

A Redox-Active Frustrated Lewis Pair for the Activation and N-O Scission of Nitrosonium Cations

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KEYWORDS: Frustrated Lewis Pairs, Non-Innocent Substituents, Multi-electron activation, NO Bond Scission

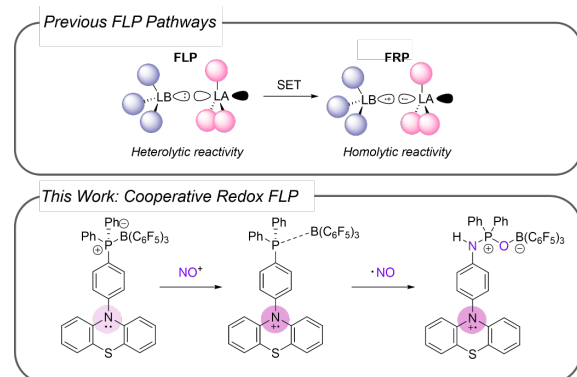
ABSTRACT: Frustrated Lewis pairs (FLPs) have revolutionized main-group chemistry by enabling reactivity traditionally associated with transition metals. However, existing FLP systems are predominantly restricted to two-electron heterolytic or homolytic bond activation mechanisms. In this work, we present a phosphine functionalized with a peripheral redox-active phenothiazine moiety and exploration of its unique behaviour within an FLP framework. The resulting FLP exhibits unprecedented reactivity, allowing for the activation of the highly oxidizing nitrosonium cation with subsequent N-O bond scission. This reaction is facilitated by the redox-active functionality, by first being oxidized by a single electron, then producing a reactive FLP to activate the substrate, resulting in a total of 3-electron bond activation reaction. This novel transformation underscores the potential of incorporating redox-active groups to expand the scope of FLP chemistry paving the way for new avenues in main-group bond activations.

INTRODUCTION

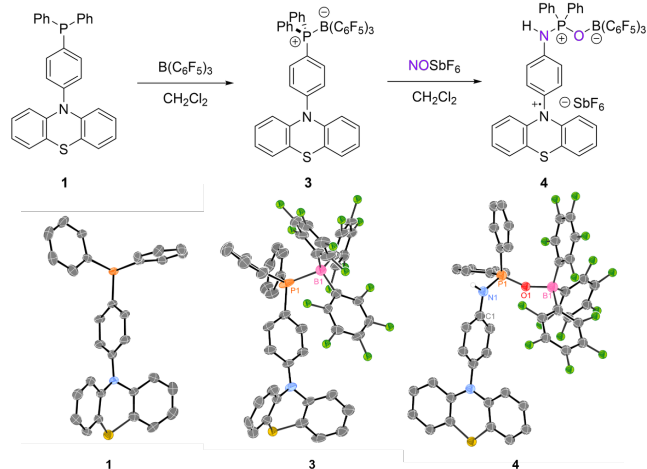
The activation of small molecules is significant for a range of chemistries, as it represents a fundamental step in processes such as stoichiometric sequestration and catalytic transformations to synthesize new molecules. These processes have long been facilitated by transition metal complexes and often proceed via two-electron oxidative addition/reductive elimination pathways.¹⁻³ Ligand design around the metal complex plays a central role in facilitating increasingly challenging transformations, and in some cases, allowing for cooperative participation in bond activation between the ligand and the metal-center.^{4,5} This is particularly illustrated by the use of redox-active ligands, which serve as additional electron reservoirs to modulate the oxidation state of metal complexes during small-molecule activation, particularly with first-row transition metals.⁶⁻⁹

The notion that transition metals are crucial for small-molecule activation has shifted with the advent of frustrated Lewis pair (FLP) chemistry. This began with the reversible heterolytic activation of dihydrogen using sterically encumbered phosphines and boranes.¹⁰ In the 20 years since this initial discovery, combinations of Lewis acids and bases have activated a plethora of inert small-molecules.¹¹⁻¹³ The predominant mechanism of bond activation being two-electron heterolytic processes, akin to oxidative addition observed in transition metal catalysis. More recently, a second bond activation pathway has been uncovered within FLPs, where a single electron transfer first occurs between the Lewis base and acid, leading to a frustrated radical pair (FRP). These systems can homolytically activate bonds in a two-electron process complementary to FLPs and have further expanded the scope of small-molecule activation (Scheme 1).¹⁴⁻¹⁶

