

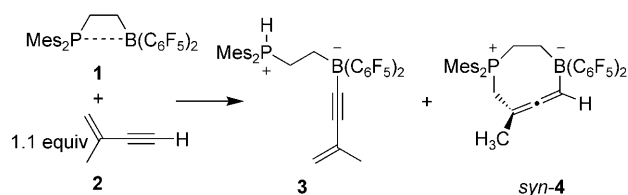
Formation of Cyclic Allenes and Cumulenes by Cooperative Addition of Frustrated Lewis Pairs to Conjugated Enynes and Diynes**

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Dedicated to Professor Günther Wilke on the occasion of his 85th birthday

Allenes and cumulenes are not only synthetically important substrates;^[1] they are also structurally interesting organic compounds, especially when incorporated into small and medium-sized ring systems. In this context allene and cumulene units may introduce substantial strain if their carbon frameworks become markedly distorted from the usual geometries.^[2] Therefore, the synthesis of cyclic allenes or cyclic cumulenes sometimes presents a challenge.^[3,4] Herein we report on the facile addition reactions of an intramolecular frustrated Lewis pair to an enyne and two conjugated diynes which lead directly to the formation of the respective eight-membered-ring cyclocumulene derivatives under very mild conditions.

Our new reaction makes use of the remarkable features of frustrated Lewis pairs. Pairs of strong Lewis acids and bases that bear substituents bulky enough to prevent formation of the adduct can potentially react cooperatively with a variety of substrates.^[5] Most notably such systems have been used for the heterolytic activation of dihydrogen and concomitantly for metal-free catalytic hydrogenation of several functionalized alkenes^[6] and bulky imines.^[7–9] Frustrated Lewis pairs have been shown to add to olefinic substrates,^[10,11] to terminal alkynes,^[11,12] to N_2O ,^[13] to organic carbonyl compounds^[11,14] and even to carbon dioxide.^[15] The intramolecular frustrated Lewis pair **1** (Scheme 1) was shown to be especially reactive in some of these binding or activation reactions of small molecules.^[11,15–17]



Scheme 1. Reaction of the frustrated Lewis pair **1** with butenyne **2**.

We treated the Lewis pair system **1** with 2-methyl-1,3-butenyne (**2**) and found a remarkable new reaction pathway. Treatment of the Lewis pair **1**, which was generated in situ by hydroboration of dimesitylvinyphosphine^[16] with $HB(C_6F_5)_2$,^[18] with an equimolar amount of butenyne **2** in pentane at room temperature resulted in an instantaneous reaction to yield a white precipitate which was isolated in 80% yield. The NMR analysis revealed a mixture of two compounds in a 1:2 ratio. Single crystals suitable for the X-ray crystal structure analysis were obtained for both compounds: **3** by diffusion of heptane into a benzene solution, and **4** from a layered CH_2Cl_2 /pentane mixture at $-36^\circ C$. We used these data along with the NMR spectra obtained for the mixture to identify the two products.

The minor product arises by deprotonation of the CH-acidic acetylene^[12] by the basic phosphorus component of the Lewis pair **1** to give a phosphonium cation (^{31}P NMR: $\delta = -3.4$ ppm, 1H : $\delta = 7.53$ ppm, $^1J_{PH} = 468$ Hz); the formally resulting acetylide anion was then trapped by the electrophilic borane functionality of the Lewis pair to give a boron acetylide. In the crystal the zwitterion **3** features a tetracoordinate boron atom with $B-C(sp^3)$ and $B-C(sp)$ bond lengths of 1.646(3) Å ($B1-C2$) and 1.587(3) Å ($B1-C3$), respectively [$B-C(aryl)$: 1.654(3) Å ($B1-C31$), 1.657(3) Å ($B1-C41$)] (Figure 1). The zwitterion displays an antiperiplanar conformation of the central $B1-C2-C1-P1$ unit in the solid state [dihedral angle $-168.5(1)^\circ$, $P1-C1$ 1.802(2) Å]. It shows typical “phosphonium” C-P-C angles at the phosphorus atom [$C1-P1-C11$ $118.0(1)^\circ$, $C1-P1-C21$ $108.7(1)^\circ$, $C11-P1-C21$ $114.8(1)^\circ$] (for details see the Supporting Information).

