JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by CARLETON UNIVERSITY

Communication

ROMP-Boranes as Moisture Tolerant and Recyclable Lewis Acid Organocatalysts

Fernando Vidal, James McQuade, Roger Lalancette, and Frieder Jaekle

J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.0c05454 • Publication Date (Web): 05 Aug 2020

Downloaded from pubs.acs.org on August 5, 2020

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

ROMP-Boranes as Moisture Tolerant and Recyclable Lewis Acid Organocatalysts

Fernando Vidal, James McQuade, Roger Lalancette, and Frieder Jäkle*

Department of Chemistry, Rutgers University-Newark, 73 Warren Street, Newark, New Jersey 07102, United States.

KEYWORDS “Frustrated” Lewis pairs, triarylboranes, recyclable catalyst, ROMP, reductive amination.

ABSTRACT: Although widely used in catalysis, the multi-step syntheses and high loadings typically employed are limiting broader implementation of highly active tailor-made arylborane Lewis acids and Lewis pairs. Attempts at developing recyclable systems have thus far met with limited success, as general and versatile platforms are yet to be developed. We demonstrate a novel approach that is based on the excellent control and functional group tolerance of ring-opening metathesis polymerization (ROMP). The ROMP of highly Lewis acidic borane-functionalized phenylnorbornenes afforded both a soluble linear copolymer and a crosslinked organogel. The polymers proved highly efficient as recyclable catalysts in the reductive *N*-alkylation of arylamines under mild conditions and at exceptionally low catalyst loadings. The modular design presented herein can be readily adapted to other finely tuned triarylboranes, enabling wide applications of ROMP-borane polymers as well-defined supported organocatalysts.

The remarkable success of main-group Lewis acids (LA) in general, and electron-deficient triarylboranes (BAr_3) such as $B(C_6F_5)_3$ in particular, is clearly evident in the wide variety of chemical transformations they have been applied to,[1] many of them associated with the concept of “frustrated” Lewis pairs (FLPs).[2] Striking examples include hydrogenation,[3] hydrosilylation,[4] CO_2 reduction,[5] defunctionalization,[6] C-H bond activation,[7] and Lewis pair (LP) polymerization.[8] Although these reactions no longer require the use of costly, scarce, and oftentimes toxic transition-metal catalysts, as homogeneous catalysts the boranes cannot be easily recycled and require separation from the products. This is exacerbated by the need for multi-step syntheses to prepare tailored halogenated BAr_3 catalysts and the high loadings typically employed in catalytic processes.[9]

Immobilization of organoboranes is essential to overcome these problems,[10] but so far very few solid supports are available, among them modified silica,[11] metal-organic frameworks (MOFs),[12] transient micelles,[13] and covalent polymer networks.[14] Limitations arise due to difficult material syntheses and manipulations, complex or inadequate characterizations, underperforming stability, catalyst leaching, and/or insufficient understanding of the true molecular environment around the catalytic site. Contrarily, polymeric materials obtained by controlled conversion of functional monomers offer access to well-defined and tunable (“homogeneous-like”) catalytic sites, convenient characterization, and facile manipulations.[15] In the rich field of boron-containing polymers, both (intrinsically less perfect) polymer modification and direct polymerization routes are commonly employed.[16] However, the direct polymerization of highly Lewis acidic BAr_3 monomers is challenging and has remained largely limited to vinyl-addition methods (Figure 1, top).[13, 17]

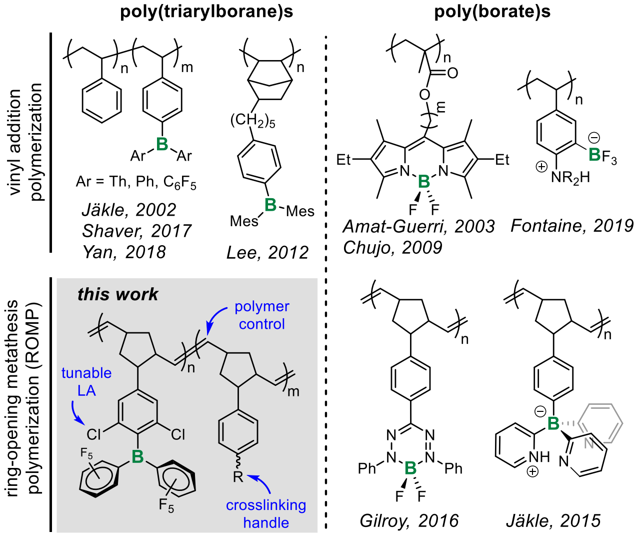
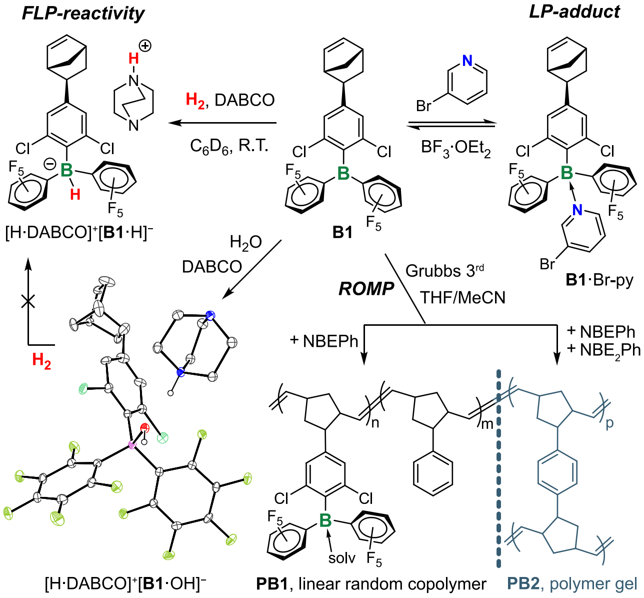


