques for organometallic syntheses. For the synthesis and treatments of the surface species, reactions were carried out using high-vacuum lines (ca. 1 mPa) and glove boxes. Benzene, toluene and pentane were distilled on NaK-benzophenone and degassed through freeze-pump-thaw cycles. Alkynes such as 3-hexyne, 1,2-diphenylethyne, and hex-2-yn-1-yloxy)trimethylsilane were purchased from Aldrich and purified by distillation (or dried under vacuum for 1,2-diphenylethyne (solid)). The alkyne derived from oleic methyl ester: methyl octadec-9-ynoate was purchased from Alfa Aesar® and distilled prior to use. B(C₆F₅)₃ (Strem Chemicals > 97%) was dried on Me₃SiCl, purified by vacuum sublimation and controlled by ¹⁹F NMR before use. Piers reagent HB(C₆F₅)₂ was synthesized following the literature procedure.⁷⁰ (4-hydroxyphenyl)biphenylphosphine was purchased from ABCR. SiO₂₋₍₇₀₀₎ was prepared from Aerosil silica (Degussa, specific surface area of 200 m²·g⁻¹), which was dehydroxylated at 700 °C under high vacuum (about 1 mPa) for 15 h to give a white solid having a specific surface area of 190 m²·g⁻¹ and 0.7 OH nm⁻². Gas-phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and an Al₂O₃/KCl on fused silica column (50 m x 0.32 mm). Elemental analyses were performed at the Mikroanalytisches Labor Pascher, Remagen (Germany). It is noteworthy that, during the elemental-analysis procedures, molecules of diethyl ether were released in some cases, especially if the aluminum atom was bonded to three oxygen atoms. DRIFT spectra were recorded on a Nicolet 6700 FT-IR by using airtight cells. Solid-state ¹H MAS, ¹³C CP/MAS and ¹⁹F MAS NMR spectra were recorded on a Bruker Avance 500 spectrometer with a conventional double-resonance 4 mm CP-MAS probe at C2P2 – ESCPE Lyon. The samples were loaded under argon in a zirconia rotor, which was then tightly closed. Chemical shifts were given with respect to TMS as external reference for ¹H and ¹³C NMR, and to BF₃·OEt₂ for ¹¹B. The ¹¹B and ³¹P solid-state NMR spectra were acquired on Bruker

Avance III 800 (^{11}B , 256.71 MHz, ^{31}P , 323.89 MHz) spectrometers at a MAS frequency of 20 kHz at UCCS Lille. The D-HMQC experiments were set up with a ^{11}B spin echo selective to the central transition, with pulses of 10 and 20 μs , with ^1H $\pi/2$ pulse of 4.1 μs on either side of the ^{11}B π pulse. The dipolar recoupling scheme (SR4_1^2)⁷¹ was applied for 800 μs . The number of scans for each t_1 increment was set to 3072. The bipodal species $[(\text{SiO})_2\text{Al}(i\text{Bu})(\text{Et}_2\text{O})]$, **1**, was prepared according to literature procedure.⁶⁶

Preparation of 2: A benzene solution of (4-hydroxyphenyl)diphenylphosphine (0.180 g, 0.647 mmol) and $[(\text{SiO})_2\text{Al}(i\text{Bu})(\text{Et}_2\text{O})]$, **1**, (2 g) was stirred at 25 °C for 12 h. After filtration, the solid was washed three times with benzene. The resulting white powder was dried under vacuum (1.34 Pa) and stored in the glovebox.

Preparation of 3a: A benzene solution of $\text{HB}(\text{C}_6\text{F}_5)_2$ (0.405 mmol, 1.5 eq.) and **2** (1g) were stirred at 25 °C for 3 h in double Schlenk. After filtration, the solid was washed three times with benzene. The resulting white powder was dried under vacuum (1.34 Pa) and stored in the glovebox.

Preparation of 3b: A benzene solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (0.405 mmol, 1.5 eq.) and **2** (1g) were stirred at 25 °C for 3 h in double Schlenk. After filtration, the solid was washed three times with benzene. The resulting white powder was dried under vacuum (1.34 Pa) and stored in the glovebox.

