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The frustrated Lewis pair induced formation of a pentafulvene [6 + 4] cycloaddition product†

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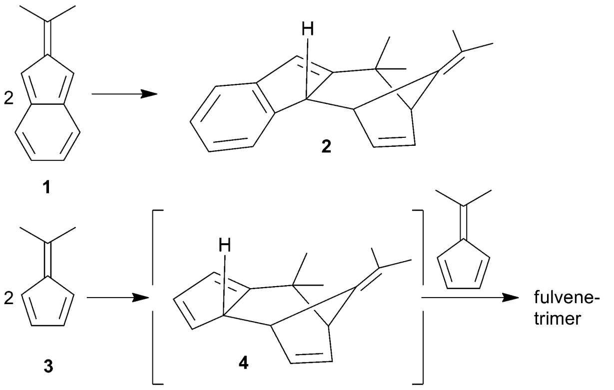
The frustrated Lewis pair $Mes_2P–CH_2CH_2–B(C_6F_5)_2$ reacts with excess 6,6-dimethylpentafulvene to yield a P/B-Lewis pair addition product to an elusive pentafulvene [6 + 4] cycloaddition dimer. This observation may open a new field of utilization of frustrated Lewis pair chemistry.

[*m* + *n*] Cycloaddition reactions are of great synthetic importance. Their detailed study has significantly contributed to the understanding of mechanistic routes taken in organic transformations.[1] The most frequently employed reaction of this type is the [4 + 2] cycloaddition, *i.e.* the Diels–Alder-reaction and its variants. Higher order cycloadditions such as the [6 + 4] or [8 + 2] cycloaddition have been studied[2] and in some cases utilized,[3] but to a much lesser extent than many of their lower congeners.

Fulvenes should be prime candidates for *e.g.* [6 + 4] cycloaddition reactions, but they mostly react by the preferred [4 + 2] reaction alternative.[4] The much more reactive isobenzofulvene **1**, however, undergoes rapid dimerization to form the respective [6 + 4] cycloaddition product **2**.[5] To the best of our knowledge, information about the [6 + 4] dimerization of simple pentafulvenes is scarce. Neuenschwander suggested the potential occurrence of a [6 + 4] intermediate **4** in the trimerization reaction of 6,6-dimethylfulvene **3** (Scheme 1). We have now found a unique way to generate the framework of the 6,6-dimethylpentafulvene [6 + 4] dimer with the aid of frustrated Lewis pair chemistry.

Frustrated Lewis pairs have been known to undergo a number of small molecule activation reactions.[6] We had shown that the P(*o*-tolyl)$_3$/B(C_6F_5)$_3$ Lewis pair can add to non-conjugated di-acetylenes to induce additional carbon–carbon coupling.[7] The very reactive intramolecular Lewis pair **5**[8] undergoes 1,2-addition reactions to olefins or acetylenes[9] but also is able to undergo 1,4-addition reactions to conjugated enynes and diynes.[10]



Scheme 1 Dimerization reactions of fulvene derivatives.

When the intramolecular frustrated Lewis pair **5** was stirred with a *ca.* 10 fold excess of 6,6-dimethylfulvene **3** in pentane at room temperature a slow reaction occurred to give a colorless precipitate. It was collected after a total of 7 days reaction time and isolated in 43% yield as an off-white solid. Single crystals suited for the X-ray crystal structure analysis were obtained from benzene/heptane by the diffusion method. It showed that we had isolated the formal addition product (**6**) to the *endo*-[6 + 4] dimer (**4**) of 6,6-dimethylpentafulvene **3** (see Fig. 1 and Scheme 2). The core of the structure contains the tricyclic ring system formally derived from the pentafulvene [6 + 4] dimerization. It features a bridgehead C=C double bond (C7–C8: 1.318(4) Å), the endocyclic C3–C4 double bond (1.313(5) Å) and the exocyclic C=CMe$_2$ bond (C11–C12: 1.319(4) Å). The (C_6F_5)$_2$B–CH$_2$–CH$_2$–PMes$_2$ system **5** is found 1,2-attached at the five-membered ring (C9–P: 1.882(3) Å, C10–B: 1.651(4) Å). The resulting P/B containing heterocycle attains a rigid boat conformation (see Fig. 1). The overall structure can formally be described as the regioselective *exo*-1,2-addition product of the P/B Lewis pair **5** to the C9=C10 carbon–carbon double bond of the *endo*-[6 + 4] dimer of 6,6-dimethylfulvene.

