# 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]

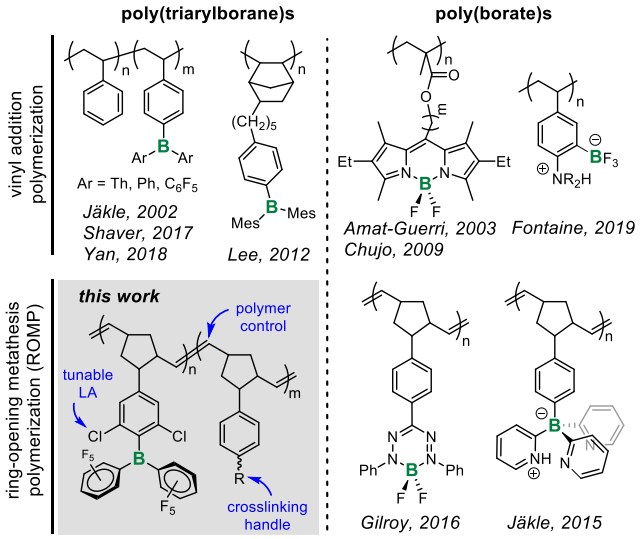


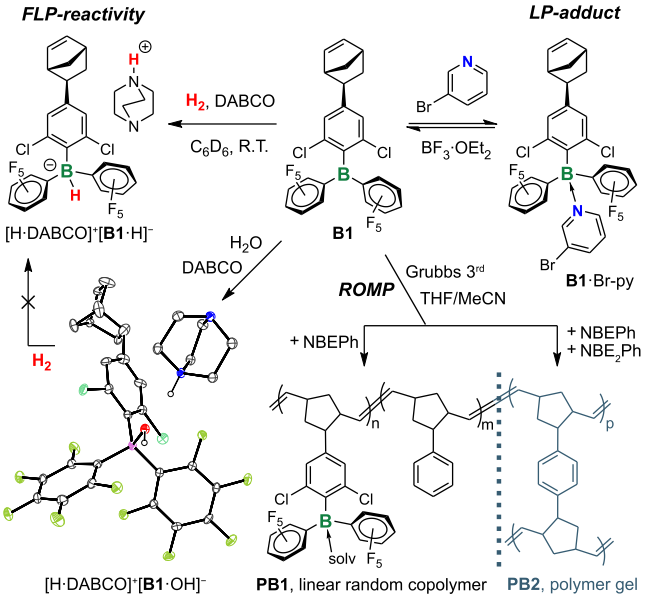

**Figure 1.** Selected examples of poly(triarylborane)s and poly(borate)s obtained by direct polymerization methods.

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 $[H{\cdot}Solv]^+[\mathbf{B1}{\cdot}OH]^-$ 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 $^1$H, $^{19}$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 $[H{\cdot}DABCO]^+[\mathbf{B1}{\cdot}OH]^-$ 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 $[H{\cdot}DABCO]^+[\mathbf{B1}{\cdot}H]^-$ 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 $^1$H NMR all corroborate this archetypal FLP-mediated transformation.

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



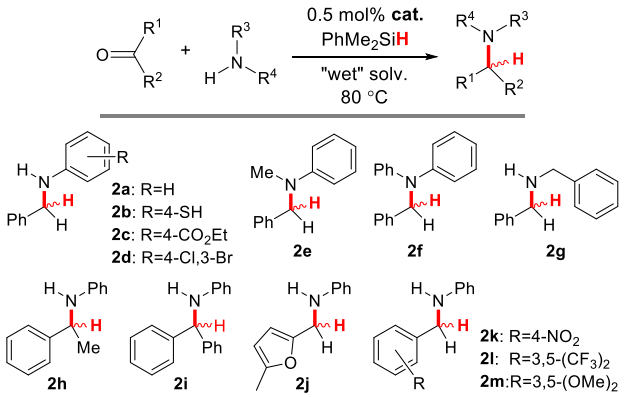

Encouraged by the high Lewis acidity and FLP activity of **B1**, as well as the premise of recyclability based on the favorable stability, we pursued the ROMP with Grubbs' 3$^{rd}$ generation catalyst (**G3**). Using a [**G3**]/[M] ratio of 1:100 in anhydrous THF, a linear random copolymer **PB1** was obtained containing 90 mol% of (*exo*)-5-phenyl-2-norbornene (NBEPh) and 10 mol% of **B1** (Scheme 1 and SI). $^1$H 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 $^1$H, $^{19}$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 $[BenzNH_3]^+[LA{\cdot}OH]^-$ 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) | $PhMe_2SiH$ (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; $PhMe_2SiH$ = 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 $^1H$ NMR. [c]Determined by GC/MS.

