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Frustrated Lewis Pairs

An Unprecedented Ga/P Frustrated Lewis Pair: Synthesis, Characterization, and Reactivity

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Abstract: Frustrated Lewis pairs (FLPs) represent a new paradigm of main-group chemistry. The Lewis acidic centers in FLP chemistry are typically B and Al atoms in the studies reported over the past decade, and most of them are tri-coordinated with strong electron-withdrawing groups. Herein, a Ga/P system is reported which contains an unprecedented four-coordinated Lewis acidic Ga center. This Ga/P species performs classical addition reactions toward heterocumulenes, alkyne, diazomethane, and transition metal complex. Regioselective formation of the products can be rationalized by DFT calculations. The penta-coordinated gallium atom center in these products is rare in the FLP chemistry. This study enriches the diversity of FLPs and demonstrates that a four-coordinated Lewis acidic site with a donor-acceptor bond can also be FLP active.

The chemistry of frustrated Lewis pairs (FLPs) has attracted significant attention and has flourished over the past decade,[1–3] with the potential to play significant roles in main group chemistry. FLPs combine both Lewis acidic and basic centers via sterically or electronically induced frustration, exhibiting remarkable activity for catalysis and small molecule activation.[4] Recent studies revealed that even the classical Lewis acid–base adducts show FLP reactivity, which broadened the definition of FLPs.[5] In addition to the main-group elements typically used in FLPs, the transition metals[6] and even rare-earth metals[7] can also be used as Lewis acids in FLP chemistry. Therefore, the territory of FLPs is constantly developing.

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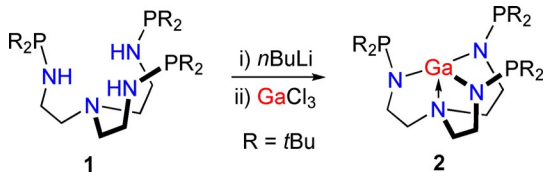
The activities of FLPs largely depend on the Lewis acid and the Lewis base components. The Lewis-base center of FLPs is typically a P- or N-based Lewis bases or *N*-heterocyclic carbene. Generally, the Lewis-acidic center of FLPs is coordinatively unsaturated (three-coordinate) and the most common example being borane with strong electron-withdrawing groups (e.g., $B(C_6F_5)_3$). Although aluminum has also been explored as a Lewis-acidic site in the past few years,[8] the use of the heavier gallium as a Lewis acid in FLPs was rare.[9,10]

Herein, we report a straightforward one-step synthesis of an unprecedented Ga/P FLP, in which the Lewis acidic Ga center is tetra-coordinated with a N→Ga donor-acceptor bond. Density functional theory (DFT) calculations and reactivity toward several substrates were investigated.

Compound **1** was easily prepared by the reaction of $N[CH_2CH_2NH_2]_3$ with three equivalents of tBu_2PCl in the presence of three equivalents of DBU.[11] Treatment of compound **1** with three equivalents of *n*BuLi at room temperature (RT) for 6 h, followed by the dropwise addition of $GaCl_3$ in toluene at −30 °C and further stirring at RT overnight formed a suspension, from which **2** was isolated as a white solid in 85% yield (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum showed a single signal at 89.3 ppm for three equivalent phosphorus atoms.



Scheme 1. The synthesis of compound **2**.

The molecular structure of compound **2** was confirmed by single-crystal X-ray diffraction.[12] As shown in Figure 1, compound **2** exhibited three-fold symmetry, consistent with the single phosphine signal and three proton resonances observed in the solution of $^{31}P\{^1H\}$ and ^1H NMR spectra, respectively. Compound **2** contains a four-coordinated gallium atom, which is bound to three anionic nitrogen atoms in an almost ideally planar arrangement and has an additional N4→Ga1 donor–acceptor bond perpendicular to this plane. The bond lengths of Ga1–N_{amido} (in average) and Ga1–N_{amine} were determined to be 1.877 and 2.059(2) Å. The average bond distance of Ga1···P (3.129 Å) is longer than the sum of the covalent radii for Ga and P (2.35 Å),[13] indicating the negligible interaction between P and Ga1.

