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Communication

Synthesis and Photochemical Uncaging of Alkene-Protected, Polymer-Bound Vicinal Frustrated Lewis Pairs

Emily A. Latif, Jeremy D. Hilgar, and Nathan A. Romero*

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ABSTRACT: Polymeric materials bearing Frustrated Lewis Pair (FLP) functionality are promising candidates for use as heterogeneous catalysts and adaptive materials, but synthetic access to FLP-functional polymers remains limited due to the incompatibility of FLPs with standard polymerization chemistries. Herein, we describe a synthetic approach that "cages" highly reactive vicinal phosphine-borane FLPs as covalent alkene adducts, which are stable to Ni-mediated vinyl addition polymerization. We discovered that the caged FLP adducts can be photochemically activated to liberate vicinal FLPs, enabling spatiotemporally controlled release of FLPs from polymeric precursors.

Building on established applications of molecular Frustrated Lewis Pairs (FLPs) in metal-free small molecule activation,[1−5] catalysis,[6−9] and controlled polymerization,[10,11] there is emerging interest in polymeric systems that contain FLPs (Figure 1a).[12,13] Frustrated LA or LB functionality can be incorporated into polymeric scaffolds[12,13] to construct heterogeneous FLP catalyst systems, which may derive enhanced catalytic activity or reusability from the bulk properties of the macromolecular material.[14−18] Reciprocally,

the macromolecular properties of FLP polymers can be regulated through reversible covalent reactions of FLPs with small molecules, as showcased by Shaver[19−22] and Yan.[23−25] Collectively, FLP polymers hold vast potential as materials whose dynamic molecular reactivity and multi-length-scale structure could be leveraged in tandem to achieve advanced properties and functions.[26]

Yet, *bifunctional FLP polymers* have proven to be synthetically elusive, precluding access to FLP polymers capable of triggered FLP release or FLP polymers that reversibly bind small molecules while maintaining constant topology (Figure 1b). The primary obstacle to these advanced FLP polymer architectures is the incompatibility of FLPs with conventional monomer functionalities and polymerization chemistries. New protecting group strategies are needed for orthogonal protection−deprotection of both LA and LB components of the FLP. To this end, our work seeks to develop synthetic tools for controllably generating FLPs from inert precursors, as both a gateway to studying new FLP polymer architectures and a means of triggering FLP release on-demand. Unmasking latent FLP functionality with (spatio)temporal precision could ultimately be harnessed to externally regulate catalytic FLP reactivity within polymeric matrices,[27] or to achieve localized release of FLP payloads, akin to drug delivery polymer systems.[28,29]

Herein, we demonstrate that FLP-alkene adducts serve as protected FLP precursors, enabling the synthesis of polymer-bound "caged" FLPs that can be controllably "uncaged" (Figure 2). Fontaine and co-workers followed a similar approach to polymerize styrene-based aminoborane-functional
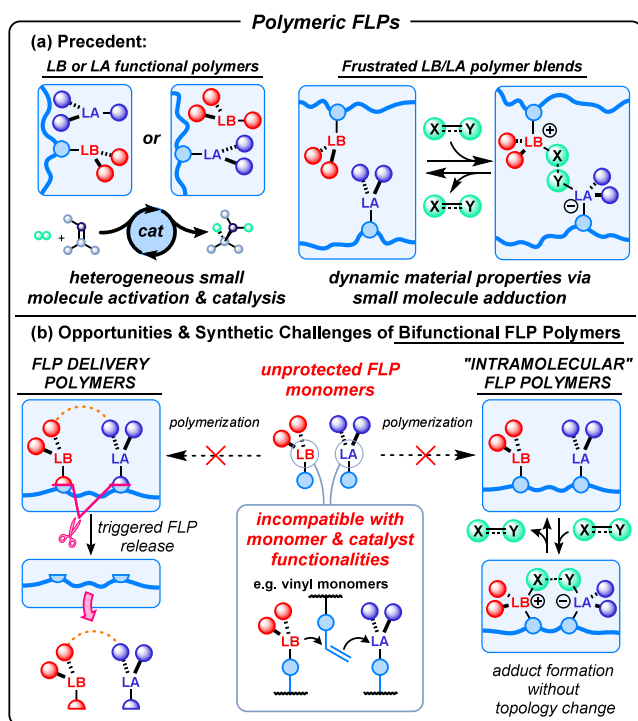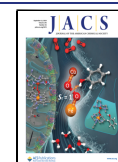