Nonetheless, in both scenarios, bond-activation is limited to two-electron processes, and more challenging, multi-electron transformations have yet to be achieved. To expand the scope and complexity of bond activations, we hypothesized that a peripheral electron reservoir could be appended to an FLP to facilitate novel small molecule activation by providing an additional electron to reduce reactive substrates, as well as generating a more reactive FLP by producing a radical cation on the Lewis base partner. Ourselves, and others, have recently found interest in introducing redox-active functionalities into Lewis acids to modulate Lewis acidity.¹⁷⁻¹⁹ Beyond this, one recent example highlights the potential synergy between redox-active ligands and main-group elements. Hwang and co-workers found that a phosphorus complex bearing a redox-active pincer ligand can facilitate the 4e⁻ activation of O₂ at the phosphorus center.²⁰ Herein, we expand this concept to frustrated Lewis pairs and report the synthesis of a phosphine bearing a distal redox-active phenothiazine motif (**1**) and its reactivity with the Lewis acid B(C₆F₅)₃.



Scheme 1, Top: Illustration of FLP and FRP combinations. Bottom: This work demonstrates a new activation approach using a cooperative redox-active FLP.



Scheme 2: Synthesis of 3 and subsequent oxidation with NOSbF₆ (top). Solid-state structures for each compound (bottom). In all cases, ellipsoids are shown at 50% probability. For clarity, hydrogen atoms and weakly coordinating anions are omitted. Selected atomic distances (Å): 3: C1-P1: 1.803(5), P1-B1: 2.227(1). 4: C1-N1: 1.415(5), N1-P1: 1.644(3), P1-O1: 1.520(3), O1-B1: 1.558(5).

Excitingly, we discovered that the phenothiazine provides an additional electron that facilitates the activation of NO⁺ and promotes a unique, metal-free N-O bond-scission reaction.

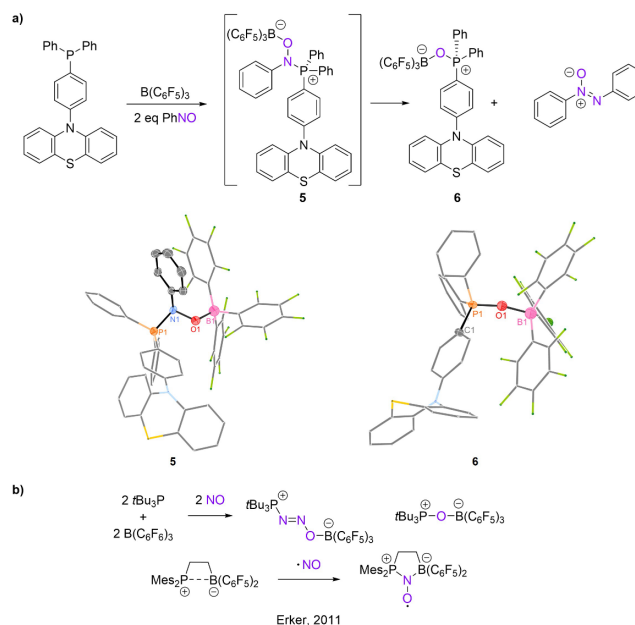
RESULTS AND DISCUSSION

1 was synthesized through the lithiation of 10-(4-bromophenyl)phenothiazine and reaction with Ph₂PCl, resulting in near quantitative yields, with a ³¹P NMR resonance at δ: -6.0 ppm. Single crystals suitable for X-ray diffraction were grown from a saturated solution of pentane and confirmed the formation of the **1** (Scheme 2).

