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Controlling the Lewis Acidity and Polymerizing Effectively Prevent Frustrated Lewis Pairs from Deactivation in the Hydrogenation of Terminal Alkynes

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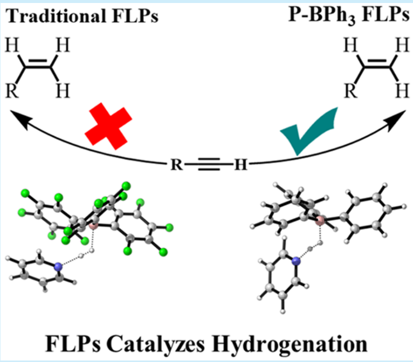
ABSTRACT: Two strategies were reported to prevent the deactivation of Frustrated Lewis pairs (FLPs) in the hydrogenation of terminal alkynes: reducing the Lewis acidity and polymerizing the Lewis acid. A polymeric Lewis acid (P-BPh_3) with high stability was designed and synthesized. Excellent conversion (up to 99%) and selectivity can be achieved in the hydrogenation of terminal alkynes catalyzed by P-BPh_3. This catalytic system works quite well for different substrates. In addition, the P-BPh_3 can be easily recycled.



For a long time, it has been generally believed that the activation of hydrogen must involve the participation of metals,[1] especially precious metals.[2] In 2006, a metal-free hydrogen activation method, called frustrated Lewis pairs (FLPs) catalytic hydrogenation, was first proposed by Stephan et al.[3] FLPs consist of a Lewis base (an electron donor) and a Lewis acid (an electron acceptor) with steric hindrance. Subsequently, such a metal-free catalytic system has been widely studied.[1,4]

Since the concept of FLPs was proposed, FLPs chemistry has been widely used in the hydrogen activation[5] and the hydrogenation of many different unsaturated compounds, such as imines,[6] enamines,[4f,7] olefins,[4c,8] poly aromatics,[9] internal alkynes,[10] ketones,[11] aldehydes,[9a,12] silyl-enol ethers,[13] and CO_2.[5i,14] Although many successes have been achieved for the catalytic hydrogenation promoted by FLPs, the terminal alkyne is an exception. Ansa-aminohydroborane, which showed excellent reactivity for the hydrogenation of internal alkynes (up to 100% conversion), has no any catalytic ability for the hydrogenation of terminal alkynes.[10a] The pyridone borane complex showed some catalytic reactivity for terminal alkynes with low conversion.[10d] Much experimental and theoretical researches revealed that the Lewis acids used for the classical FLPs, such as tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), could react with the terminal alkynes via deprotonative borylation pathway, producing a stable alkynyl borates in which the terminal carbon of alkynes tightly binds with the boron of these Lewis acids.[10a,15] As a result, the FLPs are deactivated for the hydrogenation. We rationalize that a borane compound with reasonable Lewis acidity should prevent the formation of alkynyl borates and retain the ability to split H_2 in the presence of Lewis bases, thus avoiding the deactivation of FLPs in the hydrogenation.

On the basis of a theoretical analysis on the H_2 activation ability and binding energies between different Lewis acids and terminal alkynes using the B3LYP-D3(BJ)/6-311+G* method including solvent influence (Supporting Information (SI), Figures S1 and S2), triphenylboron (BPh_3) was chosen as a potential compound to investigate the possibility of terminal alkynes hydrogenation catalyzed by FLPs. Although the Lewis acidity of BPh_3 is weaker than that of $B(C_6F_5)_3$, theoretical calculations on the H_2 activation by BPh_3/Py (Py: pyridine) and $B(C_6F_5)_3$/Py Lewis pairs gives close energy barriers for H_2 splitting (26.2 and 27.2 kcal/mol, respectively). The H−H distances are 0.949 and 0.807 Å in the transition states TS_{BPh3} and $TS_{B(C6F5)3}$, respectively (Figure 1a). The later one is quite close to those using classical FLPs, such as 0.79 Å for $B(C_6F_5)_3/(tBu)_3P$,[16] 0.787 Å for $B(C_6F_5)_3/KHCO_3$,[14d] and 0.85 Å for $Mes_2P\text{-}C_2H_4\text{-}B(C_6F_5)_2$.[17]