Figure 1. (a) Emerging applications of FLP polymers. (b) Synthetic challenges in accessing bifunctional FLP polymers.
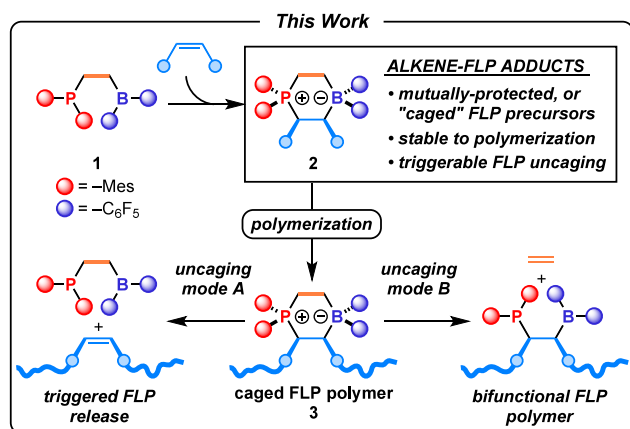
Figure 2. Strategy used in this work to prepare caged FLP polymers **3** capable of uncaging vicinal FLPs.

monomers by masking the aminoborane FLPs as adducts with HF,[30] but this system lacks a mechanism for discrete external control of uncaging. The focus of our work is FLP-alkene adducts **2**, which are derived from ethylene-bridged phosphine-borane **1**. Vicinal FLP **1** was first reported by Erker and co-workers[31] and exhibits potent small molecule reactivity due to the proximity of the LA and LB.[31–34] Caged FLP polymers **3** have two possible uncaging pathways: "*uncaging mode A*" releases molecular vicinal FLP **1**, leaving an alkene within the polymer backbone, while "*uncaging mode B*" generates a bifunctional, vicinal FLP polymer through the release of ethylene. Since both uncaging modes represent promising avenues toward new polymeric FLP-based materials, we sought to develop a synthetic route to caged FLP polymers **3** and to study their uncaging behavior.

We designed norbornadiene-derived FLP adduct **5** as a caged monomer (Figure 3), which features a strained cyclic
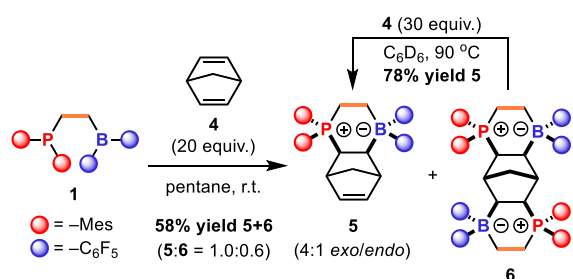

Figure 3. Synthesis of caged monomer **5** and thermal conversion of diaddition product **6** to monomer **5**.

alkene primed for either ring-opening metathesis polymerization[35] or vinyl addition (VA) polymerization.[36,37] Monomer **5** was synthesized by addition of excess norbornadiene (**4**) to FLP **1** and isolated as a mixture of diastereomers (ca. 4:1 *exo*-**5**/*endo*-**5**). *Exo*-**5** was assigned as the major diastereomer based on X-ray diffraction (XRD) analysis (Figure S56). We also isolated diaddition product **6** (XRD analysis in Figure S57; additional discussion in Figure S13), which—although undesired—could be efficiently converted to monoadduct **5** by heating **6** at 90 °C with excess norbornadiene (Figure S14). While thermally reversible at elevated temperatures, adducts **5** and **6** can be purified by silica gel column chromatography, demonstrating their kinetic stability under ambient conditions.