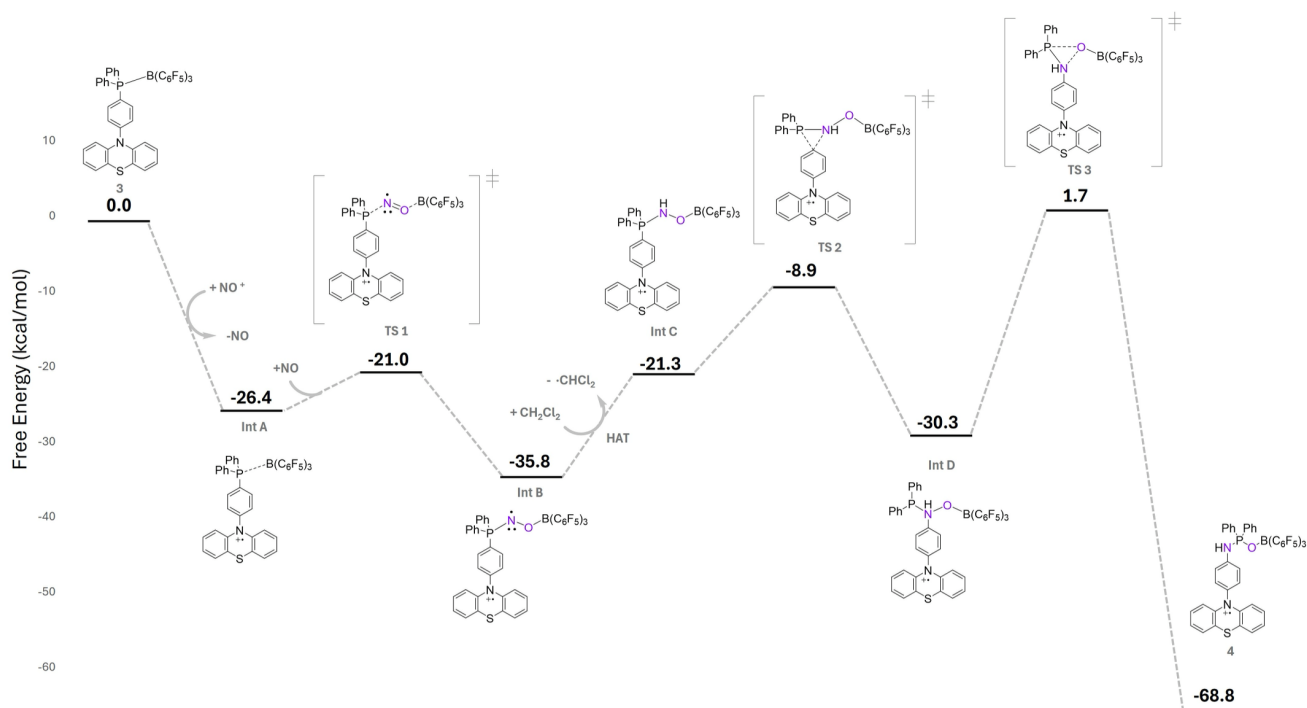
To understand the impact of the distal phenothiazine, cyclic voltammetry was undertaken and showed two overlapping oxidations: an irreversible event at 0.72 V and a quasi-reversible event at 0.92 V vs Ag/AgCl (Figure S1-E). Since **1** can be oxidized at both the phenothiazine N and at the phosphorus center, we synthesized the P(V) phosphine oxide (**2**) by stirring **1** overnight with 3 equivalents of H₂O₂. **2** was isolated in 79 % yield, with a notable change in the ³¹P NMR resonance to δ: 28.7 ppm (Figure S2-C). Cyclic voltammetry of **2** exhibited a single reversible oxidation event at 0.80 V vs Ag/AgCl, suggesting that oxidizing the phosphorus center allows for a selective redox-event at the phenothiazine (Figure S2-E).

To further corroborate this observation, we synthesized the Lewis acid-base adduct of **1** with B(C₆F₅)₃ through an equimolar reaction in CH₂Cl₂. The product, **3**, (Scheme 2) was isolated in quantitative yield and multinuclear NMR analysis suggested that a strong adduct was formed, with a ³¹P NMR resonance at δ: 18.4 ppm; an ¹¹B NMR resonance at δ: -6.8 ppm, and very broad resonances in the ¹⁹F NMR spectrum at δ: -123.5 (*o*-F), -154.5 (*p*-F), and -162.7 (*m*-F) ppm, indicating restricted rotation around the P-B bond. This adduct was unambiguously confirmed using X-ray crystallography, having a P-B bond length of 2.227(1) Å. Cyclic voltammetry of **3** indicates a single, quasi-reversible oxidation event at 0.89 V vs Ag/AgCl. However, there is a small secondary feature at 0.63 V, similar to the first oxidation event observed in **1**, suggesting that there may be some lability to the adduct (Figure S3-F). It should be noted that there is no interaction between **3** and the electrolyte (NBu₄PF₆), however, care should be taken when doing electrochemistry with highly electrophilic boranes, as they require specialized, weakly coordinating electrolytes.²¹