More importantly, the Gibbs free energy changes to form the B−C bond are 13.9 and −6.1 kcal/mol for BPh_3+Ph−C≡CH+Py and $B(C_6F_5)_3$+Ph−C≡CH+Py systems, respectively

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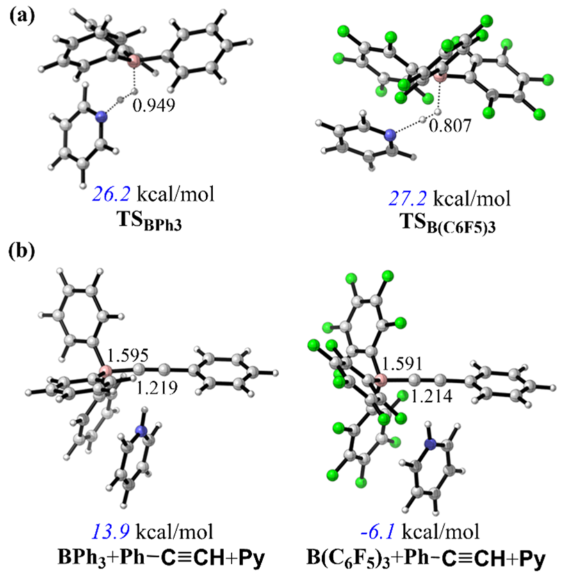


Figure 1. Optimized structures of (a) transition states of H_2 activation and (b) $BPh_3/B(C_6F_5)_3$+Ph−C≡CH+Py complexes. The italic values are (a) activation energies and (b) Gibbs free energy changes in kcal/mol. The other values are distances in Å. See SI for calculation details.

(Figure 1b), indicating that the formation of alkynylborates between BPh_3 and terminal alkyne is highly unfavorable, whereas that between $B(C_6F_5)_3$ and terminal alkyne is obviously exothermic. These theoretical results were further confirmed by NMR experiments. The ^{11}B signal in the NMR spectra of $B(C_6F_5)_3$ and BPh_3 appear at 57.5 and 68.7 ppm, respectively, which are consistent with the literature data.[18] When equivalent molar of phenylacetylene (Ph-C≡CH) was mixed with $B(C_6F_5)_3$, the ^{11}B signal shifted to −12.0 ppm (Figure 2.1), due to the formation of the B−C bond between $B(C_6F_5)_3$ and the Ph-C≡CH. In addition, because of the isomerization of 1,1-carboboration reactions between $B(C_6F_5)_3$ and the Ph-C≡CH, a corresponding doublet was observed (Figure 2.1).[15i] Even though the Lewis acid−base interaction between $B(C_6F_5)_3$ and Py is strong[18c] (^{11}B signal for $B(C_6F_5)_3$/Py adduct: −4.2 ppm), adding Py into the $B(C_6F_5)_3$/Ph-C≡CH system cannot break the B−C bond of the alkynylborates. The ^{11}B NMR of the mixture of BCF, Py, and Ph-C≡CH also shows two peaks at −13.9 and −16.4 ppm, which correspond to the products of 1,2-addition and C−H deprotonation, respectively.[5e,15b] When using BPh_3 as Lewis acid, the situation is totally different. After adding Ph-C≡CH, the ^{11}B signal of BPh_3 does not have any shift (Figure 2.2). It suggests that BPh_3 does not bind with Ph-C≡CH. No matter whether there is Ph-C≡CH or not, adding Py results in the shift of ^{11}B signal from 68.7 to 4.2 ppm due to the formation of BPh_3/Py adduct. Even the samples were treated at 120 °C for 12 h, and the same results can be obtained (SI, Figure S3). However, when Py was replaced by a stronger base, such as $N(CH_2CH_2NPr^i)_3P$, it could induce deprotonation of Ph-C≡CH and $[N(CH_2CH_2NPr^i)_3PH][PhC{\equiv}C\text{-}BPh_3]$ was formed, which exhibited the ^{11}B chemical shift at −13 ppm.[15j]