Figure 1. Selected examples of poly(triarylborane)s and poly(borate)s obtained by direct polymerization methods.

Despite the great success of ROMP for immobilizing other homogeneous organocatalysts,[18] and unlike the case of tetracoordinated borates (Figure 1, bottom right),[19] the ROMP of triarylboranes remains unexplored to the best of our knowledge. Herein, we propose a versatile new approach to polymeric Lewis acids and Lewis pairs by ROMP of functional norbornenes that offers the following benefits (Figure 1, bottom left): (a) a modular monomer platform, allowing facile tuning of the steric/electronic environment at boron, (b) perfect compatibility between the growing site of the polymer main-chain and the LA, (c) retention of structural integrity and catalytic activity after polymerization, and (d) facile manipulation of the polymer architecture to impart recyclability.

The synthesis of the tricoordinate organoborane monomer **B1**, inspired by other 2:1 hetero-tri(aryl)boranes with enhanced H_2O tolerance,[20] was accomplished on gram scale and in 48% combined yield as illustrated in Scheme S1 (SI). The Lewis acidity of **B1** (acceptor number, AN = 73, as determined by the Gutmann-Beckett method in $CDCl_3$) is close to that of $B(C_6F_5)_3$ (AN = 81.8)[21]. As expected, **B1** forms classical LPs with coordinating solvents, such as MeCN or THF, and the corresponding hydroxo complexes $[H{\cdot}Solv]^+[$**B1**$\cdot OH]^-$ in the presence of air and moisture (Figures S30-S33). Importantly, these species remain stable at room temperature for >10 days in MeCN, enabling benchtop manipulations, and even at 80°C show less than ~25% degradation over 72 hours (Figures S12-S19). We also verified that, in combination with the appropriate LB, **B1** is competent to engage in an FLP-mediated intermolecular activation of H_2 (Scheme 1 and Figures S41-S43). First, a stoichiometric mixture of **B1** and 1,4-diazabicyclo[2.2.2]octane (DABCO) forms a non-interacting pair in C_6D_6 as indicated by ^1H, ^{19}F, and ^{11}B NMR spectra that are identical to those of the isolated species. Second, a solution of **B1**/DABCO rapidly and irreversibly activates H_2O to form the $[H{\cdot}DABCO]^+[$**B1**$\cdot OH]^-$ ion pair *via* deprotonation of the Brønsted acidic **B1**-aqua complex (Figures S37-S40). Finally, replacing an inert atmosphere of N_2 with H_2 furnishes the ammonium hydridoborate $[H{\cdot}DABCO]^+[$**B1**$\cdot H]^-$ in 85% yield after 3 days at room temperature. A doublet at −19.8 ppm in the ^{11}B NMR, an upfield shift of the ^{19}F NMR resonances, and a characteristic B-H broad signal at 3.64 ppm in the ^1H NMR all corroborate this archetypal FLP-mediated transformation.

Scheme 1. Reactivity of norbornene monomer B1 and its polymerization to generate ROMP-boranes.