These encouraging data suggested that the phenothiazine motif could act as an electron reservoir, and we sought to chemically oxidize the adduct **3**. One equivalent of nitrosonium hexafluoroantimonate (NOSbF₆) was slowly added to a solution of **3** in CH₂Cl₂ at room temperature, resulting in an immediate color change from colorless to dark red. The solvent was removed *in-vacuo* to yield a dark red solid in a 91 % yield. Broad resonances in the ¹H NMR spectrum suggested the formation of a paramagnetic product, which was corroborated using EPR spectroscopy. Analysis at room temperature showed a triplet resonance centered at *g* = 2.0061 with a nitrogen hyperfine coupling pattern, aligning with a simulated spectrum of a phenothiazine centered radical (Figure S4-A). Interestingly, the ¹¹B NMR spectrum had a sharp peak at δ: -11.7 ppm, and the corresponding ¹⁹F NMR spectrum also had sharp resonances at δ: -135.1 (*o*-F), -158.7 (*p*-F), and -165.7 ppm (*m*-F). Taken together, these suggest that the boron center is tetracoordinate and the sharp signals indicate it is removed from where the unpaired electron is located. Finally, the ³¹P NMR spectrum had a broad resonance at δ: 20.6 ppm. Excitingly, single crystals suitable for X-ray diffraction were grown from a concentrated CH₂Cl₂/pentane mixture and the structure of **4** was fully elucidated. The solid-state structure of **4** showed that not only did the single-electron oxidation of the phenothiazine motif occur, but the resulting neutral NO formed was activated between the P/B FLP. Once activated, the N=O bond was cleaved, and subsequent N-atom migration into a P-C(aryl) bond results in the formation of a Lewis acid-base adduct between B(C₆F₅)₃ and a phosphinamide bearing a pendant radical cation (Scheme 2). X-ray diffraction data indicated a C1-N1 bond length of 1.415(5) Å, and a N1-P1 bond length of 1.644(3) Å, suggestive of single bonds. The P1-O1 bond length was found to be 1.520(3) Å, and the O1-B1 length of 1.558(5) Å, similar to previously reported phosphine oxide adducts with B(C₆F₅)₃.²² This observed activation of NO⁺ is unprecedented in the FLP literature as FLP combinations tend to be incompatible with highly oxidizing substrates.



Scheme 3: (a) Reactivity of adduct 3 with nitrosobenzene and solid-state structures for species 5 and 6. In all cases, ellipsoids are shown at 50% probability. Common scaffolds are shown in wireframe. For clarity, hydrogen atoms are omitted. Selected atomic distances [Å]: 5: C1-P1: 1.789(2), P1-N1: 1.692(7), N1-O1: 1.447(6), O1-B1: 1.520(4). 6: C1-P1: 1.796(1), P1-O1: 1.515(0), O1-B1: 1.546(3). (b) Established reactivity of intra- and intermolecular FLPs with NO.



Scheme 4: The potential energy surface depicting the plausible mechanism for the NO-insertion into **3** to yield **4**. Free energy changes for the elementary steps were calculated at the ω B97XD (Grimme D2-dispersion)/cc-pVQz level of theory in a polarized continuum solvation model for dichloromethane.

The N-H moiety was confirmed using IR spectroscopy with an observed vibration at 3578 cm^{-1} . While we cannot unequivocally determine where the H-atom comes from, there is literature precedent that chlorinated solvents, such as CH_2Cl_2 , can be an H-atom donors.²³⁻²⁶ This was further corroborated by changing the solvent to *o*-difluorobenzene, which is not an H-atom donor. In this case, **4** was not observed, and the only product isolated from this reaction mixture was a fluorophosphonium radical dication (**11**, Figure S23), a possible byproduct of SbF_6^- decomposition by the highly reactive $3^{+\cdot}$. Furthermore, when trace dichloromethane is introduced in *o*-difluorobenzene, product **4** is only observed (Figure S12). Additional isolation attempts of this radical cation using *tris*(4-bromophenyl)ammoniumyl hexachloroantimonate as the oxidant led to a similar chlorophosphonium radical dication, again presumably through decomposition of the SbCl_6^- (**12**, Figure S24).