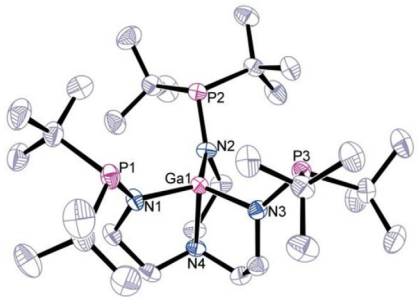


Figure 1. Molecular structure of **2** (thermal ellipsoids shown at 50% probability). Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): N1–Ga1 1.880(2), N2–Ga1 1.880(2), N3–Ga1 1.871(2), N4–Ga1 2.059(2), N1–P1 1.681(2), N2–P2 1.677(2), N3–P3 1.686(2); N1-Ga1-N4 89.05(8), N2-Ga1-N4 89.30(8), N3-Ga1-N4 89.51(9), Ga1-N1-P1 123.41(11), Ga1-N2-P2 123.21(11), Ga1-N3-P3 122.47(12).

To probe the electronic character of **2**, DFT calculations were performed. The optimized geometry revealed that no covalent interaction exists between the Ga1 and P centers, consistent with the X-ray structure (Figure 2 and Table S4 in the Supporting Information). The calculated contribution from the *p* orbital

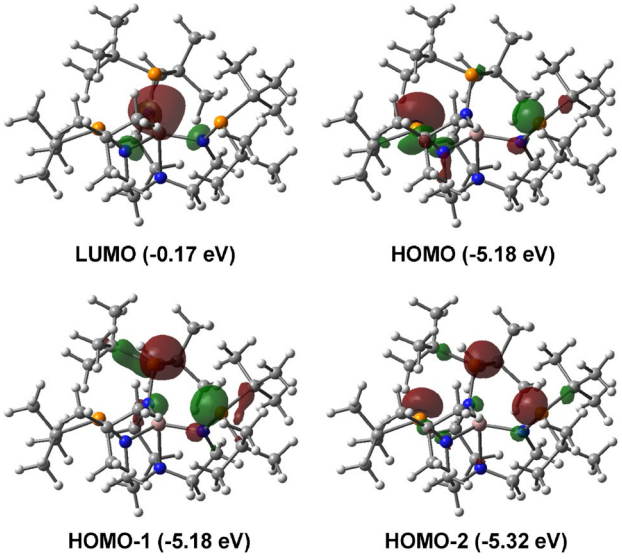
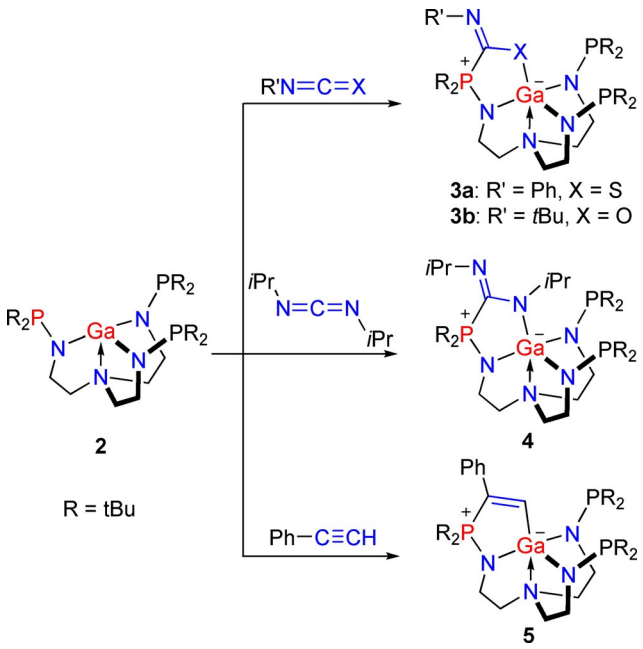


Figure 2. Schematic of the frontier molecular orbitals of **2** (isovalue = 0.05).