We have initially pursued VA polymerization of monomer **5** to simplify characterization of the uncaging process, as the resultant VA polymers possess a fully saturated backbone (Table 1). We used $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$ as a convenient

Table 1. Vinyl Addition Polymerization of Caged Monomer 5 and Comonomer 7

entry	sample	isolated yield	theor. $n{:}m$[a]	exp. $n{:}m$[b]	M_n (Da)[c]	$Đ$[c]	wt % at 175 °C[d]
1	**8a**	46%	5:95	5:95	3.7×10^6	7.1	95%
2	**8b**	61%	10:90	7:93	9.3×10^5	4.2	93%
3	**8c**	56%	20:80	9:91	3.2×10^5	2.1	89%
4	**8d**	<20%	50:50	13:87	5.1×10^4	1.5	85%
5	**8e**	0%	100:0	–	–	–	–

[a]Estimated from feed ratio of monomers **5**:**7**. [b]Actual comonomer content estimated from ^{1}H NMR spectra. [c]M_n and dispersity (M_w/M_n) determined by SEC. [d]Weight percent at 175 °C determined by TGA.

initiator that is highly active in VA polymerization without requiring exogenous activating agents.[38–40] Caged polymers **8a–d** were obtained successfully when employing pentylnorbornene **7** as a comonomer (Table 1, entries 1–4). ^{1}H, ^{31}P, ^{19}F, and ^{11}B NMR spectra confirm that the key phosphonium-borate functionality remains in-tact in polymers **8** (Figures S15–S19). Based on differential conversion rates observed for *exo*-**5** and *endo*-**5**, polymers **8** are likely enriched in or consist exclusively of caged FLP adducts with *exo*-configurations (Figure S24).[41,42] The actual degree of functionalization for polymers **8** plateaus at higher feed ratios (n:m) of monomer **5**, reflecting sluggish incorporation of the sterically bulky monomer **5** relative to **7**. Decreased molar mass and lower isolated yields observed at higher feed ratios are also consistent with inefficient incorporation of the bulky monomer **5**. The fact that monomer **5** does not undergo homopolymerization to **8e** (Table 1, entry 5) suggests sequential insertion of **5** is unfavorable. Thus, a random or gradient-like distribution of the caged FLP units is most likely for polymers **8a–d**, rather than block-like structures. Whereas trace diene impurities from **7** led to poor uniformity and partial cross-linking in **8a** and **8b** (see SI, Section 3 for additional details), these undesired reactivities appear minimal for polymers **8c** and **8d**, which showed dispersities (Đ) of 2.1 and 1.5, respectively, that are typical of VA polynorbornenes prepared using $(\eta^6\text{-}C_6H_5CH_3)\text{-}Ni(C_6F_5)_2$ and similar Ni(II) initiators.[40,43–45] Although as yet unoptimized, this VA polymerization system afforded the opportunity to study the uncaging of caged FLP polymers **8**.