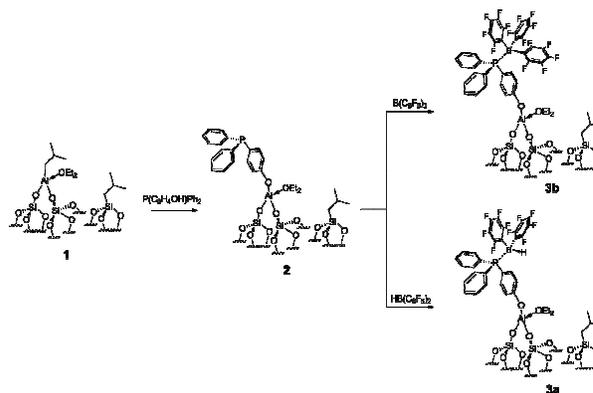
Procedure for the hydrogenation experiments. Typically, an accurate amount of the catalyst (around 65 mg) was loaded into a 21 mL Parr autoclave within the glove box. Then 1 ml of pentane, previously distilled over NaK, further purified by freeze-pump-thaw cycles, was introduced. 3-hexyne, previously distilled and purified by freeze-pump-thaw cycle was then added. The desired amount of hydrogen purified over deoxo catalyst and zeolite was added to the autoclave before heating to 80 °C. After stirring for appropriate time *via* a magnetic stirrer, all hydrocarbons were distilled to a liquid nitrogen cooled schlenk flask under high vacuum (about 1 mPa, gentle heating was applied to the autoclave to ensure complete evaporation) and analyzed by GC (HP 5890 chromatograph fitted with an $\text{Al}_2\text{O}_3/\text{KCl}$ (50 m x 0.32 mm) capillary column, FID detector for hydrocarbons). Conversion and selectivity were calculated with respect to carbon number. The recycling experiments were performed by adding 3-hexyne and pentane directly to the autoclave in the glovebox after having all hydrocarbons distilled and the solid catalyst remained in the autoclave. When 1 equivalent (with respect to phosphine content) of Piers' reagent was employed, the Lewis acid was first dissolved in toluene and mixed with the catalyst in the autoclave. After 20 minutes of stirring, toluene was first evaporated, then 3-hexyne and pentane were added to the dried solid in the glovebox. Hydrogenation of the other substrates was performed in the same manner in benzene. After the given reaction time, the autoclave was quenched and gently depressurized. The solution was analyzed by GC (HP 5890 equipped with HP5 (30 m x 0.32 mm) capillary column and FID).

Results and discussion

Silica was first dehydroxylated under high vacuum at 700 °C for 12 h to afford SiO_{2-700} which only presents isolated silanols. Treatment of this silica with $\text{Al}/i\text{Bu}_3$ in diethylether afforded bipodal surface species $[(\text{SiO})_2\text{Al}(i\text{Bu})(\text{Et}_2\text{O})]$ **1**, with a concomitant transfer of isobutyl ligand onto an adjacent silicon atom, to yield an adjacent $[\text{Si}-i\text{Bu}]$ fragment,⁶⁶ as confirmed by DRIFT (Figure 1, a), elemental analysis (0.8 wt% Al) and ^1H MAS NMR (Figure S1a), ^{13}C CP/MAS NMR (Figure 2a). This material was then treated with (4-hydroxyphenyl)diphenylphosphine (1.3 eq. per grafted aluminum) in diethylether for 12 h at room temperature. Repeated washings with diethylether, followed by evacuation of the volatiles, afforded a white powder (Scheme 2).