of Ga1 atom to the lowest unoccupied molecular orbital (LUMO) (−0.17 eV) is 42% (Table S5 in the Supporting Information), suggesting that it could act as an electrophilic center. The lone pairs of electrons of the P atoms are located in the highest occupied molecular orbital (HOMO; −5.18 eV), HOMO−1 (−5.18 eV), and HOMO−2 (−5.32 eV). Although the HOMO and LUMO orbitals have the appropriate orientation, the Wiberg bond index for the Ga1–P bond was only 0.07, consistent with the absence of significant donor–acceptor interactions between the P and Ga1 atoms. In contrast, a slightly stronger donor–acceptor bonding between the N4 and Ga1 was detected, exemplified by the Wiberg bond index of 0.16 for the Ga1–N4 bond. For comparison, the Wiberg bond indices for other Ga1–N bonds are 0.37.

According to the DFT calculations, compound **2** could exhibit FLP-type reactivity. Therefore, we investigated the reactivity of compound **2** towards organic substrates typically used in FLP chemistry. Initially, we performed the reactions of **2** with heterocumulenes in THF at RT. As shown in Scheme 2, treatment of **2** with phenyl isothiocyanate and tert-butyl isocyanate yielded species **3a** and **3b** in almost quantitative yields based on the in situ $^{31}P\{^{1}H\}$ NMR spectrum. The $^{31}P\{^{1}H\}$ NMR spectrum showed two signals for unequivalent phosphorus atoms of **3a** and **3b** (85.3 and 34.6 ppm for **3a**; 87.4 and 28.2 ppm for **3b**), consistent with the formulation of these products. Under identical conditions, compound **2** reacted with the symmetrical heterocumulene, *N,N′*-diisopropylcarbodiimide, to produce compound **4** in 64% isolated yield (Scheme 2). Two phosphine signals for **4** were observed at 88.7 and 28.8 ppm in its $^{31}P\{^{1}H\}$ NMR spectrum.



Scheme 2. Reactions of compound **2** with heterocumulenes and phenylacetylene.

The structures of **3a** and **4** were further determined by single-crystal X-ray diffraction (Figure 3).[12] The most salient feature for these species was the new five-membered heterocycle formed by addition of **2** with C=X double bonds in the heterocumulenes. The generation of **3** and **4** indicated that compound **2** exhibited typical features of a FLP, as the examples of addition reactions between heterocumulenes and FLPs have been widely reported.

In addition, the reaction of **2** was further extended to alkyne. Treatment of phenylacetylene with **2** produced compound **5** with a new five-membered heterocycle. The $^{31}P\{^{1}H\}$ NMR spectrum showed two signals at 87.8 and 41.2 ppm for the unequivalent phosphorus atoms. Crystallographic analysis

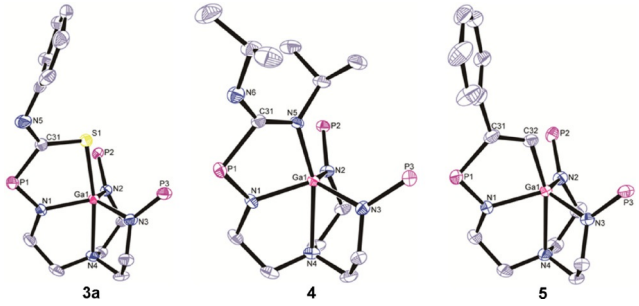
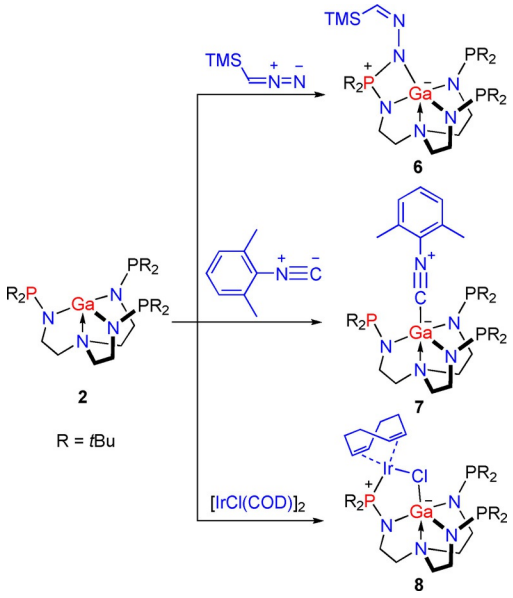