To elucidate the uncaging reactivity of alkene-caged FLPs, we used adduct **9**[46] as a molecular model system for the caged FLP repeat units in polymers **8**, facilitating analysis by NMR spectroscopy (Figure 4). We initially probed for thermal uncaging of adduct **9**. After heating at 80 °C, we observed partial conversion to norbornene (**NBE**) and FLP **1**, with no
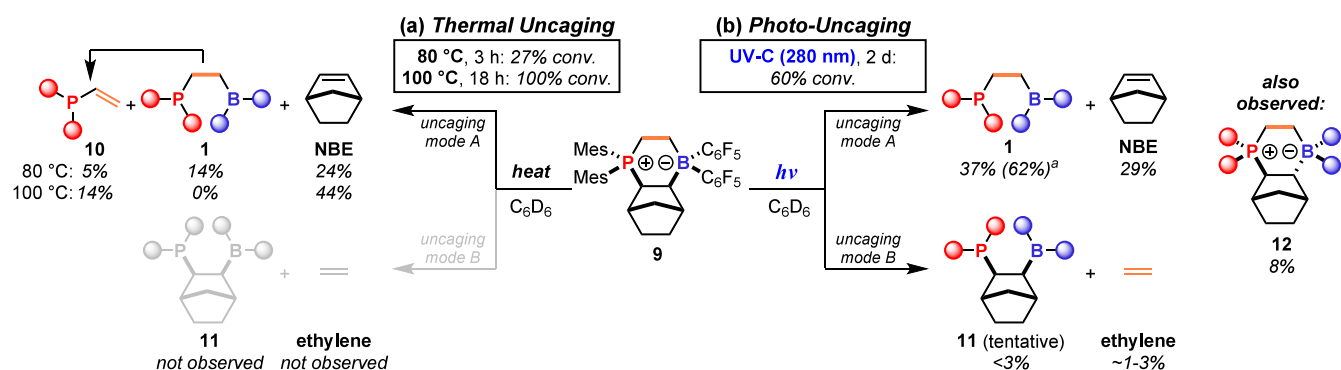
Figure 4. (a) Thermal uncaging and (b) photochemical uncaging studies with model FLP-alkene adduct **9**. % Conversion and % yields determined from ^{1}H NMR spectra relative to an internal standard. ^{a}Yield in parentheses is % yield based on recovered starting material (BRSM). See the SI for details.

ethylene present to suggest uncaging via mode B (Figure 4a). However, vinylphosphine **10**, formed by retro-hydroboration of **1**, was also present after heating **9** at 80 °C, and extended heating above 100 °C resulted in complete decomposition to **10** (Figures S26 and S27). Polymer **8c** exhibited similar behavior at 80 and 100 °C, with no FLP **1** observed at 100 °C (Figure S47). Broad alkene resonances observed in ^{1}H NMR spectra at these temperatures likely correspond to norbornenyl repeat units in the resulting polymer. TGA data show significant weight loss events beginning near 100 °C for polymers **8a–d** (Figure S23), suggesting similar thermal reactivity patterns in the solid state and in solution. These studies reveal that at the temperatures required for appreciable thermal uncaging, decomposition of FLP **1** is inevitable.

Seeking to obviate thermal retro-hydroboration of uncaged vicinal FLPs, we considered photochemical activation of phosphonium[47−52] borate[53,54] **9** as an alternative trigger for uncaging (Figure 4b). Photolysis of adduct **9** with a UV-C LED (λ_{peak} = 280 nm) readily afforded NBE and FLP **1** as the major products (62% yield **1** BRSM), revealing *uncaging mode A* as the predominant pathway. Crucially, vinylphosphine **10** was not observed in all photochemical reactions (Figures S28−S30). FLP **1** persisted for >3 days after irradiation was stopped and showed negligible reformation of adduct **9** (Figure S30). Ethylene was also observed during UV-C photolysis in smaller quantities, implying formation of vicinal phosphine-borane **11** via *uncaging mode B*. As we were not able to isolate this putative vicinal FLP for definitive characterization, the assignment of **11** remains tentative at this stage. Based on the resonances attributed to **11** in NMR spectra, **11** is presumed to be a minor photoproduct relative to FLP **1** (**1**:**11** = >10:1; see discussion in SI, Section 4c and Figures S27−S30). Adduct **12**, a *trans*-diastereomer of **9**, was also isolated as a minor byproduct in UV-C photoreactions (Figure 4b; XRD analysis in Figure S58). The stereochemical configuration of **12** suggests that it may be an "interrupted" product of a stepwise uncaging pathway (see Figure S43 and SI Section 4i for further mechanistic discussion).