The DRIFT spectrum of the resulting material, **2**, displays new bands at 1501 and 1591 cm^{-1} , as well as in the 3000-3035 cm^{-1} range assigned to the aromatic ring stretchings $\nu(\text{Csp}^2=\text{Csp}^2)$ and $\nu(\text{Csp}^2-\text{H})$, respectively (Figure 1,b) and attributed to the (4-hydroxyphenyl)diphenylphosphine fragment. The presence of residual alkyls ($\nu(\text{Csp}^3-\text{H})$ at 2800-3000 cm^{-1}) is in agreement with the presence of the inert $\text{Si}-i\text{Bu}$ fragment. The aluminum content displays minor change (0.75 wt%) after the grafting. The protonolysis of the aluminum isobutyl fragment by (4-hydroxyphenyl)diphenylphosphine ligand is evidenced by the near quantitative amount of *isobutane* evolved (0.9 eq. per grafted aluminum). This is confirmed by the elemental analysis of carbon (7.0 wt%) and phosphorus (0.9 wt%) (21 C/Al; 1.04 P/Al) which is consistent with one molecule of (4-hydroxyphenyl)diphenylphosphine grafted on an aluminum atom, alongside a $\text{Si}-i\text{Bu}$ fragment (th. 22, without diethylether, see experimental section). Although not accounted for in the mass balance analysis, the diethylether molecule is still present at the aluminum center, as seen by NMR (*vide infra*). The surface species on this material, **2**, can therefore be described as $[(\text{SiO})_2(\text{AlO}-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2(\text{Et}_2\text{O}))]$ (Scheme 2).

The ^1H MAS NMR spectrum of **2** (Figure S1b) displays a new



Scheme 2. Formation of surface phosphine **2** and supported frustrated Lewis pairs (FLP), **3a** and **3b**.

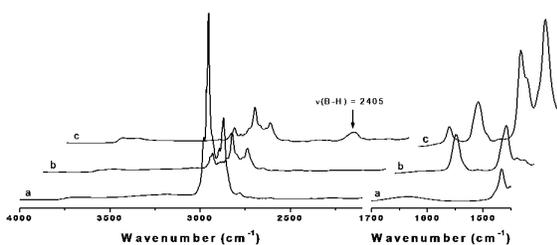


Figure 1. DRIFT spectra of 1 (a), 2 (b) and 3a (c).

signal at 7.1 ppm, characteristic of the aromatic protons of the (4-hydroxyphenyl)diphenylphosphine. The signal at 0.14 ppm in the spectrum of **1** (Figure S1a), assigned to the CH₂ protons of the isobutyl aluminum fragment is no longer present. The protonolysis of the isobutyl aluminum fragment is further evidenced in the ¹³C CP/MAS spectrum by the disappearance of the signal at 20.2 ppm and the decrease in intensity of the signal at 25.6 ppm (Figure 2b), which now corresponds solely to the isobutyl silicon carbons. The intense signals at 120-140 ppm are assigned to the C_{Ar}-H carbons and the broad and weak signal at 161.3 ppm correspond to the quaternary C_{Ar}-O carbons of the (4-hydroxyphenyl)diphenylphosphine moiety. The presence of the diethylether molecule coordinated to the aluminum center is evidenced by the signals at 13 and 67 ppm.⁶⁷⁻⁶⁹ Material **2** shows in the ³¹P MAS NMR spectrum a signal at δ = -6 ppm (Figure 2c), similar to the chemical shift of (p-hydroxyphenyl)diphenylphosphine in C₆D₆ (-6.3 ppm). These combined elements demonstrate that (4-hydroxyphenyl)diphenylphosphine reacts selectively through protonolysis of supported Al-*i*Bu fragment by the phenolic moiety to achieve formation on the targeted phosphine species.

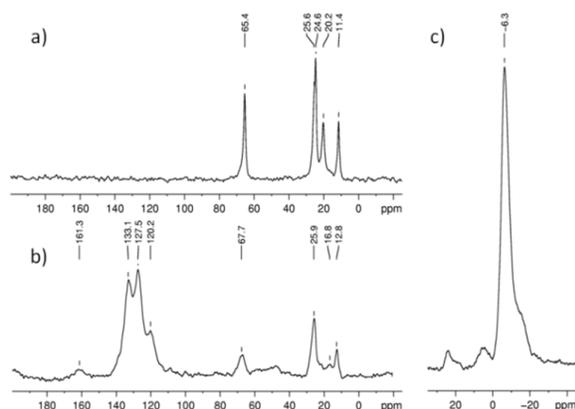


Figure 2. ¹³C CP/MAS NMR spectra of 1 (a) and 2 (b) (125.7 MHz, 30 000 scans, relaxation delay of 2 s, CP contact time of 2 ms, 10 kHz spinning speed) and ³¹P CP/MAS NMR spectrum of 2 (c) (202.4 MHz, 6 000 scans, relaxation delay of 2 s, CP contact time of 2 ms, 10 kHz spinning speed).