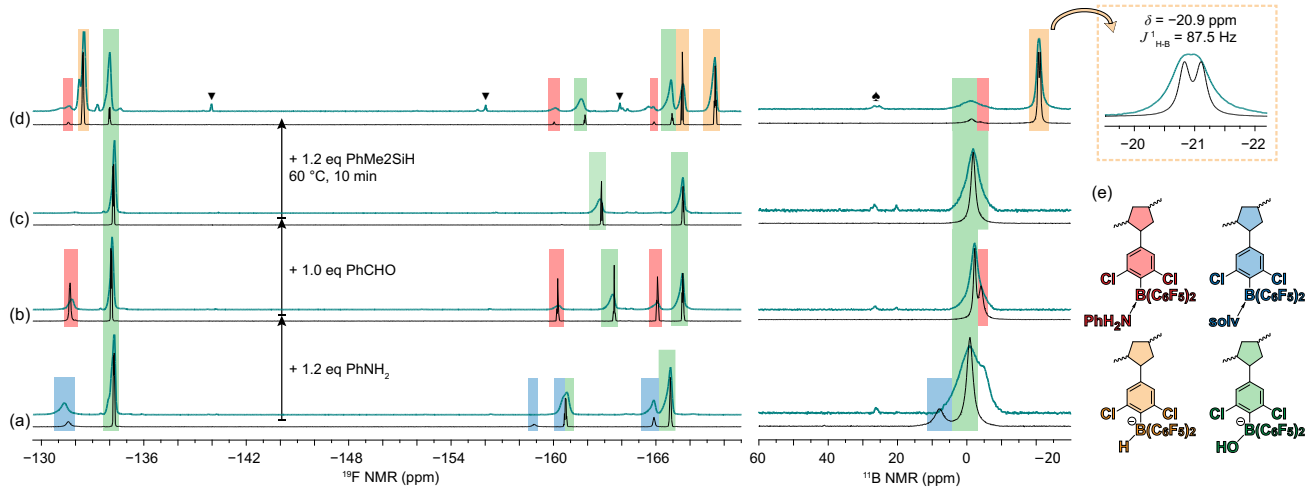



**Figure 2.** Sequential $^{19}F$ NMR and $^{11}B$ NMR spectra (wet THF-$d_8$, 25 °C) during the *in-situ* model reductive *N*-alkylation: (a) 5 mol% of catalysts **B1** (black line) and **PB1** (dark cyan line); (b) 1.2 eq. of aniline; (c) 1.0 eq. of benzaldehyde; (d) 1.2 eq. of dimethylphenylsilane, 60 °C, 10 min. (e) Schematic structures of borane species detected in solution (▼) $C_6F_5H$; (♠) $Ar_2BOH$ and $ArB(OH)_2$.

In an effort at developing a more general recycling approach, polymer resin **PB2** containing $3.33 \times 10^{-4}$ mol/g of borane units was synthesized by addition of a crosslinking agent (1,4-di(norbornen-2-yl)benzene, $NBE_2Ph$) 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).

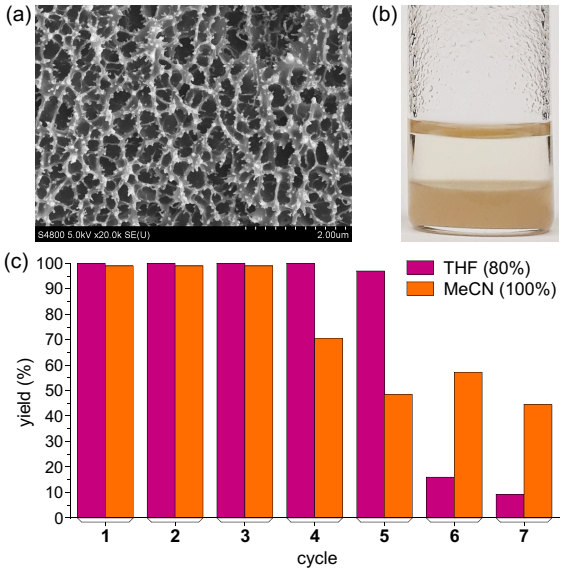



**Figure 3.** (a) SEM of swollen resin **PB2**. (b) Photograph of ROMP-borane gel **PB2** in 80:20 (v:v) THF/MeCN. (c) Consecutive reaction yields in the reductive amination of aniline/benzaldehyde catalyzed by recycled 5 mol% **PB2** (for details of reaction conditions see SI).

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.

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(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.

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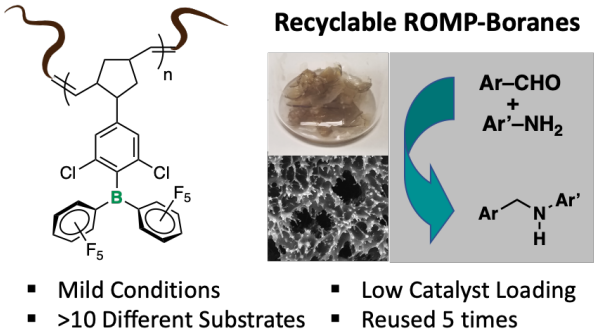
Recyclable ROMP-Boranes
n
Cl
Cl
B
F5
F5
Ar–CHO
+
Ar'–NH2
Ar
N
H
Ar'
Mild Conditions
>10 Different Substrates
Low Catalyst Loading
Reused 5 times