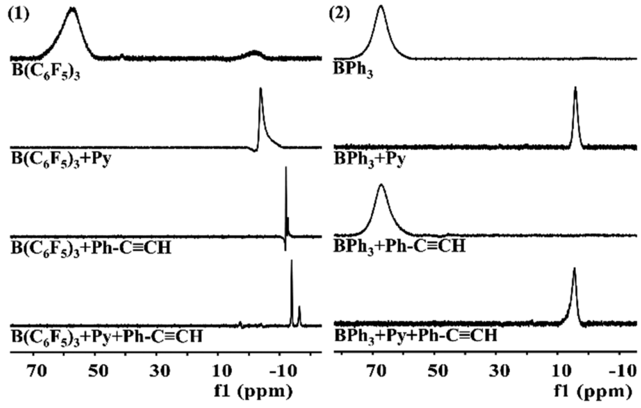
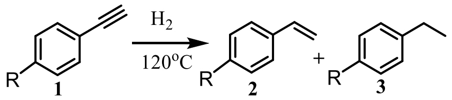


Figure 2. ^{11}B spectra of (1) $B(C_6F_5)_3$ and (2) BPh_3 in the presence of equivalent Py, Ph-C≡CH, and Py/Ph-C≡CH, respectively, in $CDCl_3$.

Above theoretical and experimental results reveal that, being different from classical FLPs, BPh_3/Py may serve as a catalyst for the hydrogenation of terminal alkynes. Activation barrier of H_2 splitting for TS_{BPh3} is a little high, indicating that a higher temperature is necessary for the cleavage of H_2. It is interesting to find that 11.6% conversion from phenylacetylene to styrene and ethylbenzene can be obtained in the presence of BPh_3/Py at 120 °C in 12 h (Scheme 1). As expected, $B(C_6F_5)_3$/Py cannot promote the reaction at all under the same conditions. The BPh_3/Py system is not stable during the reaction (SI, Figure S9), which may be responsible for the low conversion of hydrogenation.

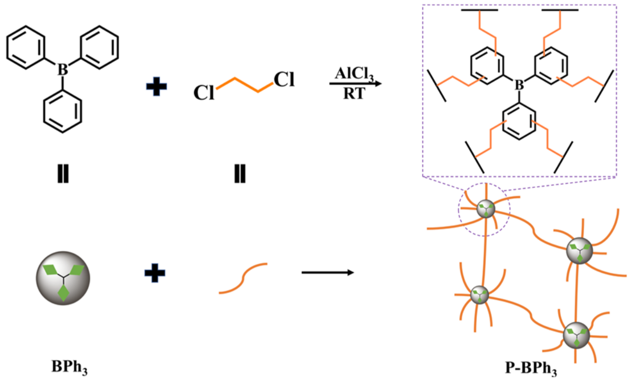
Scheme 1. Terminal Alkynes Hydrogenation Catalyzed by $B(C_6F_5)_3$/Py and BPh_3/Py



Catalyst	R	Con. (%)	Sel. (%)
$B(C_6F_5)_3$/Py	-H	0	—
	$-CH_2CH_3$	0	—
BPh_3/Py	-H	12	100 (2:3=98:2)
	$-CH_2CH_3$	13	100 (2:3=96:4)

To enhance the stability of BPh_3 and provide an example for recyclable FLPs, a polymeric-BPh_3 (P-BPh_3) was designed and synthesized. Alkane was introduced to polymerize with BPh_3 by the Friedel−Crafts reaction at room temperature (Scheme 2). The P-BPh_3 was characterized by solid-stated NMR, TGA, XPS, SEM, XRD, and FT-IR (see SI for details). Both the signals of aromatic carbons, methylene carbons, and boron can