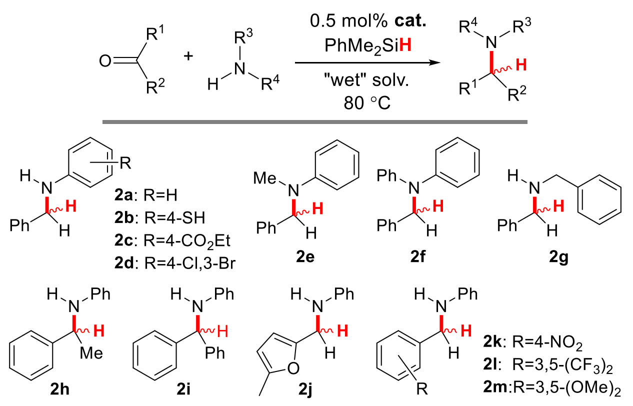
Encouraged by the high Lewis acidity and FLP activity of **B1**, as well as the premise of recyclability based on the favorable stability, we pursued the ROMP with Grubbs' 3rd generation catalyst (**G3**). Using a [**G3**]/[M] ratio of 1:100 in anhydrous THF, a linear random copolymer **PB1** was obtained containing 90 mol% of (*exo*)-5-phenyl-2-norbornene (NBEPh) and 10 mol% of **B1** (Scheme 1 and SI). ^1H NMR analyses of reaction aliquots indicated full monomer conversion within less than 3 min (Figure S22), thus polymerizations were quenched after 5 min with excess vinylene carbonate (VC) as terminating agent.[22] The fast polymerization kinetics are attributed to both the favorable *exo*-geometry of the norbornene moiety (*endo*-isomers polymerize more slowly) and the high Lewis acidity of the monomer itself. As such, **B1** acts as a scavenger for 3-bromopyridine, Br-py (the dissociating L-type ligand on **G3**), and thus accelerates the ROMP propagation rate. Indeed, a stoichiometric mixture of **B1** and Br-py in C_6D_6 confirmed the instantaneous formation of the LP **B1**·Br-py (Scheme 1, and Figures S34-S36). Subsequent addition of excess $BF_3{\cdot}OEt_2$ regenerated the free borane **B1** almost quantitatively. Based on these findings, $BF_3{\cdot}OEt_2$ was injected into the polymerization mixture prior to isolation to remove Br-py. Then, precipitation in wet MeCN on the benchtop under air yielded the polymers in the form of white colloidal suspensions. Spectroscopic analyses of **PB1** by ^1H, ^{19}F, and ^{11}B NMR confirmed the presence of stabilized triarylborane moieties as a mixture of solvent (MeCN/THF) adducts and hydroxylated species (Figures S23-S25).

Next, we set out to explore the catalytic performance of the molecular and ROMP-boranes. We selected the reductive amination of carbonyls as a convenient model reaction to probe their utility as recyclable catalysts in the presence of H_2O.[23] At the outset, using 5 mol% of **B1** and 1.2 eq of $PhMe_2SiH$ as reducing agent, the reductive *N*-alkylation of aniline with benzaldehyde under inert conditions produced *N*-benzylaniline in quantitative yield within 24 h at 20 °C (Table S3, entries 1-4).[24] This is remarkable as neither BPh_3 nor $B(C_6F_5)_3$ display any catalytic activity at room temperature and are only effective at 100 °C.[23a, 23c] Increasing the temperature to 60 °C (80 °C) in THF (MeCN) lowered the reaction time to a matter of minutes (Table S3, entries 5-6). Importantly, these reactions can be performed by simple manipulation on the benchtop using undried solvents and reagents (Table S3, entries 7-8), and regardless of the MeCN/THF vol:vol content (Table S4). To investigate whether **B1** remains active, competence checks were performed by replenishing the testing NMR tubes with a second load of all the reagents 24 h after the first reaction was completed (Table S3). Under identical reaction conditions, **B1** showed no loss of activity regardless of the reaction temperature and exposure to moisture and air.[25] Furthermore, up to 6 consecutive refilling cycles in wet CD_3CN furnished quantitative yields with only 1 mol% of **B1** (Figures S109-S110).[26] Gratifyingly, the polymeric ROMP-borane catalyst **PB1** performed similarly well under homogeneous conditions in a wet MeCN/THF solvent mixture, rapidly yielding 100% of *N*-benzylaniline with only 1.2 eq of hydrosilane (see SI).

Having confirmed the catalytic proficiency in the *N*-alkylation of aniline, we further explored the substrate scope of the molecular and polymer-bound catalysts. Anilines containing electron-withdrawing and donating groups, as well as secondary arylamines, underwent reductive amination in quantitative yields with loadings of **B1** and **PB1** as low as 0.5 mol% (Table 1, entries 1-6). Conversions could be extraordinarily fast, as exemplified by the reaction between benzocaine and benzaldehyde (turn-over-frequency, TOF = 2400 h^{-1}, entry 3). An exception is the reductive amination of the more basic benzylamine which did not proceed even with a large hydrosilane excess, likely due to irreversibly deactivation of the [BenzNH$_3$]$^+$[LA·OH]$^-$ species (entry 7).[23a] Variation of the keto component also gave excellent results as acetophenone, 5-methylfurfural and substituted benzaldehydes were converted to product in high yield by only 0.5 mol% of **B1** or **PB1** as the catalyst (Table 1, entries 8-13). The lower reactivity of benzophenone is attributed to steric effects.