The reaction of material **2** with the Lewis acid HB(C₆F₅)₂ or tris(pentafluorophenyl)borane (1.3 eq.) was carried out in benzene for 3 h at room temperature. After multiple washings, materials **3a** and **3b** were obtained respectively, as white powders. These new materials were first analyzed by DRIFT spectroscopy. The DRIFT spectrum of **3a** (Figure 1c) is moderately altered in the 2800-3200 cm⁻¹ range but displays new bands at 1645, 1515, and 1472 cm⁻¹, characteristic of ν(C=C) vibrations from the pentafluorophenyl rings.^{51,52,72} Importantly, a band at 2405 cm⁻¹ appeared. This frequency is in line with ν(BH) of HB(C₆F₅)₂ coordinated to a Lewis base, such as THF.^{73,74} **3b** features similar characteristic bands in the DRIFT spectrum, apart the absence of the peak at 2405 cm⁻¹ (Figure S2).

The boron (0.27 wt% on **3a** and 0.26 wt% on **3b**), and aluminium (0.72 wt% on **3a** and 0.7 wt% on **3b**) loadings on both materials have been determined by elemental analysis (B/Al = 0.92 on **3a** and B/Al = 0.88 on **3b**). The amount of carbon was found to be 10.56 and 12.16 wt% for **3a** and **3b** respectively, corresponding to 33 and 38 C/Al. These data are in agreement with the expected coordination of Piers' reagent and BARf on **2**, and support the formation of proposed surface species **3a** and **3b** in Scheme 2.

The ¹H MAS-NMR and ¹³C CP/MAS spectra of **3a** and **3b** are not changed compared to that of precursor **2** (provided in Figures S3 and S4), as the new species do not comprise additional protons and no significant shift is induced by borane coordination (there is indeed a boron hydride in **3a** that could not be detected by solid state NMR, even on a ¹H-¹¹B}-J-HMQC MAS spectrum: such signals are notoriously difficult to observe by liquid state NMR).⁷⁴ The ¹³C CP/MAS spectra comprise a broad signal in the aromatic region due to multiple C-F coupling. The presence of the Lewis acid on **3a** and **3b** can be confirmed by ¹¹B and ¹⁹F solid-state NMR. The ¹⁹F solid-state NMR spectrum of **3a** displays three large signals around -126, -158 and -165 ppm, as defined by deconvolution of the spectrum (Figure S5a). The intensities and chemical shifts of these three signals are characteristic of the *ortho*, *para* and *meta* fluorine atoms, respectively, on the coordinated HB(C₆F₅)₂ with triphenylphosphine in agreement with literature data.⁷⁵ The solid state ¹⁹F NMR spectrum of **3b** (Figure S5b) shows three large signals (-134, -160, -167 ppm) having the comparable chemical shifts as reported for the molecular adduct [PPh₃•BARf].⁷⁶

The more informative ¹¹B spectrum of **3a** displays a single signal at -24 ppm, previously attributed in homogeneous studies to the tetrahedral boron from [PPh₃•HB((C₆F₅))] adduct (figure S6).⁷⁵ The ³¹P NMR signal has shifted from -6.3 ppm in **2** to 10.1 ppm in **3a**. The ¹¹B-³¹P correlation spectrum in Figure 3 was acquired using the D-HMQC pulse sequence, which correlates nuclei through their dipolar coupling.^{77,78} The signal at 10.1 ppm in the ³¹P dimension correlates with the signal at -24 ppm in the ¹¹B dimension.

