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Communication

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Room-Temperature Activation of Hydrogen by Semi-Immobilized Frustrated Lewis Pairs in Microporous Polymer Networks

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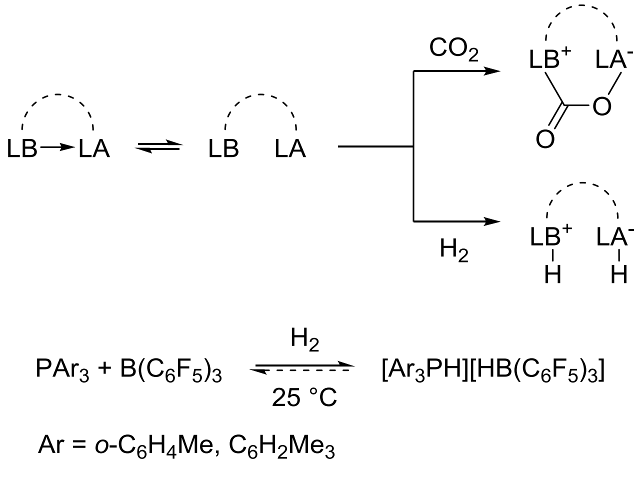
Supporting Information Placeholder

ABSTRACT: Porous polymer networks based on sterically encumbered triphenylphosphine motifs, mimicking the basic sites employed in frustrated Lewis pair chemistry, were synthesized *via* Yamamoto polymerization and their interactions with the strong Lewis acid $B(C_6F_5)_3$ probed. The combinations yield semi-immobilized frustrated Lewis pairs, one of which is able to cleave dihydrogen heterolytically at ambient temperature and low hydrogen pressure.

Over the last decade, microporous polymer networks have garnered attention as materials for a wide variety of applications.[1,2] Emanating from rigid organic building blocks, materials with very small pores between 0.5 and 2 nm, accessible surface areas of up to 6400 m^2g^{-1} as well as high thermal and chemical stability[3] have been synthesized by a number of polymerization methods such as metal-mediated homocoupling reactions, metal-catalyzed cross-coupling reactions, condensation reactions, and many others.[2,4] In contrast to MOFs and COFs these materials do not exhibit crystallinity but, emerging from C–C bond forming reactions, they can forgo the use of heteroatoms entirely, allowing for a pure hydrocarbon skeleton. This feature is especially advantageous when designing catalysts with highly sensitive active sites as it enables the exclusion of non-orthogonal functional groups.



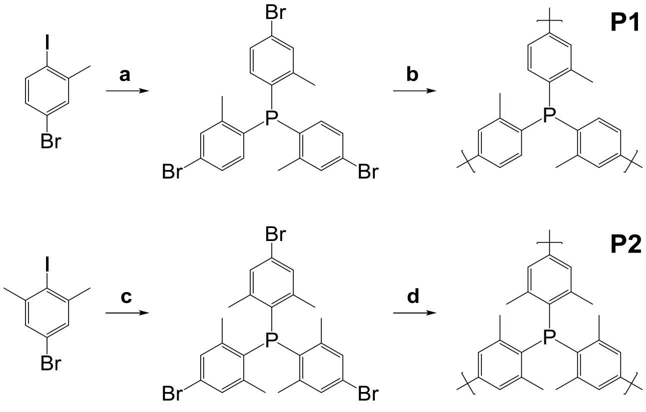
Scheme 1: Equilibrium state of a generic frustrated Lewis pair (LA: Lewis acid, LB: Lewis base) and activation of carbon dioxide and hydrogen (top); (non-)reversible activation of hydrogen by reported FLPs[5,6] (bottom)

Such types of functional groups can be found as catalytic sites in frustrated Lewis pairs (FLPs).[7] The members of this emerging class of molecular catalysts are solely based on main group elements and in most cases consist of a boron-based Lewis acid (LA) and a Lewis base (LB), usually comprising phosphorus or nitrogen as basic sites.[8] Both active sites are sterically encumbered by bulky moieties in order to prevent them from forming a strong covalent bond and consequently quench their opposing reactivities. Small molecules (H_2, CO_2 etc.) fitting in between these bulky groups can be activated through double polarization by the acidic and basic sites, leading to (zwitter)ionic products (see Scheme 1).[6,7,9] For this activation to take place, the steric hindrance must not be sufficient to prohibit any interaction; in solution a weak but reversible coordination must be possible lest the polarization be precluded entirely.[10] Subsequently, the activated intermediate(s) can be used for reactions with a number of substrates. The most intensely researched application for this type of catalyst is the heterolytic splitting of dihydrogen and its subsequent use in the reduction of C=C[11], C=N[12], and C=O[13] double bonds as well as cleavage of silylenolethers[14], among others. Lewis acid and base can be part of the same molecule, *i.e.* both intra- and intermolecular FLPs are capable of activating small molecules.[9] In many cases though the mechanistic properties of an activation process are deceptively simple. Even in cases of both active sites within the same molecule theoretical studies rather suggest intermolecular activation *via* a twofold head-to-tail interaction between two intramolecular FLP molecules.[15]