Scheme 2. Synthesis of P-BPh_3



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be clearly observed in the solid-state NMR (Figure 3). All of them show close chemical shifts to those in the liquid NMR,

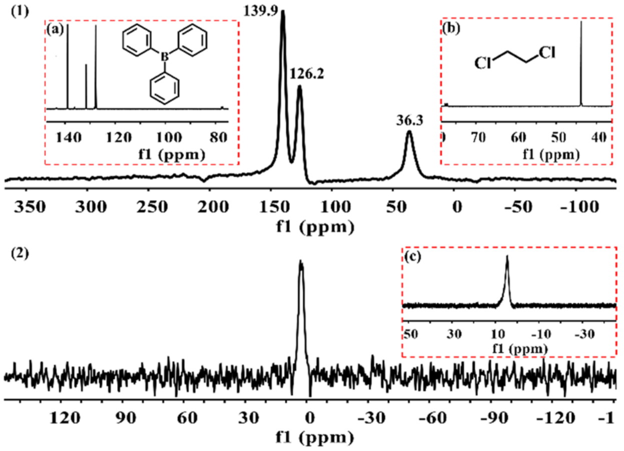


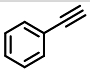
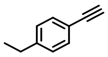
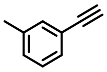
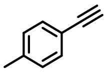
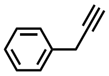
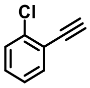
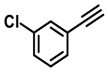
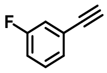
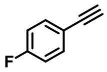
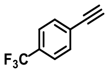
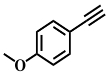
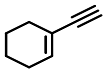
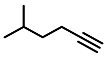
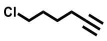
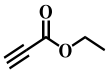
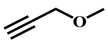
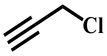
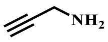
Figure 3. (1) Solid-state ^{13}C NMR spectrum of P-BPh_3 and (2) solid-state ^{11}B NMR spectrum of P-BPh_3/Py. Insets: liquid ^{13}C NMR spectrum of (a) BPh_3 and (b) dichloroethane in $CDCl_3$, and (c) liquid ^{11}B NMR spectrum of BPh_3/Py in $CDCl_3$.

indicating that the polymerization happened and the three-coordinate structure of B is maintained. Besides NMR, the C—C bond of the linker in P-BPh_3 can also be evidenced by XPS (SI, Figure S4) and FT-IR (SI, Figure S5). The content of B in P-BPh_3 is 4.4 wt %, determined by EDX of SEM (SI, Table S1). It is worth noticing that the polymerization with dichloroethane extremely enhances the stability of P-BPh_3. The decomposition temperature of P-BPh_3 is higher than 450 °C, determined by TGA (SI, Figure S8). On the contrary, slow degradation is observed below 150 °C on the TGA of BPh_3.

It is exciting to find that 99% conversion of 4-ethylphenylacetylene is achieved when P-BPh_3 was used as the Lewis acid of FLPs at 120 °C (entry 1, SI, Table S2). Lewis bases, as the important part of FLPs for H_2 splitting, have crucial influence on the hydrogenation of terminal alkynes. Reactions with both pyridine and methyl substituted pyridine give excellent conversions (entries 1−3). However, electrophilic substitution, which weakens the electron-donor ability of pyridine, results in poor bases for the hydrogenation (entries 4 and 5). Although bases with steric hindrance are favorable for H_2 splitting according to the concept of FLPs,[2−4] this is not the case for the hydrogenation of terminal alkynes (entries 6−8), suggesting that steric hindrance may prevent the access of alkynes.

By using P-BPh_3/Py as the catalytic system, we further explored the substrate scope of terminal alkynes hydrogenation promoted by this unusual FLPs (Table 1). The investigated substrates include both aromatic and nonaromatic alkynes. For all the aromatic alkynes (entries 1−11), whether it is an electron donor or acceptor modification on the aromatic ring, more than 99% conversions of alkynes were obtained with 99% selectivity of alkene and alkane. Comparing with the aromatic alkynes, the aliphatic alkynes are less reactive (entries 12−18). Especially, when propargyl amine was used as substrate, no hydrogenation happened, which may be the result of strong interaction between the −NH_2 group and Lewis acid center.