The remarkable similarities between the molecular and polymer-bound catalysts reflected in Table 1 suggests that the structure/reactivity dependence of the LA was retained when embedded in the polymer framework. Direct stepwise monitoring of the model catalytic reaction by NMR spectroscopy in wet THF-*d*$_8$ provided further evidence (Figure 2). The resonances in the ^{19}F and ^{11}B NMR spectra of **PB1** matched almost perfectly with those of **B1**, except for the expected broadening of the polymer signals. These signals indicated that the triarylborane moieties engaged in Lewis and Brønsted acid/base equilibria prior to the addition of the reducing agent. However, a dominant borohydride complex, ([**P/B1**–H]$^-$), characterized by a doublet at −20.9 ppm in the ^{11}B NMR, was systematically found at the end of the catalytic process regardless of the solvent and moisture content (Figures S60-S77). This is in good agreement with the expected hydrosilylation mechanism (Scheme S2). The catalyst resting state, although not previously reported for other BAr$_3$,[23a, 23c] was remarkably stable in wet MeCN over seven days at room temperature, which bodes well for developing recyclable catalyst systems.[27]

Table 1. Substrate scope for reductive amination. [a]



Entry #	Product	Time (min)	PhMe$_2$SiH (eq.)	Yield (%) [b] B1	Yield (%) [b] PB1
1	**2a**	60	1.2	100	100
2	**2b**	30	1.2	99	99
3	**2c**	5	1.2	100	100
4	**2d**	60	3.5	100	100
5	**2e**	1440	1.2	100	100
6	**2f**	60	1.2	100	100
7	**2g**	1440	3.5	0	0
8	**2h**	1440	3.5	67.1 [c]	62.2 [c]
9	**2i**	1440	3.5	2.8 [c]	1.1 [c]
10	**2j**	60	3.5	100	100
11	**2k**	30	1.2	100	100
12	**2l**	1440	1.2	100	73.3
13	**2m**	1440	1.2	100	100

[a] Amine = 2.88 mmol; ketone = 2.40 mmol; catalyst = 0.012 mmol; PhMe$_2$SiH = 2.88 or 8.40 mmol; solv. = 2 mL (MeCN for **B1**; MeCN/THF 75:25 for **PB1**); [mesitylene] = 0.6 M (IS). [b] Determined by ^{1}H NMR. [c] Determined by GC/MS.

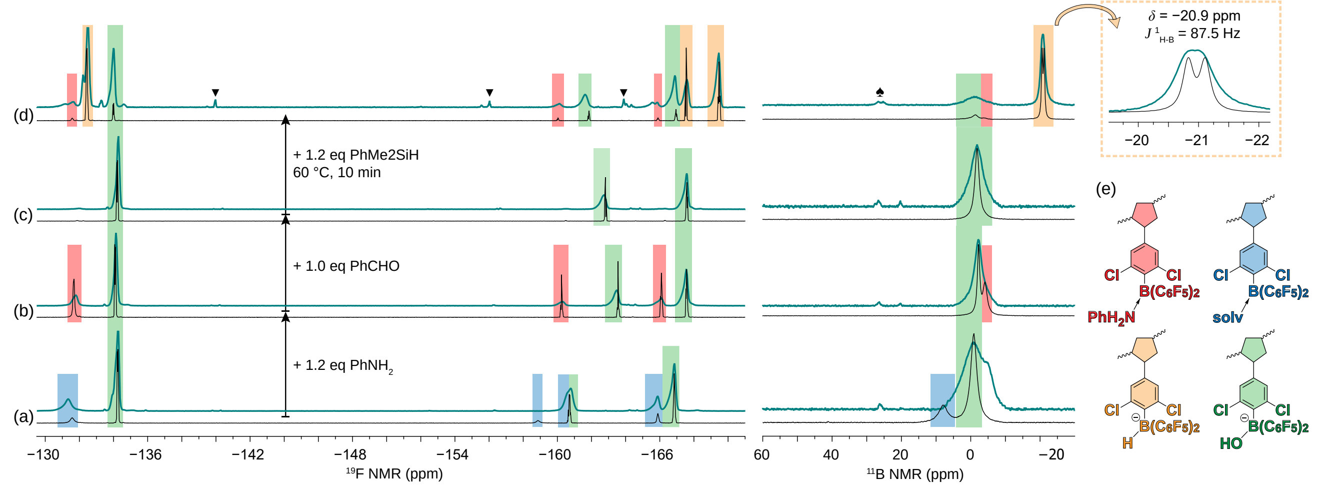


Figure 2. Sequential ^{19}F NMR and ^{11}B NMR spectra (wet THF-*d*$_8$, 25 °C) during the *in-situ* model reductive *N*-alkylation: (a) 5 mol% of catalysts **B1** (black line) and **PB1** (dark cyan line); (b) 1.2 eq. of aniline; (c) 1.0 eq. of benzaldehyde; (d) 1.2 eq. of dimethylphenylsilane, 60 °C, 10 min. (e) Schematic structures of borane species detected in solution (▼) C$_6$F$_5$H; (♠) Ar$_2$BOH and ArB(OH)$_2$.