Furthermore, using scalar coupling filtering, namely ¹¹B{³¹P}-J-HMQC 1D spectrum, the signal at -24 ppm is observed, unambiguously confirming the presence of a P-B bond, and thus formation of an adduct. This definitively rules

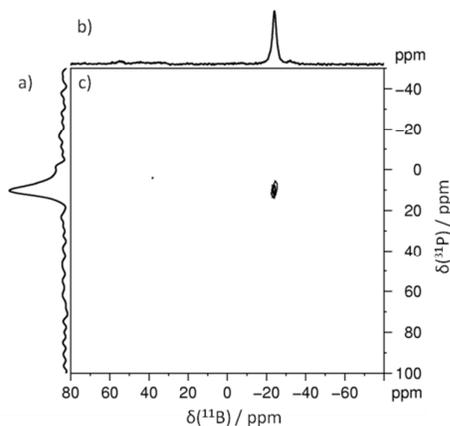


Figure 3. MAS-D-HMPC experiment of **3a** to a pair of nuclei (^{11}B , ^{31}P).

out the assignment of the signal to the $[\text{HB}(\text{C}_6\text{F}_5)_4]$ anion, which also features a ^{11}B chemical shift of -25.5 ppm, close to that of **3a**.²⁹ Similarly the same experiment performed on **3b** (Figure S7), leading to a correlation between signals $\delta(^{11}\text{B}) = -9$ ppm and $\delta(^{31}\text{P}) = 17$ ppm confirmed the coordination of BARF to **2** as reported in the literature.⁷⁶ We have thus prepared by surface organometallic chemistry two new supported materials based on a tethered phosphine (Lewis base) combined with Piers' reagent or BARF (Lewis acid). These well-defined materials were evaluated in the highly challenging heterogeneous hydrogenation of 3-hexyne to Z-3-hexene.

FLP are known to catalyze hydrogenation of organic substrates containing double or triple bonds. Substrates containing heteroatoms are generally fairly easy to reduce due to the polarity of the molecules which facilitates the transfer of the Lewis acidic proton. However, hydrogenation of unactivated alkynes is more challenging. Only one recent example reported by Papai and Repo of a homogeneous system demonstrates hydrogenation of 3-hexyne yielding mainly Z-3-hexene. Their system is based on a bridged B/N FLP

(2-[bis(pentafluorophenyl)boryl]-N,N-dialkylanilines),⁶ that requires a multiple-step synthesis.⁷⁹ Furthermore, its homogeneous nature also prevents recycling of the catalyst.

Stereoselective heterogeneous catalytic hydrogenation of 3-hexyne has been demonstrated with **3a** and **3b** at 80°C in a batch reactor. Already after 2 hours (10 bar H_2 , 2 mol% catalyst in pentane), **3a** converts 3-hexyne to mainly Z-3-hexene (86% selectivity) with a conversion of 13% (Table 1, Entry 1). The minor products are hexane (about 4%), E-3-hexene (about 4.5%), E-2-hexene (about 3%) and Z-2-hexene (about 2.5%). Formation of 2-hexenes stems from isomerization of Z-3-hexene through hydroboration/retrohydroboration reactions, as observed in homogeneous catalysis.⁶ Interestingly, the substrate scope can be extended to other alkynes with some restrictions (Table 2). If 1,2-diphenylethyne can be advantageously converted to Z-1,2-diphenylethylene albeit with a lower reaction rate probably due to steric hindrance, both (hex-2-yn-1-yloxy)trimethylsilane and methyl octadec-9-ynoate yield corresponding Z-alkenes very selectively (>99%) though in modest quantities. We suspect a strong interaction of the Lewis pair with the polar moieties of these particular substrates. Remarkably, the molecular analogous FLP: $\text{HB}(\text{C}_6\text{F}_5)_2/\text{PPh}_3$ system is inactive in hydrogenation of 3-hexyne. Such observation has previously been observed when using Piers' reagent along with different Lewis bases.⁶ The reason is due to a protonation of $\text{B}-\text{C}_6\text{F}_5$ from the phosphonium ion, obtained after H_2 activation on the Frustrated Lewis pair, leading to release of pentafluorobenzene and loss of the Lewis acidity (see Scheme 3).⁸⁰ Such bi-molecular decomposition process is common in homogeneous catalysis. Advantages of a heterogenized system (beside already mentioned reasons, *vide supra*) are fixing the active sites on the surface and consequently avoid bi-molecular decomposition processes. Such phenomenon has already been observed in homogeneous catalysis for example in alkene and alkyne metathesis reaction with molecular complexes based on Mo and W.^{81,82}