Figure 3. Molecular structures of **3a**, **4**, and **5** (thermal ellipsoids shown at 50% probability). Hydrogen atoms and tert-butyl moieties in the P*t*Bu$_2$ were omitted for clarity. Selected bond lengths (Å): For **3a**: N1–Ga1 2.004(2), N2–Ga1 1.933(2), N3–Ga1 1.912(2), N4–Ga1 2.257(2), Ga1–S1 2.3749(8), S1–C31 1.716(3), C31–N5 1.287(4); for **4**: N1–Ga1 1.996(2), N2–Ga1 1.942(2), N3–Ga1 1.949(2), N4–Ga1 2.387(2), N5–Ga1 2.020(2), N5–C31 1.347(3), C31–N6 1.300(3); for **5**: N1–Ga1 2.029(3), N2–Ga1 1.946(3), N3–Ga1 1.926(3), N4–Ga1 2.354(3), C32–Ga1 1.999(3), C31–C32 1.332(4).

of **5** confirmed that the new five-membered ring was formed through the addition of the C–C triple bond in phenylacetylene to the Ga and P atoms in compound **2** (Figure 3).[12] Similarly, the Ga atoms in all products were penta-coordinated, adopting an approximate trigonal-bipyramid geometry ($\tau >$ 0.7).[14]

Regioselective formation of the products was further investigated by DFT calculations. Considering the reaction of compound **2** with phenylacetylene, the Gibbs activation energy for the formation of **5** via the transition-state **TS$_{2/5}$** (10.9 kcal mol^{-1}) was significantly lower than that (26.5 kcal mol^{-1}) of the formation of **5′** via **TS$_{2/5'}$** (Figure 4 and Figures S45–S47 in the Supporting Information). The charges via natural population analysis of the sp-hybridized carbons in phenylacetylene were determined to be −0.01 and −0.22 a.u., respectively. Therefore, the terminal carbon of phenylacetylene is more nucleophilic, which can reasonably explain that lower activation energy of **TS$_{2/5}$**. Therefore, the formation of **5** is kinetically favorable process, consistent with the experimental observation that this reaction finished within 15 min at RT. Only the kinetically favored product was observed in this reaction even at 80 °C.

Compound **2** can be considered as a hidden FLP, although it contains an electron-donating group (N4) on the Lewis acid Ga center. Thus, we further investigated the reactivity of **2**. Treatment of **2** with (trimethylsilyl) diazomethane led to the formation of compound **6**, which was formed by the coordination of the terminal N atom to Ga1 and P1 to form a four-membered heterocycle (Scheme 3). Two signals were observed at 87.6 and 55.3 ppm in the $^{31}P\{^1H\}$ NMR spectrum for compound **6**. In contrast, the in situ $^{31}P\{^1H\}$ NMR spectrum of the reaction of **2** with 2, 6-dimethylphenyl isocyanide only showed a single signal at 81.8 ppm, suggesting that the three phosphorus atoms were equivalent in solution. Finally, **7** was isolated as a yellow solid in 65% yield. The molecular structures of both **6** and **7** were confirmed via X-ray analysis (Figure 5). All gallium



Scheme 3. The reactivity of compound **2**.