In an effort at developing a more general recycling approach, polymer resin **PB2** containing 3.33×10^{-4} mol/g of borane units was synthesized by addition of a crosslinking agent (1,4-di(norbornen-2-yl)benzene, NBE$_2$Ph) during a second block copolymer chain extension by ROMP (Scheme 1 and SI). The crosslinker was added in the second block to ensure full conversion of **B1** before gelation takes place and because the expected architecture with grafted triarylborane chains should provide favorable access for substrates and reagents. The ROMP-resin successfully promoted the reductive *N*-alkylation of aniline with benzaldehyde in quantitative yields either as swollen organogel (80% THF) or as heterogeneous particles (100% MeCN) in bench-top reactions (Figures 3 and S111-S116). Excitingly, high yield of *N*-benzylaniline (94.1%) was obtained with just 0.5 mol% catalyst and in the absence of solvent, hinting at a path to greener and easier alternatives that avoid wasteful product purifications (Figures S117-S119). However, a more rapid decrease in activity with neat reagents in consecutive cycles compared with THF/MeCN solutions points to a beneficial stabilizing effect of coordinating solvents under open-air conditions. Thus, further improvements are expected from optimization of the recycling procedure and implementation of continuous-flow methods. In comparison, a control polynorbornene resin prepared without **B1** monomer was unable to catalyze this reaction (Figure S120).

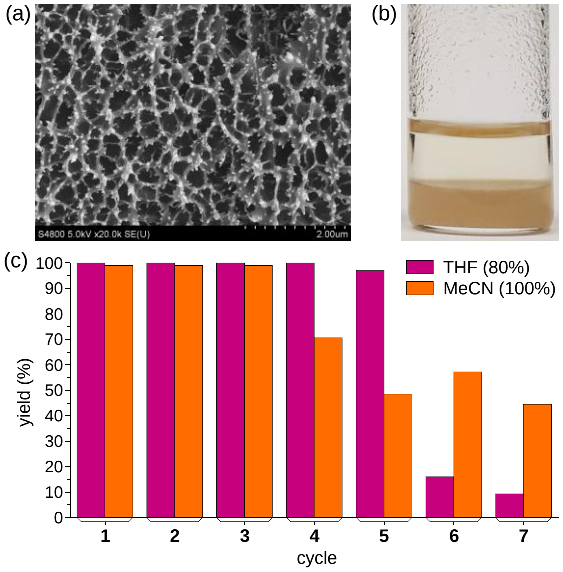


Figure 3. (a) SEM of swollen resin **PB2**. (b) Photograph of ROMP-borane gel **PB2** in 80:20 (v:v) THF/MeCN. (c) Consecutive reaction yields in the reductive amination of aniline/benzaldehyde catalyzed by recycled 5 mol% **PB2** (for details of reaction conditions see SI).

In summary, the attachment of a chemically and sterically tuned triarylborane to a solid support was realized by ROMP of a functionalized phenylnorbornene. Outstanding catalytic performance was achieved as exemplified in the bench-top reductive *N*-alkylation of arylamines, requiring far lower temperatures and catalyst loadings than previously reported. The immobilization and recycling of the organocatalyst was accomplished by integration into a covalently crosslinked polymer network. The modular synthetic strategy lends itself to constructing other heterogenized BAr$_3$ whose FLP activity and scope can be tailored by design. Further development of ROMP-boranes is also expected to offer access to boron-containing materials with desirable stimuli-responsive, self-healing, and optoelectronic properties.[16b, 17e, 28]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

Full details on monomer and polymer synthesis and characterization, NMR data, and catalytic reaction protocols, (PDF). Crystallographic data for [H·DABCO]$^+$[**B1**·OH]$^-$, (CIF).

AUTHOR INFORMATION

Corresponding Author

*fjaekle@newark.rutgers.edu.

Funding Sources

NSF CHE-1609043, CHE-1904791, CRIF-0443538, MRI-1229030, MRI-1039828; Rutgers University SEED grant (202607), New Jersey Higher Education Equipment Leasing Fund (ELF III 047-04)

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank Dr. Lazaros Kakalis for assistance with solid-state ^{11}B NMR measurements. This material is based upon work supported by the National Science Foundation (NSF) under Grants CHE-1609043 and CHE-1904791. The Bruker 500 MHz NMR spectrometer (MRI-1229030), the SEM (MRI-1039828) and the X-ray diffractometer (CRIF 0443538) used in this study were acquired with support by the NSF and Rutgers University. Equipment in the Polymer and Nanomaterials Facility at Rutgers University Newark (PolyRUN) was acquired with support by the New Jersey Higher Education Equipment Leasing Fund (ELF III 047-04) and maintained with support from Rutgers University through SEED grant 202607.

REFERENCES

(1) (a) Oestreich, M.; Hermeke, J.; Mohr, J. A unified survey of Si–H and H–H bond activation catalysed by electron-deficient boranes. *Chem. Soc. Rev.* **2015,** 44, 2202-2220. (b) Lawson, J. R.; Melen, R. L. Tris(pentafluorophenyl)borane and Beyond: Modern Advances in Borylation Chemistry. *Inorg. Chem.* **2017,** 56, 8627-8643.