The major product of this reaction, the cyclic allene *syn-4*, was formed by regioselective 1,4-addition of the P/B Lewis

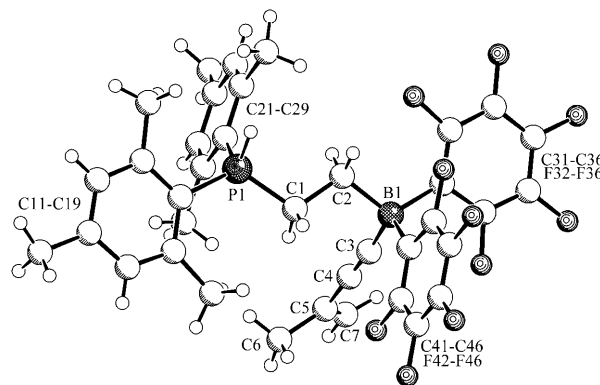


Figure 1. Molecular structure of the zwitterion **3**.

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pair **1** to the conjugated butenyne **2**. The phosphorus atom is attached to the former =CH₂ terminus. We observe corresponding [P]–CH₂ NMR resonances at $\delta = +32.8$ ppm (³¹P), $\delta = 27.6$ ppm (¹³C, ¹J_{PC} = 43.7 Hz), and $\delta = 3.07, 2.85$ ppm (¹H). The diastereotopic splitting of the ¹H NMR methylene signals is caused by the introduction of the axially chiral allene moiety within the eight-membered ring. Consequently, we also observe the typical NMR resonances of a pair of mesityl substituents at phosphorus and a pair of C₆F₅ groups at boron (¹¹B NMR: $\delta = -14.5$ ppm). The allene unit itself exhibits very typical ¹³C NMR resonances of the central sp-hybridized carbon atom ($\delta = 204.5$ ppm) and of the adjacent C(sp²) atoms [=CH $\delta = 103.4$ ppm (¹³C), $\delta = 5.85$ ppm (¹H); =C(CH₃): $\delta = 81.7$ ppm (¹³C)].

In the crystal compound *syn*-**4** features an eight-membered cyclic allene structure (Figure 2). The phosphorus center is attached to the former terminal enyne C(sp²)

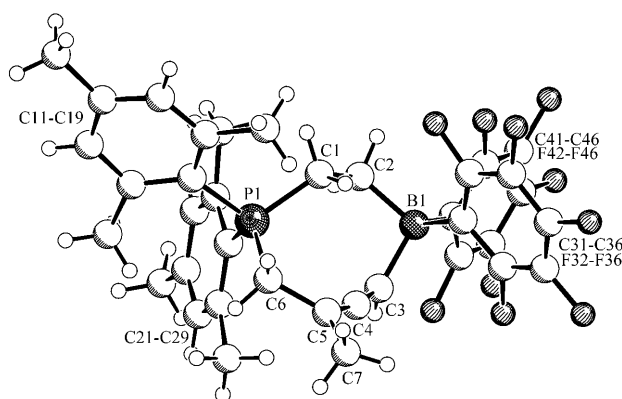


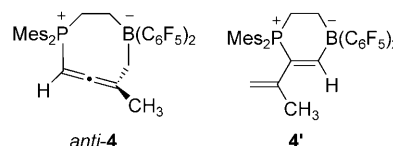
Figure 2. Molecular structure of the cyclic allene *syn*-**4**.

carbon atom [P1–C6 1.816(4) Å, C6–P1–C1 107.5(2)°] and the boron atom binds to the former ≡C–H unit of the acetylene [B1–C3 1.633(6) Å, C2–B1–C3 102.6(3)°]. The eight-membered heterocyclic framework is nonplanar [dihedral angle P1–C1–C2–B1 –89.8(4)°]. The endocyclic allene unit features internal bond lengths of 1.305(6) Å (C3–C4) and 1.311(6) Å (C4–C5); it deviates slightly from linearity [C3–C4–C5 169.0(4)°]. The substituent planes at the allene termini do not deviate much from the expected perpendicular arrangement [angle between the C6–C5–C7 and B1–C3–H planes 79.6°, bond angles C6–C5–C7 116.7(4)°, C6–C5–C4 118.3(4)°, C4–C3–B1 121.6(4)°] (for details see the Supporting Information).