Table 1. Catalytic hydrogenation of 3-hexyne and other alkynes at 80°C by **3a** and **3b**.

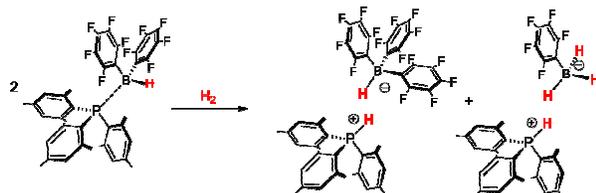
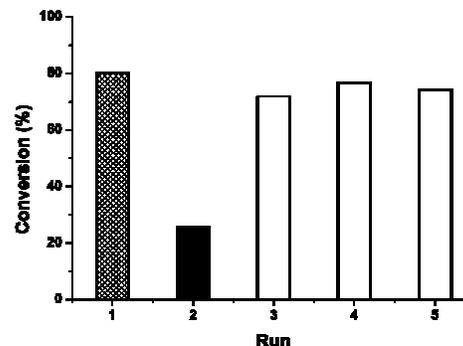
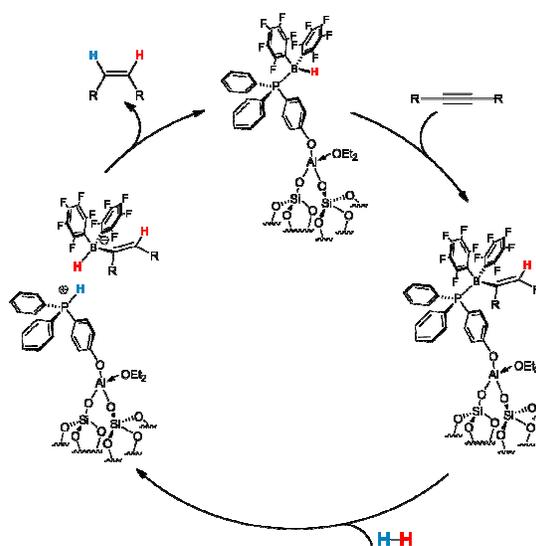
Entry	Catalyst	Catalyst (mol%)	Time (h)	Pressure H_2 (bar)	Conversion (%)	Selectivity (%)				
						Z-3-hexene	E-3-hexene	E-2-hexene	Hexane	Z-2-hexene
1	3a	2	2	10	13.2	86.9	4.3	2.6	3.7	2.5
2	3a	2	4	10	34.7	85.3	5.2	3.1	4.3	2.1
3	3a	2	8	10	99.2	83.8	5.6	3.5	4.2	2.9
4	3a	2	16	10	99.6	83.4	6.2	3.6	4.2	2.6
5	3a	2	4	20	74.8	86.8	4.3	2.7	3.7	2.5
6	3a	2	4	40	98.7	78.5	6.8	4.0	8.0	2.6
7	3a	1	4	40	80.1	85.1	4.5	2.8	5.3	2.3
8	3b	1	4	40	9.0	81.7	5.0	2.7	6.0	4.6

Table 2. Catalytic hydrogenation of selected alkynes by 2 mol% **3a** at 80 °C, 16 h, 10 bar hydrogen.