Whereas a great number of Lewis basic polymers has been published, since these are easy to obtain and often display interesting CO_2 adsorption properties, only a handful of Lewis acidic moieties into porous polymers have been reported[16,17], none of which are used for catalytic applications. Due to the use of very strong Lewis acids such as tris(pentafluorophenyl)borane (commonly abbreviated to BCF) or related compounds, these catalysts are often highly sensitive to external factors such as humidity or oxygen, which makes their handling challenging. To overcome this issue, extensive studies towards electronic fine-tuning have produced robust Lewis acids which can be handled without the use of inert gas techniques.[18] Recent advances have furthermore afforded so-called “inverse” FLPs based on a weak and more robust Lewis acid but which are used in conjunction with a very strong and sensitive Lewis base on the other hand.[19]

In order to be able to enhance stability and recyclability and to further increase the appeal of FLPs, the incorporation of frustrated Lewis pairs into solid materials, e.g. a microporous polymer network, seems an advantageous endeavor. In this work we focused on the generation of frustrated Lewis pairs emerging from porous polymers comprising sterically encumbered phosphine moieties, which are impregnated with a readily available strong Lewis acid. We demonstrate the ability of these semi-immobilized FLP systems to activate dihydrogen at ambient temperature and low hydrogen pressure.

The syntheses of the phosphine polymers were carried out according to the synthesis procedure for porous polymer networks *via* Yamamoto polymerization[20] starting from tris(*p*-bromophenyl)phosphine derivatives (see Scheme 2) with increasing steric demand around the phosphorus atoms. The structure of unmethylated triphenylphosphine polymer has been described previously.[21,22] Due to the use of less reactive aryl chloride starting material harsher synthesis conditions were required, whereas in this work a milder synthesis protocol[23] was applied due to the exclusive use of the more reactive brominated species.



Scheme 2: Syntheses of triarylphosphine polymers; a) *i*-PrMgCl, THF, 0 °C, 1 h, then PCl_3, THF, -78 °C to r.t., 12 h; b) $Ni(COD)_2$, DMF/THF, r.t., 15 h c) *n*-BuLi, Et_2O, -78 °C, 2 h, then PCl_3, Et_2O, -78 °C to r.t., 12 h d) $Ni(COD)_2$, DMF/THF, r.t., 22 h

Purification *via* Soxhlet extraction with methanol and drying *in vacuo* at 80 °C yields the product networks (Figure S1). Tris(2-methylphenyl)phosphine polymer **P1** was collected as white and light solid whereas tris(2,6-dimethylphenyl)phosphine polymer **P2** has an intense yellow color and fluffy texture. **P1** and **P2** feature surface areas of 1045 and 947 $m^2\ g^{-1}$, respectively, with **P2** featuring a remarkable hysteresis (see Figure 1). These results are in line with the reported surface area of unmethylated triphenylphosphine polymer of 1284 $m^2\ g^{-1}$.[21] The decrease in surface area can thus be interpreted as a result of the increased monomer weight and pore blocking by increasing amounts of methyl groups.

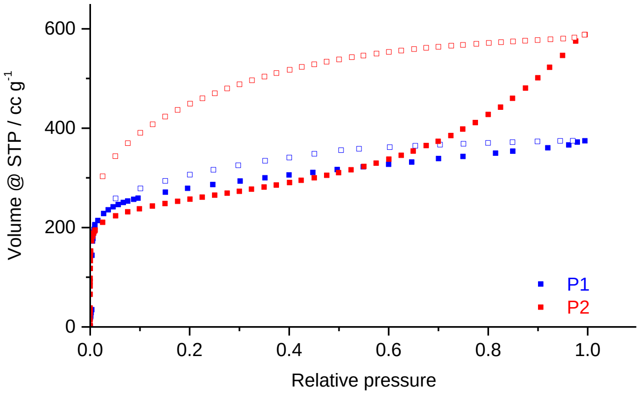


Figure 1: Nitrogen sorption isotherms of P1 (blue) and P2 (red)