(2) (a) Stephan, D. W. The broadening reach of frustrated Lewis pair chemistry. *Science* **2016,** 354, aaf7229. (b) Jupp, A. R.; Stephan, D. W. New Directions for Frustrated Lewis Pair Chemistry. *Trends Chem.* **2019,** 1, 35-48. (c) Paradies, J. Mechanisms in Frustrated Lewis Pair-Catalyzed Reactions. *Eur. J. Org. Chem.* **2019,** 2019, 283-294.

(3) (a) Chen, D.; Wang, Y.; Klankermayer, J. Enantioselective Hydrogenation with Chiral Frustrated Lewis Pairs. *Angew. Chem. Int. Ed.* **2010,** 49, 9475-9478. (b) Erős, G.; Mehdi, H.; Pápai, I.; Rokob, T. A.; Király, P.; Tárkányi, G.; Soós, T. Expanding the Scope of Metal-Free Catalytic Hydrogenation through Frustrated Lewis Pair Design. *Angew. Chem. Int. Ed.* **2010,** 49, 6559-6563. (c) Scott, D. J.; Fuchter, M. J.; Ashley, A. E. Designing effective 'frustrated Lewis pair' hydrogenation catalysts. *Chem. Soc. Rev.* **2017,** 46, 5689-5700.

(4) (a) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. A Novel B(C$_6$F$_5$)$_3$-Catalyzed Reduction of Alcohols and Cleavage of Aryl and Alkyl Ethers with Hydrosilanes. *J. Org. Chem.* **2000,** 65, 6179-6186. (b) Hoshimoto, Y.; Ogoshi, S. Triarylborane-Catalyzed Reductive N-Alkylation of Amines: A Perspective. *ACS Catal.* **2019,** 9, 5439-5444.

(5) (a) Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. Reducing CO2 to Methanol Using Frustrated Lewis Pairs: On the Mechanism of Phosphine–Borane-Mediated Hydroboration of CO$_2$. *J. Am. Chem. Soc.* **2014,** 136, 10708-10717. (b) Chen, J.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. Selective Reduction of CO$_2$ to CH$_4$ by Tandem Hydrosilylation with Mixed Al/B Catalysts. *J. Am. Chem. Soc.* **2016,** 138, 5321-5333.

(6) (a) Yang, W.; Gao, L.; Lu, J.; Song, Z. Chemoselective deoxygenation of ether-substituted alcohols and carbonyl compounds by B(C6F5)3-catalyzed reduction with (HMe2SiCH2)2. *Chem. Commun.* **2018,** 54, 4834-4837. (b) Fang, H.; Oestreich, M. Reductive Deamination with Hydrosilanes Catalyzed by B(C$_6$F$_5$)$_3$. *Angew. Chem. Int. Ed.* **2020,** 59, 11394-11398.

(7) (a) Légaré, M. A.; Courtemanche, M. A.; Rochette, E.; Fontaine, F. G. Metal-free catalytic C-H bond activation and borylation of heteroarenes. *Science* **2015,** 349, 513-516. (b) Légaré Lavergne, J.; Jayaraman, A.; Misal Castro, L. C.; Rochette, É.; Fontaine, F.-G. Metal-Free Borylation of Heteroarenes Using Ambiphilic Aminoboranes: On the Importance of Sterics in Frustrated Lewis Pair C–H Bond Activation. *J. Am. Chem. Soc.* **2017,** 139, 14714-14723.

(8) Hong, M.; Chen, J.; Chen, E. Y.-X. Polymerization of Polar Monomers Mediated by Main-Group Lewis Acid–Base Pairs. *Chem. Rev.* **2018,** 118, 10551-10616.

(9) Carden, J. L.; Dasgupta, A.; Melen, R. L. Halogenated triarylboranes: synthesis, properties and applications in catalysis. *Chem. Soc. Rev.* **2020,** 49, 1706-1725.

(10) Ma, Y.; Zhang, S.; Chang, C.-R.; Huang, Z.-Q.; Ho, J. C.; Qu, Y. Semi-solid and solid frustrated Lewis pair catalysts. *Chem. Soc. Rev.* **2018,** 47, 5541-5553.

(11) (a) Szeto, K. C.; Sahyoun, W.; Merle, N.; Castelbou, J. L.; Popoff, N.; Lefebvre, F.; Raynaud, J.; Godard, C.; Claver, C.; Delevoye, L.; Gauvin, R. M.; Taoufik, M. Development of silica-supported frustrated Lewis pairs: highly active transition metal-free catalysts for the Z-selective reduction of alkynes. *Catal. Sci. Technol.* **2016,** 6, 882-889. (b) Zakharova, M. V.; Masoumifard, N.; Hu, Y.; Han, J.; Kleitz, F.; Fontaine, F.-G. Designed Synthesis of Mesoporous Solid-Supported Lewis Acid–Base Pairs and Their CO$_2$ Adsorption Behaviors. *ACS Appl. Mater. Interfaces* **2018,** 10, 13199-13210.