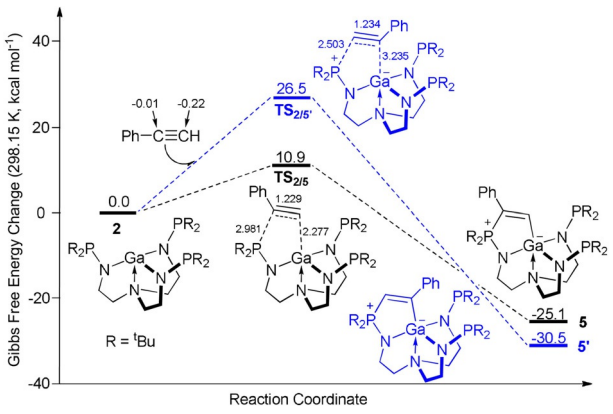


Figure 4. Energy profiles (kcal mol^{-1}) for the addition reactions of phenylacetylene and **2** calculated at the PCM-B3LYP-GD3BJ/Def2TZVP level. The pathways for the formation of **5** and **5′** are labelled in black and blue, respectively. Distances are provided in Å.

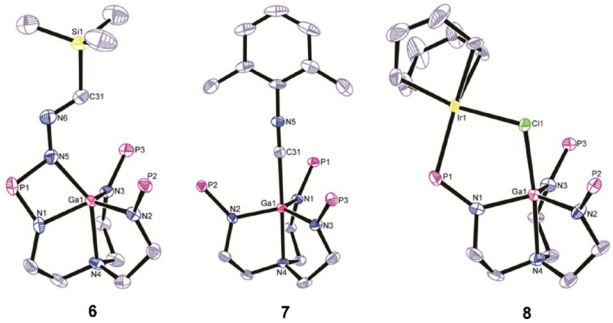


Figure 5. Molecular structures of **6**, **7**, and **8** (thermal ellipsoids shown at 50% probability). Hydrogen atoms and tert-butyl moieties in the P*t*Bu$_2$ were omitted for clarity. Selected bond lenghts (Å): For **6**: N1–Ga1 1.987(5), N2–Ga1 1.898(5), N3–Ga1 1.919(4), N4–Ga1 2.268(5), N5–Ga1 2.064(5); for **7**: N1–Ga1 1.9285(16), N2–Ga1 1.9312(17), N3–Ga1 1.9278(16), N4–Ga1 2.2295(16), Ga1–C31 2.196(2); For **8**: N1–Ga1 1.941(6), N2–Ga1 1.927(6), N3–Ga1 1.921(6), N4–Ga1 2.214(6), Ga1–Cl1 2.3933(19), Cl1–Ir1 2.3483(16).

centers in these products were penta-coordinated, which is novel in the addition products of other FLP systems.[9,10]

In addition, compound **2** was also reacted with the dimeric species $[IrCl(COD)]_2$, from which the addition product **8** was isolated in 67% yield. The $^{31}P\{^1H\}$ NMR spectra showed a single signal at 23.6 ppm, consistent with the formulation of bimetallic product. The structural features of **8** were further examined by X-ray diffraction (Figure 5). A new five-membered ring was formed by the coordination of P to Ir and Cl to Ga. The geometry of the Ir atom is tetra-coordinated and that of the Ga atom is penta-coordinated ($\tau = 0.92$).[14] The calculated Wiberg bond indices of Ga1–Cl1 and Ir1–Cl1 are 0.38 and 0.39, respectively. This is the first example of Ga-based FLP that can react with transition-metal species although the reactions of transition-metal complexes with other FLP systems have been previously reported.[15]

In summary, we developed a Ga/P species **2** based on a heptadentate N_4P_3 precursor containing three rigid nitrogen-phosphorus units. This Ga/P system exhibited FLP-type reactivity, reacting with a series of organic substrates and even transition metal complex. This study further demonstrated that the four-coordinated Lewis acidic site with donor-acceptor bond can also be exhibited FLP-type reactivity, which further expands the territory of the FLP chemistry. The construction of FLP systems to incorporate different Lewis acidic center (i.e., early transition metals or rare-earth metals) based on this heptadentate N_4P_3 ligand and their potential catalytic properties for small molecule activation are currently under investigation.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: density functional calculations · frustrated Lewis pairs · gallium · heptadentate N_4P_3 ligand · phosphorus

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