Table 1. Substrate Scope of Alkynes Hydrogenation Catalyzed by P-BPh_3/Py[a]

Entry	Alkynes	Conversion (%)[b]	Selectivity (%)[b] Total (%)	Selectivity (%)[b] Alkene(%):Alkane (%)
1		>99	>99	90:10 (71 [c])
2		>99	>99	88:12
3		>99	>99	88:12
4		>99	>99	94:6 (76 [c])
5		>99	>99	68:32
6		>99	>99	87:13 (81 [c])
7		>99	>99	86:14
8		>99	>99	85:15
9		>99	>99	82:18
10		>99	>99	73:27
11		>99	>99	94:6 (82 [c])
12		>99	>99	91:9
13		64	>99	88:12
14		>99	>99	79:21
15		>99	>99	93:7
16		98	>99	91:9
17		53	>99	99:~
18		96	>99	17:83
19		0	~	~

[a] Reaction conditions: alkynes (1 mmol), P-BPh_3 (10 wt % of the substrate); base (0.5 mmol); solvent toluene (1 mL); pressure of H_2, 5 MPa, 120 °C, 12 h. [b] Determined by GC and GC-MS. [c] The isolate yield of alkenes (molar ratio).

The recyclability and long-term stability of the catalysts are vital for practical application in industry. Although FLPs have achieved great successes for H_2 activation, recyclable FLPs were rarely reported.[19] P-BPh_3 provides a simple example of recyclable and highly stable Lewis acid for FLPs. After the hydrogenation of alkynes, the P-BPh_3 can be recovered by easy solid−liquid separation. Without further treatment, the P-BPh$_3$ was reused 12 times and an obvious loss of catalytic activity was observed (Figure 4)due to the high stability of P-BPh$_3$.

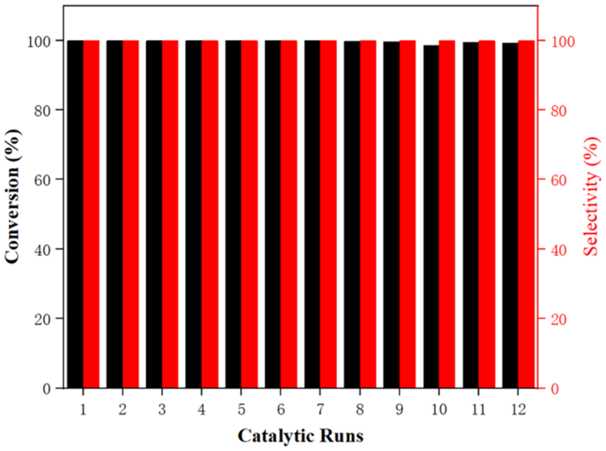


Figure 4. Reusability of P-BPh$_3$ in the hydrogenation of phenylacetylene.

In summary, we have successfully developed a highly stable polymeric Lewis acid (P-BPh$_3$) for effective metal-free hydrogenation of terminal alkynes. In the past, such a hydrogenation reaction is impossible for classical FLPs due to the tight bond between the Lewis acid and terminal alkynes, making the FLPs deactivated.[10a,15] In the presence of P-BPh$_3$/Py, excellent conversion and selectivity can be achieved for the hydrogenation of terminal alkynes with different functional groups. In addition, because P-BPh$_3$ is extremely stable with decomposition temperature being higher than 450 °C, its catalytic activity remains quite good after recycling 12 times. This work demonstrates the importance of a rational Lewis acidity and polymerization for avoiding the deactivation of FLPs. The simple synthesis route, high stability, and reactivity of P-BPh$_3$ may provide a new way for FLPs application.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01073.

Experimental and theoretical calculation details, original spectra, and Cartesian coordinates of the optimized structures (PDF)

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Notes

The authors declare no competing financial interest.

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