To better understand the importance of the phenothiazine radical cation, we explored the reaction of the neutral **3** with nitrosobenzene in CH_2Cl_2 . While this substrate cannot oxidize the phenothiazine, we found it was able to be activated by the FLP, yielding **5**, as confirmed by X-ray crystallography (Scheme 3, **b**). This structure showed a P1-N1 bond length of $1.692(7)\text{ \AA}$, a N1-O1 bond length of $1.447(6)\text{ \AA}$, and an O1-B1 bond length of $1.520(4)\text{ \AA}$. These bond lengths are reminiscent of what Erker and co-workers observed when activating nitrosobenzene with an intramolecular FLP.²⁷ Isolation of **5** proved to be difficult as it rapidly decomposed to the phosphine oxide/ $\text{B}(\text{C}_6\text{F}_5)_3$ adduct, **6**. This compound has a distinct ^{31}P NMR resonance at δ : 44.4 ppm; an ^{11}B resonance at δ : 1.5 ppm; along with ^{19}F NMR resonances at δ : -132.4 (*o*-F), -158.5 (*p*-F), and -164.4 (*m*-F) ppm, indicating a tetra-coordinate borate species. The phosphine oxide/ $\text{B}(\text{C}_6\text{F}_5)_3$ adduct was independently synthesized through the reaction of the phosphine oxide **2** with one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$, and was verified through multinuclear NMR analysis as well as X-ray crystallography (Scheme 3, **a**). We pondered the fate of the N-Ph moiety in this reaction, and

interestingly, we found the ^1H NMR spectrum of the crude reaction mixture between **3** and nitrosobenzene showed two distinct doublet resonances in the aromatic region (at 8.20 and 8.42 ppm). Following purification by flash chromatography (20% EtOAc/Hex), we identified the byproduct as azoxybenzene, consistent with literature reports of its formation from reactions between phosphines and nitrosobenzene.²⁸

The observed activation and scission of the *in-situ* generated nitric oxide is quite unexpected. NO has found significant interest due to its non-innocent redox behavior, in biology as a signaling molecule, but also broadly as ligands in transition metal chemistry, as they are exceptional π -acceptors and can modulate reactivity based on binding modes.^{29,30} While it has been shown that under some circumstances, coordinated NO can undergo migratory insertion reactions at a transition metal center,^{31,32} the further scission of the N-O has been a challenge. Nevertheless, this has been achieved using reactive transition metal complexes; first reported by Cummins and Protasiewicz, whereby a high valent Cr(VI) nitrido complex was synthesized through the deoxygenation of the Cr-nitrosyl precursor using a reactive vanadium(III) triaryl species.³³ This has been subsequently expanded towards a broader scope of Group 6 metal complexes and heterometallic species, to name a few.^{24,34-36}

The observed reactivity of **3** with NO^+ has few parallels in a main-group context. Erker and Warren have shown that intramolecular FLPs can facilitate 1,1-activation of NO, resulting in persistent *N*-oxyl radicals (Scheme 3, **b**).^{37,38} To compare, the authors reported that intermolecular FLPs react differently with NO, proceeding through a well-established disproportionation pathway to give N_2O and R_3PO (Scheme 3, **b**).³⁹ To verify that the phenothiazine radical cation is central to the observed reactivity, we performed control experiments with **1** and **3** with one and two equivalents of gaseous NO, respectively. These experiments resulted in the formation of the phosphine oxide with concurrent formation of N_2O (See SI, Section 3), confirming that the oxidized phenothiazine radical

cation is necessary for the observed reactivity. To further elucidate the role of this moiety, we undertook additional control experiments. Due to solubility challenges of the $\text{Ph}_3\text{P-B}(\text{C}_6\text{F}_5)_3$ adduct, we explored the reaction on NOSbF_6 with $(p\text{-tol})_3\text{P-B}(\text{C}_6\text{F}_5)_3$ in the absence of a redox-active moiety. This reaction led to a mixture of which both the initial adduct and the phosphine oxide- $\text{B}(\text{C}_6\text{F}_5)_3$ adduct could be identified (**9**, Figure S8). We further added *N*-phenylphenothiazine (N-PhPtz) to provide an oxidizable motif to this adduct. As anticipated, the addition of $[\text{NO}][\text{SbF}_6]$ led to the single electron oxidation of N-PhPtz to the corresponding radical cation **7** (confirmed by single crystal X-ray diffraction, Figure S22), as well as the phosphine oxide-BCF adduct (^{31}P NMR δ : 45 ppm). Furthermore, trace amounts of $[(p\text{-tol})_3\text{P}=\text{N-P}(p\text{-tol})_3]^+$ also crystallized from the reaction mixture (^{31}P NMR δ : -8.0 ppm, **10**, Figure S25). However, this is not an unexpected product as similar species were reported from the reaction of phosphines with nitrosonium cations.²⁴