Organic solvents such as toluene, bromobenzene, dichloromethane and THF are readily absorbed by the polymers, which exhibit strong swelling properties and form gel-like mixtures with these solvents. To probe the properties of the synthesized materials as Lewis bases, their behavior towards Lewis acids such as commercially available tris(pentafluorophenyl)borane (commonly abbreviated as BCF) has to be examined. When a substance is pre-dissolved in the absorbed solvent it can be introduced into the pores of the polymer. Choosing a volatile solvent facilitates drying of the obtained material. BCF is well soluble in aromatic and chlorinated solvents. To gain information on the interaction between BCF as a Lewis acid and the bulky Lewis base, no other Lewis acidic or basic functions may be present. Therefore, inside the glovebox, BCF and porous phosphine polymer were suspended in DCM, which is volatile, non-coordinating, neither acidic nor basic, readily dissolves BCF, and leads to rapid swelling of the polymer. When impregnated with BCF solutions in non-coordinating solvents, e.g. DCM, the Lewis acid is readily absorbed into the polymer. The impregnation of the yellow polymer network **P2** was accompanied by darkening of the color while colorless **P1** remained colorless. Washing with coordinating solvents such as diethyl ether or THF restores the original network. Even weakly coordinating solvents such as methanol or acetone are coordinated preferably over the bulky phosphine moieties.

Both polymers (see Figure 2) as well as their composites with BCF exhibit strong fluorescence under UV irradiation (bottom row) at 254 (weak) and 366 nm (strong). BCF is readily absorbed by the polymer and quenches the fluorescence (see supporting information) especially for polymer P1 pointing to a stronger interaction with the Lewis acid. (Figure S1) Furthermore, after addition of BCF the finely dispersed polymer particles contract and sediment within a matter of minutes whereas the empty polymer particles tend to collect at the surface of DCM.

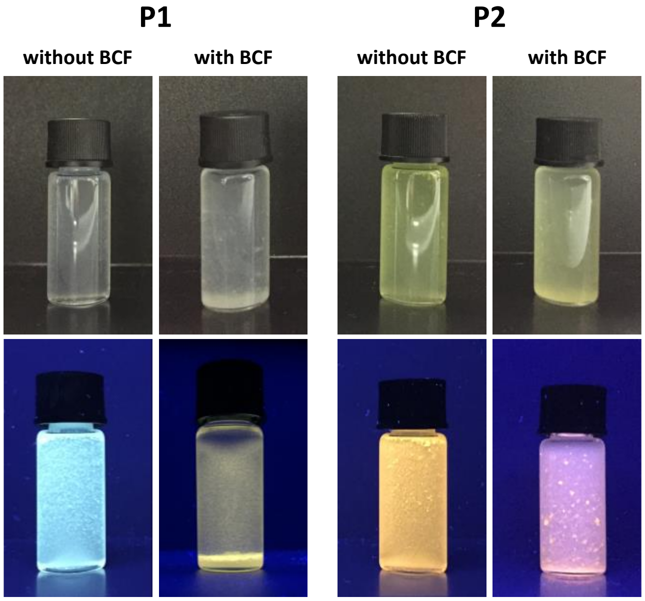


Figure 2: P1 (left block) and P2 (right block) in DCM suspension before and after addition of BCF. Top row: UV lamp off, bottom row: under irradiation of UV light (366 nm)

Solid state magic angle spinning NMR spectroscopy of the dried solids confirms the assumed structures (see Figure 3 and Figure S 2 in the supporting information). The ^{31}P NMR spectra each exhibit one main peak in the region of -34 and -36 ppm alongside a small impurity at approximately +32 ppm, indicative of small amounts of phosphine oxide present in each network. These traces of phosphine oxide have been reported previously[21] and seem to be the result of a side reaction of the Yamamoto polymerization since the polymers were synthesized under rigorously inert conditions. Additionally, **P1** and **P2** are prone to phosphine oxide formation in air at elevated temperatures over elongated periods of time and should therefore be stored under inert gas.