The addition reaction of the Lewis pair **1** to 2-methyl-1-buten-3-yne (**2**) was studied by computational chemistry. We performed accurate quantum chemical calculations at the dispersion-corrected double-hybrid density functional level (B2PLYP-D//TPSS-D,^[19] for details see the Supporting Information) employing large Gaussian AO basis sets for various possible reaction products. Similar to other addition reactions of **1** to unsaturated substrates,^[11] the formation of *syn*-**4** is very exothermic (about –19 kcal mol^{–1}) (Table 1). The regioisomer *anti*-**4** (see Scheme 2), in which the phosphorus atom is connected to the carbon atom from the triple bond of **2**, is

Table 1: Computed reaction energies (in kcal mol^{–1}) for the formation of *syn*-**4**, its regioisomer *anti*-**4**, and the related formation of the six-membered-ring product **4'**.

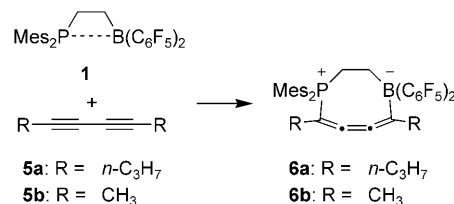
Formation of:	TPSS-D/ def2-TZVP	B2PLYP-D/ def2-TZVP
<i>syn</i> - 4 (observed)	–22.2	–18.7
<i>anti</i> - 4 (not observed)	–22.0	–17.6
4' (not observed)	–44.3	–43.5



Scheme 2. Possible isomeric addition products, *anti*-**4** and **4'**.

almost isoenergetic to *syn*-**4** (*anti*-**4** is only 0.2–1.1 kcal mol^{–1} higher in energy, which is close to the expected error of the methods). Because *anti*-**4** was not found experimentally, the preferential formation of *syn*-**4** seems not to be controlled by thermodynamics. We also considered the possible (but not observed) 1,2-addition of **1** to the triple bond of **2** leading to the formation of a six-membered-ring product **4'**. This reaction is energetically even more favored than the formation of the eight-membered-ring product *syn*-**4** by about 20 kcal mol^{–1}. This finding also indicates a kinetically controlled, rather complex reaction mechanism. In our all computational attempts so far we have not been able to locate reasonable transition states.

We were curious to learn how general this novel reaction type might be. In this respect the reaction of a conjugated diyne with the Lewis pair **1** would represent a logical but possibly challenging extension of the underlying reaction principle. Therefore, we treated **1** with 4,6-decadiyne (**5a**) (Scheme 3). When the compounds were mixed in pentane, the solution turned orange. The mixture was stirred for six days under ambient conditions to eventually produce an off-white precipitate, which was isolated in 64% yield. It contained a single product which was identified as the eight-membered heterocyclic cumulene **6a**. The product shows typical phosphonium ³¹P ($\delta = +31.6$ ppm) and borate ¹¹B NMR resonances ($\delta = -9.3$ ppm). The four separate ¹³C NMR resonances of the newly formed 1,2,3-butatriene subunit are located at $\delta = 91.9$ (=C^P), 191.4, 156.5, and 178.3 ppm (=C^B), values that are very different from the corresponding ¹³C NMR resonances of the diyne starting material **5a** ($\delta = 77.3, 66.6$ ppm).



Scheme 3. Synthesis of the cyclic cumulenes **6**.

Compound **6a** displays a chiral ring conformation in solution. This leads to the observation of the NMR signals of pairs of diastereotopic mesityl substituents at phosphorus and of diastereotopic C_6F_5 groups at boron [e.g. $\delta = -160.9$ (1F), $\delta = -161.2$ ppm (1F), $p\text{-C}_6\text{F}_5$]. Consequently, the ^1H NMR spectrum of **6a** features four separate signals of the $[\text{P}]\text{-CH}_2\text{-CH}_2\text{[B]}$ unit [$\delta = 2.78, 2.30$ ppm (P-CH_2), $\delta = 1.55, 1.12$ ppm ($\text{CH}_2\text{-B}$)].