Photouncaging of FLP **1** represents a valuable tool for modulating FLP reactivity akin to recent examples of photogenerated "Frustrated Radical Pairs" (FRPs).[55] Unlike FLP **1** and other canonical closed-shell FLPs, FRPs are typically transient, open-shell radical ion pairs (LA$^{\bullet+}$/LB$^{\bullet−}$) that react with small molecules in a homolytic fashion.[56,57] FRPs can be generated through photoexcitation of intermolecular charge transfer (CT) absorptions between a LA/LB

pair,[58] which was used to access polymeric FRPs in a recent example by Shaver.[27] We considered that "vicinal FRPs" could be generated in secondary photoreactions of **1** after uncaging from **9**, but we found that UV-C irradiation does not directly excite the intramolecular CT absorption band at 310−500 nm (Figure S53) of vicinal FLP **1** (Figure 5a). However,
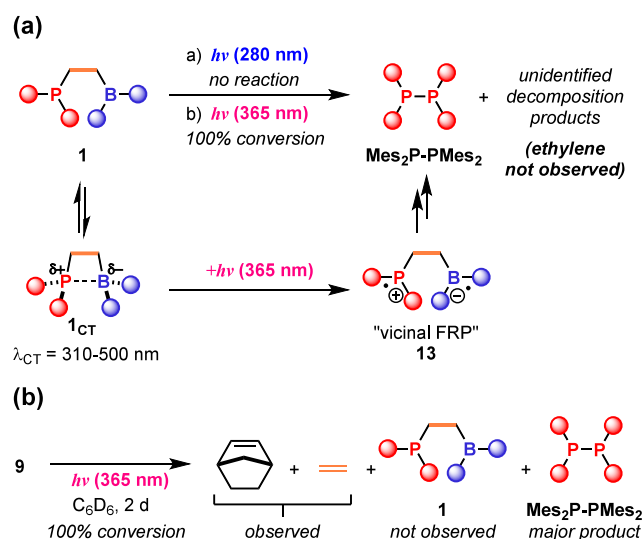

Figure 5. (a) UV-A photolysis (365 nm LED) of the CT absorption of **1** leads to decomposition. (b) UV-A photolysis of **9** results in similar decomposition products observed for direct irradiation of **1**.

photoexcitation of the CT absorption with UV-A light yielded quantitative decomposition of FLP **1** to **Mes$_2$P-PMes$_2$** as the major product (Figures S33 and S34), likely decomposing via an unstable vicinal FRP **13** (see Figure S35 for additional discussion). Likewise, UV-A irradiation of adduct **9** produced the same decomposition products (Figures S31 and S32). Thus, UV-C irradiation is key to avoiding secondary photodecomposition of uncaged FLP **1**.

Next, we leveraged the FLP photouncaging reaction to achieve photochemically triggered hydrogenation of enamine **14** and imine **16**, using adduct **9** as a latent source of catalytic FLP **1** (Figure 6a). Substrates **14** and **16** were selected to facilitate benchmarking with established literature precedent by Erker and co-workers,[59] who reported using **1•H$_2$** (the H$_2$ adduct of FLP **1**[31,32]) to achieve catalytic hydrogenation of **14** to **15** (88% yield, 20 h) and of **16** to **17** (87% yield, 45 min),
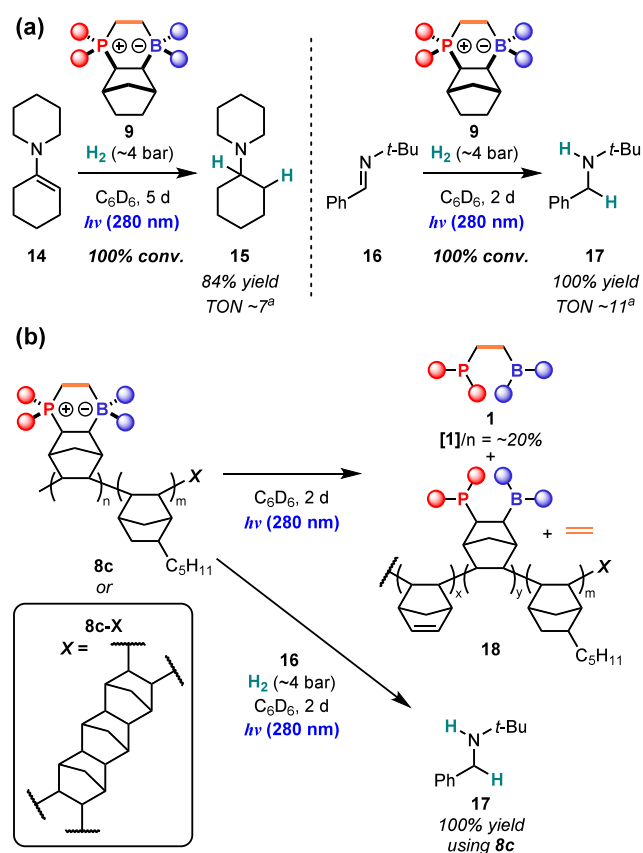
Figure 6. (a) Phototriggered hydrogenation of enamine **14** and imine **16** using **9**. % conversion and % yields determined from ^{1}H NMR spectra using an internal standard. ^{a}Turnover number (TON) relative to uncaged FLP **1**. (b) Photochemical uncaging of polymer **8c** and cross-linked polymer network **18** and photochemical hydrogenation of imine **16** using **8c**. See the SI for additional details.