Upon impregnation with BCF and subsequent solvent removal, the ^{31}P solid state NMR signals are shifted to lower field as expected when coordinating to an acidic species. It is noteworthy that nearly the entire signal of the phosphine within he polymers is shifted downfield, showing that almost all phosphine groups in the polymer networks **P1** and **P2** are accessible to the molecular Lewis acid. Notably, the extent of the shift strongly correlates with the degree of methylation of the triphenylphosphine derivative. For **P1** a shift of 14.7 ppm is observed whereas for **P2** a shift of only 6.5 ppm is observed (see Figure 3). This shift difference indicates that the bond strength decreases with increasing steric hindrance around the central phosphorus atom, which means that the higher the degree of frustration is, the weaker the emerging bond is rendered. This observation is quite remarkable. According to Heine *et al.*,[10] the formation of a FLP is usually not observed at ambient temperature in solution, *i.e.* the solution NMR spectra of the individual components do not differ from the spectra of stoichiometric mixtures. Due to the only weakly coordinating nature of the FLP, the favorable interactions gained from association of Lewis acid and base are dominated by the entropic contribution of the dissociation process. In the solid state on the other hand, after solvent removal, Lewis acid and base are forced into and kept in a "not-so-frustrated" state, so that the interaction can actually be observed, and its strength determined by the difference in the chemical shifts, Δ_δ.

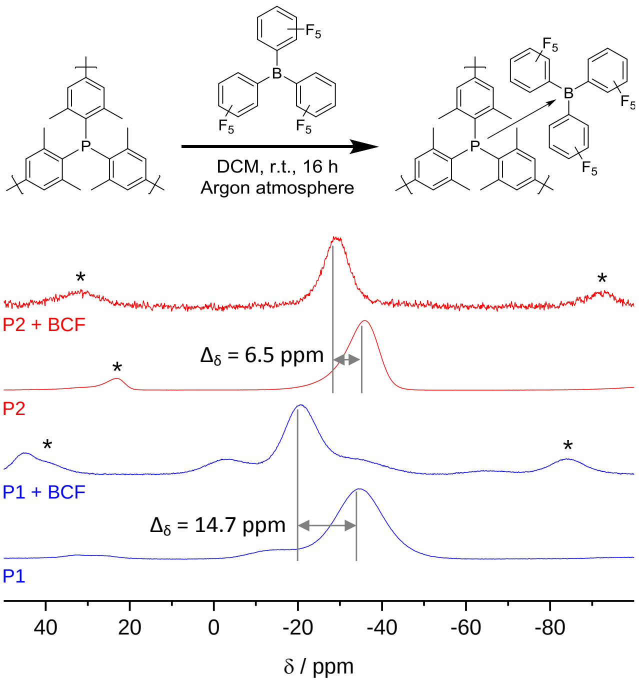


Figure 3: Impregnation procedure of triphenylphosphine derivative polymers (exemplified for P2) followed by ^{31}P NMR spectroscopy; P1 (blue) and P2 (red) before (upper spectra) and after (lower spectra) impregnation with BCF. Asterisks denote spinning sidebands.

To verify this hypothesis we compared the chemical shifts of the solid state NMR spectrum of a "dry" FLP, consisting of the molecular counterpart of **P2**, tris(2,6-dimethylphenyl)phosphine, and BCF to the solid state NMR spectrum of the phosphine molecule on its own. As expected, in the "dry" FLP, the phosphorus signal is shifted downfield by *ca.* 10 ppm compared to the phosphine (see Figure S 3 in the supporting information).