Substrate	Conversion (%)	Z-alkene (%)	E-alkene (%)
1,2-diphenylethyne	25.1	88	12
(hex-2-yn-1-yloxy)trimethylsilane	15.2	>99	trace
methyl octadec-9-ynoate	5.0	>99	trace

Kinetic studies reveal that an increase of reaction time also increases the conversion (Figure S8a), and full conversion is reached after 8 hours (Table 1, Entries 2-4). The selectivity is virtually unaffected by the reaction time (Figure S8b). Furthermore, hydrogen pressure increase has a beneficial influence on conversion (Table 1, Entries 2, 5 and 6). The selectivity remains unchanged (around 85% Z-3-hexene) except for the experiment at 40 bar with full conversion, in which the selectivity of Z-3-hexene decreases to 78% and the amount of hexane (around 8%) and other hexenes increases slightly. Higher yield of Z-3-hexene is obtained (80% conversion at 40 bar H₂, 1 mol% catalyst in pentane, 4 hours) with lower catalyst loading (table 1, entry 7). Under the same conditions, **3b** gives low conversion (9%) of 3-hexyne with a selectivity of 82% toward Z-3-hexene (Table 1, Entry 8).

These results have shown that the heterogeneous FLP **3a** catalytically reduces 3-hexyne into Z-3-hexene with high selectivity. The activity is comparable to the only example reported under homogeneous conditions and high pressure.⁶ In order to take advantage of the heterogeneous nature of this new catalyst, its recycling was studied at 40 bar, 80 °C, 1 mol% of **3a**, 4 hours reaction time. The first cycle showed a drastic drop in conversion (26%), most probably due to the loss of the Lewis acid (HB(C₆F₅)₂) during the extraction of the products under high vacuum. In these reactions, the Piers' reagent content is about 7 mg and is therefore easily stripped off with the volatile products. The selectivity remains high (86%). Nevertheless, the catalytic activity was restored, even after 5 cycles, when adding 1 equivalent of HB(C₆F₅)₂ in the recycling process (Figure 4), with retention of similar high selectivity toward Z-3-hexene. In a continuous process, rather than subsequent batch cycles, recycling would likely improve. The catalytic mechanism may be described by two pathways: i) traditional approach comprising heterolytic hydrogen splitting followed by protonation of hexyne, or ii) 3-hexyne activation *via* hydroboration accompanied by heterolytic hydrogen splitting and protonation, recently proposed by Papai and Repo based on experimental and theoretical data, and further reported more recently.^{6,16,20} Current results support the latter mechanism, as **3b** is an order of magnitude less active than **3a** which already contains a B-H moiety that can directly undergo hydroboration (first step in the proposed catalytic cycle

**Scheme 3.** Restructuration of [HB(C₆F₅)₂].[PPh₃] in solution after hydrogen addition.**Figure 4.** Catalyst recycling experiments of **3a** applied to stereoselective hydrogenation of 3-hexyne, the dark column represents direct recycling, open columns represent recycling with addition of 1 equivalent of HB(C₆F₅)₂.**Scheme 4.** Proposed mechanism for the stereoselective hydrogenation of alkyne over **3a**.

depicted in Scheme 4). Further experimental and theoretical studies may provide further mechanistic insights of this system. In particular, the substrate scope of this hydrogenation method could be extended by appropriately selecting the Lewis pair and surface tether to better accommodate polar moieties. Ongoing efforts are now dedicated to the generalization of this metal-free Z-selective hydrogenation of alkynes.

Conclusions

The first supported FLP systems, **3a** and **3b**, based on a triphenyl phosphine fragment and either Piers' reagent or BARF have been prepared and characterized. Both materials show unprecedented catalytic activity in stereoselective hydrogenation of 3-hexyne to Z-3-hexene while the molecular

counterpart is not active. Other internal alkynes can also be hydrogenated selectively to the corresponding Z-alkene, albeit in moderate yields. The obtained activity of **3a** is similar to the only homogeneous example reported catalyzed by a bridged B/N FLP. Importantly, **3a** can be recycled when adding 1 equivalent of the Lewis acid. A fully recyclable FLP could be obtained by grafting a bridged frustrated B/P Lewis pair, which will be the topic of future investigation. Current work has demonstrated a new strategy to access a metal-free active phase for the stereoselective hydrogenation of alkynes, an important step in the synthesis of natural and industrially relevant compounds.

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