under H_2 atmosphere at room temperature. In our photo-triggered experiments, excellent yields and reasonable catalytic efficiencies were observed for hydrogenation of **14** (84% yield **15**, 5 d) and **16** (100% yield **17**, 2 d). The slower reaction times compared to literature are ascribed to the gradual generation of FLP **1** in our photochemical system (Figure S30). Kinetic studies showed that hydrogenation continues after irradiation stops (Figures S44 and S45), confirming that continuous irradiation is unnecessary to maintain catalytic activity. Notably, we observed negligible hydrogenation of **14** in control reactions using FLP **1**, which we attribute to formation of an unidentified, catalytically inactive species upon direct mixing of **1** with **14** (Figure S46). This observation clarifies why successful hydrogenation of **14** required the use of **1•H$_2$** as a masked form of **1**.[59] While adduct **9** and **1•H$_2$** are both latent sources of **1**, the temporal control enabled by photouncaging **1** from **9** uniquely obviates the deleterious reaction of **1** with **14** before H_2 is introduced.

We further confirmed that polymer **8c** generates FLP **1** and ethylene under UV-C irradiation (Figure 6b), with roughly 20% of caged adducts in the starting polymer proceeding to **1** as the predominant molecular uncaging product after 2 days (Figures S48 and S49). The proposed structure of polymeric photoproduct **18** is consistent with the appearance of ethylene and broad alkene resonances in ^{1}H NMR spectra. The presence of uncaged FLPs in **18** remains tentative pending further characterization, but the ratio (y:x) should be small and

similar to the distribution seen in model studies with **9** (**11:1** = <1:10). We also incorporated caged FLP units into a cross-linked polymer network, **8c-X**, by conducting VA polymerization with 5 mol % of diene **S1** as a cross-linker (Figure 6b). As a solvent-swollen gel, **8c-X** releases FLP **1** and ethylene upon irradiation (Figure S50), confirming that the photo-uncaging reactivity is preserved in this heterogeneous system. As proof-of-concept that triggered FLP release from a polymer precursor can be utilized in catalytic applications, we achieved phototriggered hydrogenation of imine **16** to **17** using polymer **8c**, with 100% yield of **17** observed after 2 days (Figure 6b, Figure S51). While this system is selective for "uncaging mode A", ongoing efforts in our lab to optimize for "uncaging mode B" may afford bifunctional polymeric FLP materials that, among other potential applications, serve as reusable catalytic materials.

In conclusion, this work establishes the use of phosphine/borane FLP-alkene adducts as mutually protected FLPs, which enabled the incorporation of latent FLP functionality into polymers through vinyl addition polymerization. Our studies demonstrate that vicinal FLPs can be photochemically released from caged FLP polymers, uncaging persistent, closed-shell FLPs that are catalytically active. The synthetic advances in this work introduce new opportunities for stimuli-responsive delivery of FLP payloads from macromolecular scaffolds.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c09012.

Synthetic procedures, characterization data, and supplementary figures (PDF)

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