According to the molecular compounds[5,6], the combinations **P1**/BCF and **P2**/BCF should form frustrated Lewis pairs and be active towards the cleavage of dihydrogen. When used in combination with BCF, the molecular equivalent of **P1**, tris(*o*-tolyl)phosphine has been reported to activate hydrogen reversibly at ambient conditions to form $[(o\text{-}C_6H_4Me)_3PH][HB(C_6F_5)_3]$ whereas the molecular counterpart of **P2**, trimesitylphosphine, forms the hydrogen adduct $[(1,3,5\text{-}C_6H_2Me_3)_3PH][HB(C_6F_5)_3]$ which remains stable even when exposed to temperatures of up to 150 °C. To prove the hydrogen activation capability of our polymeric materials, we performed H/D isotope scrambling experiments typically employed to demonstrate FLP behavior in a new material[24] for composites of BCF with P1, P2, and their molecular counterparts, tris(*o*-tolyl)phosphine and tris(2,6-dimethylphenyl)phosphine. To that end, inside the glovebox a Young-type NMR tube was charged with a stoichiometric mixture of **P1**/BCF or P2/BCF, cyclohexane-d_{12}, and the suspension subjected to ultrasonication for 15 minutes to ensure sufficient intermixing of the poorly soluble BCF and the polymer. Subsequently, the tube was pressurized with an H_2/D_2 mixture (*ca.* 1:1 v/v) to 6 bar, and analyzed *via* ^{1}H NMR spectroscopy beginning several hours after pressurization of the tube. In both cases an emerging triplet can be observed at 4.54 ppm shortly after pressurization, indicating the formation of HD (see Figure 4). The control reaction comprising only porous phosphine polymer **P2** and solvent under H_2/D_2 pressure did not result in any conversion to HD. Although the control reaction with BCF as the sole reactant gave the scrambling product albeit at much lower rate than the BCF/**P2** composite, it must be pointed out that it has been proven theoretically[25] and experimentally under low hydrogen pressure[5] that BCF alone is not active in the heterolytic cleavage of H_2. In our case, residues of protic solvents attached to BCF or trace water on the glass surface might be responsible for providing a proton shuttle in the activation of hydrogen. Furthermore, if a composite of BCF and another highly microporous polymer network devoid of any functional groups (PPN-6, 4172 $m^2\ g^{-1}$, also prepared by Yamamoto polymerization) is used, no hydrogen activation product can be detected. It seems therefore that the impregnation procedure of a polymer has a negating effect on the activity of BCF itself. This could be caused by the highly hydrophobic and non-polarizable surface of the networks. It can therefore be assumed that the observed reactivity of the composites is not only independent of but inherently much higher than the activity of "pure" BCF. The composite tris(*o*-tolyl)phosphine/BCF gives the expected statistical H_2/HD ratio after merely a few hours. This shows that the incorporation of the active sites into the polymer imposes a strong kinetic restriction on the H/D exchange process.

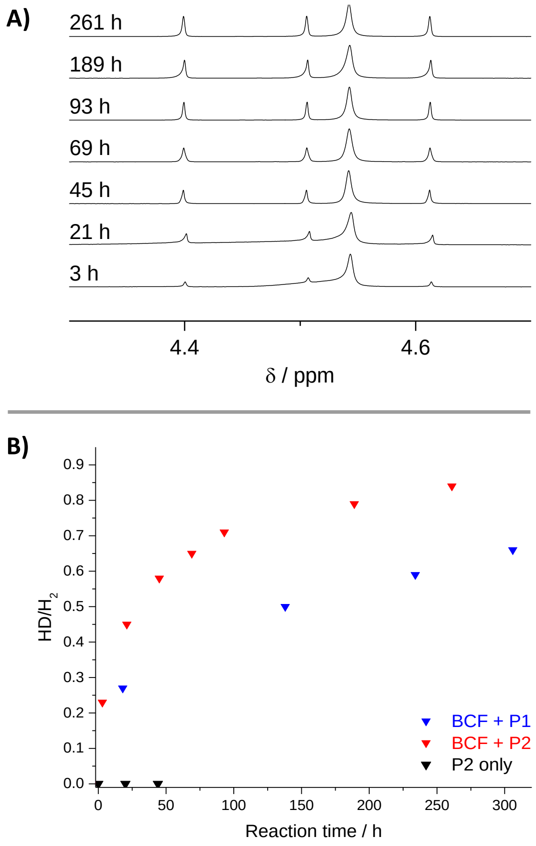


Figure 4: A) Kinetic measurement of H/D exchange determined *via* ^{1}H NMR and B) integral ratio of HD/H_2 plotted as a function of time

We hereby report the first synthesis of two semi-immobilized frustrated Lewis pairs with the basic components embedded into the backbones of microporous polymer networks. Addition of the commercially available Lewis acid, tris(pentafluorophenyl)borane, to polymers structurally akin to trimesitylphosphine yielded two functional heterogeneous hydrogen activation catalysts. Their ability to cleave dihydrogen at ambient temperature and low pressure was demonstrated *via* isotope scrambling experiments.

Further combinations of Lewis acidic and basic species need to be created to obtain heterogeneous catalyst systems capable of splitting dihydrogen at low pressures and to enable catalytic hydrogenation. Furthermore, full heterogenization of frustrated Lewis pairs could even further enhance the reactivity and applicability of such systems.

ASSOCIATED CONTENT

Supporting Information

Experimental details on synthesis of monomers and polymers and hydrogen activation. 13C-NMR of polymers and molecular model compounds, fluorescence spectra and TGA of the polymers

The Supporting Information is available free of charge on the ACS Publications website.

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