With these control experiments in mind, several potential mechanistic pathways could be accessible. We performed Density Functional Theory (DFT) calculations to gain mechanistic insight on the transformation of **3** to **4** (see SI, Section 5). It is plausible that the reaction initiates via a one-electron oxidation of the phenothiazine motif by NOSbF_6 to form NO with concurrent weakening of the P-B bond in **Int A** (spin = doublet, Scheme 4). This step was found to be exergonic by 26.4 kcal/mol and spin density plots indicate that the radical cation is delocalized across the phenothiazine fragment. This FLP can rapidly activate NO and a proceeding through a transition state (**TS 1**) 5.4 kcal/mol uphill in free energy. The activated product (**Int B**) and **Int A** differ by -9.4 kcal/mol in energy. For this reaction step, we examined an additional competitive pathway, where it proceeds via a single electron oxidation following two-steps. First the P-B Lewis adduct (**3**) completely dissociated, followed by the activation of NO solely by the phosphine with subsequent capping of the $\text{R}_3\text{P-NO}$ fragment by $\text{B}(\text{C}_6\text{F}_5)_3$ (Figure S28, CP1). It was found that this two-step competitive pathway was energetically unfavourable.

An H-atom abstraction then occurs from dichloromethane (solvent, *vide supra*), leading **Int C** (spin=triplet), which is endergonic by 14.4 kcal/mol. We also examined a competitive pathway where H-atom abstraction happens after N-O bond scission, but the highly positive calculated free energy change of the reaction deems it a thermodynamically unfavorable process (Figure S28, CP2).

A subsequent P-C bond insertion reaction can occur by the N(H)-O fragment, with a small activation barrier of 12.4 kcal/mol (**TS2**), resulting in **Int D** (spin = doublet), which is exergonic by -8.9 kcal/mol from **Int C**. This unique step highlights the importance of the oxidized phenothiazine motif, as the analogous reaction with nitrosobenzene does not yield any inserted product, but the traditional decomposition to the phosphine oxide.²⁸ Finally, P-O bond formation occurs through an oxazaphosphirane-like intermediate (**TS3**), which is reminiscent of transition states observed by Radosevich and co-workers for the deoxygenation of nitro groups using geometrically constrained phosphines.³⁹ Notably, we attempted to investigate the kinetic barrier of pathways where P-O bond formation precedes C-N bond formation, but failed in locating the corresponding transition state (Figure S28, top TS). Although the activation barrier for the final step is 32.0 kcal/mol, the formation of **4** from **Int D** is exergonic by -38.5 kcal/mol, and overall, it is -68.8 kcal/mol from **3**. This agrees with experimental observation, as this reaction proceeds rapidly by simply mixing the reagents under ambient temperature conditions.

CONCLUSION

In conclusion, we have reported a new reactivity paradigm in FLP chemistry, where utilization of a redox-active “electron-reservoir” in the FLP can lead to a three-electron activation of NO^+ . The

highly oxidizing substrate first takes an electron from the phenothiazine motif in the outer sphere of the FLP and subsequently is activated by the P/B system. Due to the highly reactive nature of the intermediate, the N-atom subsequently inserts into the P-C bond, resulting in the observed phosphinamide product. This unprecedented transformation highlights the potential of this approach to advance frustrated Lewis pair chemistry towards multi-electron transformations and closes the gap with transition metal reactivity.

ASSOCIATED CONTENT

Supporting Information

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

A PDF containing general methods, synthetic procedures, complete spectroscopic characterization of the reported compounds; control experiments; X-Ray crystallographic data (CCDC Submission: Deposition Numbers 2410239-2410245, 2463353-2463356); computational details with an additional .xyz coordinate file.

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ACKNOWLEDGMENT

Financial support was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC), the Canadian Foundation for Innovation (CFI), the Canada Research Chairs Program and the Government of Ontario. T.P.L.C. acknowledges the support of an NSERC-CGS-D Award. The computational work was performed with access to the SHARCNET and Compute/Calcul Canada facilities. Dr. Thomas Baumgartner, Dr. Howard Hunter, Charley N. Garrard, and Lucas C. Torres are thanked for helpful discussions.

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