(12) (a) Niu, Z.; Bhagya Gunatilleke, W. D. C.; Sun, Q.; Lan, P. C.; Perman, J.; Ma, J.-G.; Cheng, Y.; Aguila, B.; Ma, S. Metal-Organic Framework Anchored with a Lewis Pair as a New Paradigm for Catalysis. *Chem* **2018,** 4, 2587-2599. (b) Shyshkanov, S.; Nguyen, T. N.; Ebrahim, F. M.; Stylianou, K. C.; Dyson, P. J. In Situ Formation of Frustrated Lewis Pairs in a Water-Tolerant Metal-Organic Framework for the Transformation of CO2. *Angew. Chem. Int. Ed.* **2019,** 58, 5371-5375.

(13) Chen, L.; Liu, R.; Yan, Q. Polymer Meets Frustrated Lewis Pair: Second-Generation CO$_2$-Responsive Nanosystem for Sustainable CO2 Conversion. *Angew. Chem. Int. Ed.* **2018,** 130, 9480-9484.

(14) (a) Trunk, M.; Teichert, J. F.; Thomas, A. Room-Temperature Activation of Hydrogen by Semi-immobilized Frustrated Lewis Pairs in Microporous Polymer Networks. *J. Am. Chem. Soc.* **2017,** 139, 3615-3618. (b) Willms, A.; Schumacher, H.; Tabassum, T.; Qi, L.; Scott, S. L.; Hausoul, P. J. C.; Rose, M. Solid Molecular Frustrated Lewis Pairs in a Polyamine Organic Framework for the Catalytic Metal-free Hydrogenation of Alkenes. *ChemCatChem* **2018,** 10, 1835-1843.

(15) (a) Bergbreiter, D. E.; Tian, J.; Hongfa, C. Using Soluble Polymer Supports To Facilitate Homogeneous Catalysis. *Chem. Rev.* **2009,** 109, 530-582. (b) Altava, B.; Burguete, M. I.; Garcia-Verdugo, E.; Luis, S. V. Chiral catalysts immobilized on achiral polymers: effect of the polymer support on the performance of the catalyst. *Chem. Soc. Rev.* **2018,** 47, 2722-2771. (c) García-Loma, R.; Albéniz, A. C. Vinylic Addition Polynorbornene in Catalysis. *Asian J. Org. Chem.* **2019,** 8, 304-315.

(16) (a) Qin, Y.; Cheng, G.; Sundararaman, A.; Jäkle, F. Well-Defined Boron-Containing Polymeric Lewis Acids. *J. Am. Chem. Soc.* **2002,** 124, 12672-12673. (b) Jäkle, F. Advances in the Synthesis of Organoborane Polymers for Optical, Electronic, and Sensory Applications. *Chem. Rev.* **2010,** 110, 3985-4022. (c) Doshi, A.; Jäkle, F., Boron-Containing Polymers. In *Comprehensive Inorganic Chemistry II* Poeppelmeier, K., Ed. Elsevier: Amsterdam, **2013,** 861-891.

(17) (a) Amat-Guerri, F.; Liras, M.; Luisa Carrascoso, M.; Sastre, R. Methacrylate-tethered Analogs of the Laser Dye PM567—Synthesis, Copolymerization with Methyl Methacrylate and Photostability of the Copolymers¶. *Photochem. Photobiol.* **2003,** 77, 577-584. (b) Nagai, A.; Kokado, K.; Miyake, J.; Chujo, Y. Highly Luminescent Nanoparticles: Self-Assembly of Well-Defined Block Copolymers by π–π Stacked BODIPY Dyes as Only a Driving Force. *Macromolecules* **2009,** 42, 5446-5452. (c) Sung, W. Y.; Park, M. H.; Park, J. H.; Eo, M.; Yu, M.-S.; Do, Y.; Lee, M. H. Triarylborane-functionalized polynorbornenes: Direct polymerization and signal amplification in fluoride sensing. *Polymer* **2012,** 53, 1857-1863. (d) Cheng, F.; Bonder, E. M.; Jäkle, F. Electron-Deficient Triarylborane Block Copolymers: Synthesis by Controlled Free Radical Polymerization and Application in the Detection of Fluoride Ions. *J. Am. Chem. Soc.* **2013,** 135, 17286-17289. (e) Wang, M.; Nudelman, F.; Matthes, R. R.; Shaver, M. P. Frustrated Lewis Pair Polymers as Responsive Self-Healing Gels. *J. Am. Chem. Soc.* **2017,** 139, 14232-14236. (f) Bouchard, N.; Fontaine, F.-G. Alkylammoniotrifluoroborate functionalized polystyrenes: polymeric pre-catalysts for the metal-free borylation of heteroarenes. *Dalton Trans.* **2019,** 48, 4846-4856.