The X-ray crystal structure analysis of **6a** (single crystals were obtained by diffusion of heptane into a benzene solution) shows an eight-membered heterocycle that features a strongly nonplanar $\text{P-CH}_2\text{-CH}_2\text{-B}$ unit [dihedral angle $\text{P1-C1-C2-B1} -129.8(2)^\circ$] and a close-to-planar endocyclic 1,2,3-butatriene subunit (Figure 3). This unit exhibits a short

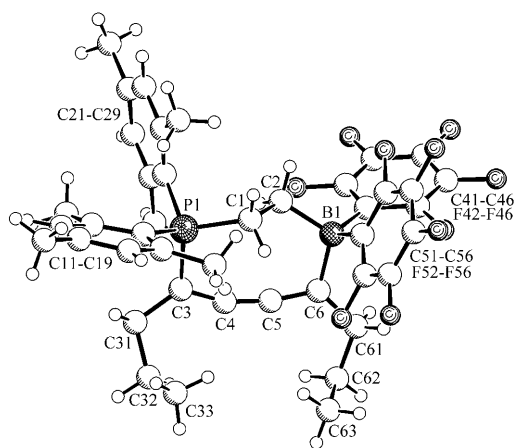


Figure 3. Molecular structure of the cyclic cumulene **6a**.

central $\text{C}(\text{sp})=\text{C}(\text{sp})$ bond ($\text{C4-C5 } 1.263(3) \text{ \AA}$) and two slightly longer adjacent $\text{C}(\text{sp})=\text{C}(\text{sp}^2)$ bonds ($\text{C3-C4 } 1.326(3) \text{ \AA}$, $\text{C5-C6 } 1.320(3) \text{ \AA}$). The central cumulene C_4 unit deviates slightly from linearity [angles $\text{C3-C4-C5 } 161.1(2)^\circ$, $\text{C4-C5-C6 } 165.0(2)^\circ$]. The planes of the substituents at the terminal cumulene $\text{C}(\text{sp}^2)$ centers are close to parallel (angle formed by the P1-C3-C31 and B1-C6-C61 planes 12.0°). The bond angles at C3 amount to $111.0(2)^\circ$ (C4-C3-P1), $124.9(2)^\circ$ (C4-C3-C31), and $123.8(2)^\circ$ (P1-C3-C31), and at C6 they are $113.0(2)^\circ$ (C5-C6-B1), $123.0(2)^\circ$ (C5-C6-C61), and $123.9(2)^\circ$ (B1-C6-C61). The lengths of the newly formed carbon-heteroatom linkages are $1.804(2) \text{ \AA}$ (P1-C3 [angle $\text{C3-P1-C1 } 105.1(1)^\circ$] and $1.651(3) \text{ \AA}$ (B1-C6 [angle $\text{C6-B1-C2 } 111.0(2)^\circ$] (for details see the Supporting Information).

The Lewis pair **1** could have undergone simple 1,2-addition reactions at the alkene (or alkyne) unit in reagent **2** (or **5a,b**). However, under the applied reaction conditions we observe in both cases the formation of the alternative 1,4-addition product, similar to the products observed recently for reactions of Lewis pairs with conjugated dienes.^[10b] Although both the heterocyclic allene *syn-4* and the heterocyclic cumulene **6a** show some distortion of their central $\text{C}=\text{C}_n=\text{C}$ moieties, the structural and spectroscopic features (and the results of the DFT calculation) indicate that these systems are probably only slightly strained. Nevertheless, they are not the thermodynamically favored isomers in the

respective reaction systems; they appear to be formed by means of a favorable kinetic pathway which must be elucidated in detail. It seems that the remarkable 1,4-addition reaction of a frustrated Lewis pair could provide a useful simple entry to the formation of cyclic systems with cumulative $\text{C}=\text{C}$ double bonds.

Experimental Section

Synthesis of **3** and *syn-4*: Dimesitylvinyolphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) in pentane (8 mL) reacted with 2-methyl-1-buten-3-yne (35 μL , 0.37 mmol) to give a mixture of **3** and *syn-4* (ratio 1:2) as a white powder (193 mg, 80%). Anal. calcd (%) for $\text{C}_{37}\text{H}_{32}\text{BF}_{10}\text{P}$: C 62.73, H 4.55; found: C 62.24, H 4.58. For more experimental details and complete characterization, see the Supporting Information.

Synthesis of **6a**: Dimesitylvinyolphosphine (100 mg, 0.34 mmol) and bis(pentafluorophenyl)borane (117 mg, 0.34 mmol) reacted with 4,6-decadiyne (55 μL , 0.34 mmol) to give an off-white powder consisting of **6a** (168 mg, 64%). Anal. calcd (%) for $\text{C}_{42}\text{H}_{40}\text{BF}_{10}\text{P}$: C 64.96, H 5.19; found: C 64.83, H 5.29. For more experimental details and complete characterization of **6a** and its similarly prepared analogue **6b**, see the Supporting Information.

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