(18) (a) Barrett, A. G. M.; Hopkins, B. T.; Köbberling, J. ROMPgel Reagents in Parallel Synthesis. *Chem. Rev.* **2002,** 102, 3301-3324. (b) Lu, J.; Toy, P. H. Organic Polymer Supports for Synthesis and for Reagent and Catalyst Immobilization. *Chem. Rev.* **2009,** 109, 815-838.

(19) (a) Pawar, G. M.; Lalancette, R. A.; Bonder, E. M.; Sheridan, J. B.; Jäkle, F. ROMP-Derived Pyridylborate Block Copolymers: Self-Assembly, pH-Responsive Properties, and Metal-Containing Nanostructures. *Macromolecules* **2015,** 48, 6508-6515. (b) Novoa, S.; Paquette, J. A.; Barbon, S. M.; Maar, R. R.; Gilroy, J. B. Side-chain boron difluoride formazanate polymers via ring-opening metathesis polymerization. *J. Mater. Chem. C* **2016,** 4, 3987-3994. (c) Novoa, S.; Gilroy, J. B. (Co)polymers containing boron difluoride 3-cyanoformazanate complexes: emission enhancement via random copolymerization. *Polym. Chem.* **2017,** 8, 5388-5395.

(20) (a) Gyömöre, Á.; Bakos, M.; Földes, T.; Pápai, I.; Domján, A.; Soós, T. Moisture-Tolerant Frustrated Lewis Pair Catalyst for Hydrogenation of Aldehydes and Ketones. *ACS Catal.* **2015,** 5, 5366-5372. (b) Dorkó, É.; Kótai, B.; Földes, T.; Gyömöre, Á.; Pápai, I.; Soós, T. Correlating electronic and catalytic properties of frustrated Lewis pairs for imine hydrogenation. *J. Organomet. Chem.* **2017,** 847, 258-262.

(21) Sivaev, I. B.; Bregadze, V. I. Lewis acidity of boron compounds. *Coord. Chem. Rev.* **2014,** 270-271, 75-88.

(22) Hilf, S.; Kilbinger, A. F. M. Functional end groups for polymers prepared using ring-opening metathesis polymerization. *Nat. Chem.* **2009,** 1, 537.

(23) (a) Fasano, V.; Radcliffe, J. E.; Ingleson, M. J. B(C6F5)3-Catalyzed Reductive Amination using Hydrosilanes. *ACS Catal.* **2016,** 6, 1793-1798. (b) Dorkó, É.; Szabó, M.; Kótai, B.; Pápai, I.; Domján, A.; Soós, T. Expanding the Boundaries of Water-Tolerant Frustrated Lewis Pair Hydrogenation: Enhanced Back Strain in the Lewis Acid Enables the Reductive Amination of Carbonyls. *Angew. Chem. Int. Ed.* **2017,** 56, 9512-9516. (c) Fasano, V.; Ingleson,

M. J. Expanding Water/Base Tolerant Frustrated Lewis Pair Chemistry to Alkylamines Enables Broad Scope Reductive Aminations. *Chem. Eur. J.* **2017,** 23, 2217-2224. (d) Hoshimoto, Y.; Kinoshita, T.; Hazra, S.; Ohashi, M.; Ogoshi, S. Main-Group-Catalyzed Reductive Alkylation of Multiply Substituted Amines with Aldehydes Using H_2. *J. Am. Chem. Soc.* **2018,** 140, 7292-7300.

(24) The direct catalytic hydrosilylation of *N*-benzylideneaniline (the intermediate imine) in anhydrous CD_3CN proceeded even faster at 20 °C (less than 30 min).

(25) Contrarily, only 17% conversion to reduced amine was observed during the second run in toluene at 20 °C, suggesting significant deactivation of **B1** in non-coordinating solvents even under moisture-free manipulations.

(26) Longer reaction times in CD_3CN were required to overcome dilution effects after each new substrate addition.

(27) Partial decomposition to boronic/borinic acids was observed in wet THF possibly due to the formation of less stable Lewis adducts.

(28) (a) Vidal, F.; Gomezcoello, J.; Lalancette, R. A.; Jäkle, F. Lewis Pairs as Highly Tunable Dynamic Cross-Links in Transient Polymer Networks. *J. Am. Chem. Soc.* **2019,** 141, 15963-15971. (b) Vidal, F.; Jäkle, F. Functional Polymeric Materials Based on Main-Group Elements. *Angew. Chem. Int. Ed.* **2019,** 58, 5846-5870. (c) Mellerup, S. K.; Wang, S. Boron-based stimuli responsive materials. *Chem. Soc. Rev.* **2019,** 48, 3537-3549. (d) Bapat, A. P.; Sumerlin, B. S.; Sutti, A. Bulk network polymers with dynamic B–O bonds: healable and reprocessable materials. *Mater. Horiz.* **2020,** 7, 694-714.

Insert Table of Contents artwork here