In solution we have also found a single diastereoisomer of **6**. It shows the ^{1}H NMR signals of two pairs of methyl groups (C12–CH$_3$/CH$_3$'; δ 1.48/1.03) and three olefinic CH signals (8-H: δ 4.65; 3-H/4-H; δ 5.91/5.98). There is a phosphonium type ^{31}P NMR resonance at δ 33.2 and a borate ^{11}B NMR signal at δ −14. Due to the chirality of the framework the

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‡ X-Ray crystal structure analyses.

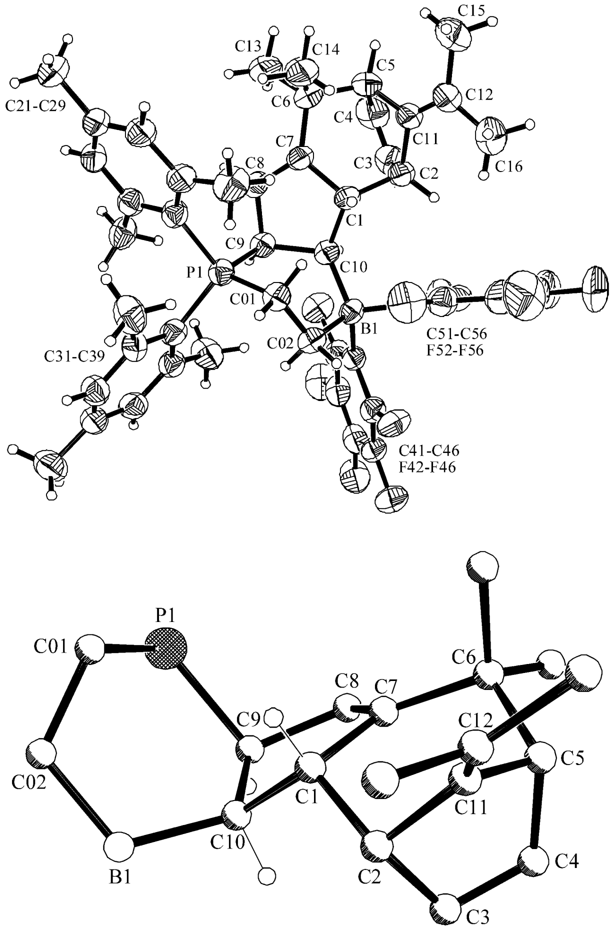
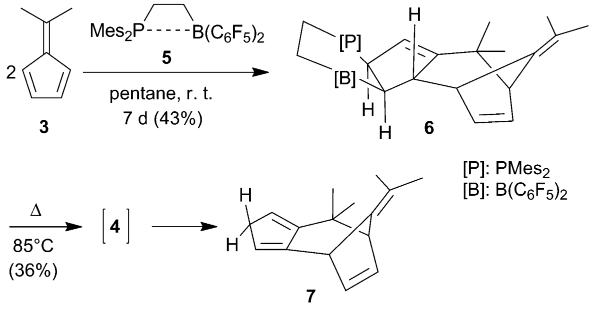


Fig. 1 Two projections of compound **6** (the lower one only contains the core atoms for clarity).



Scheme 2 Synthesis of compounds **6** and **7**.

mesityl groups at P and the C_6F_5 substituents at B are pairwise diastereotopic. Moreover, at 253 K the rotation of both the P-mesityl and B-C_6F_5 groups is frozen on the NMR time scale, so that all their core atoms feature separate individual NMR signals. Thus, we observe a total of 10 well resolved ^{19}F NMR resonances of the adduct **6** (four *ortho*, two *para* and four *meta* ^{19}F NMR signals).

Heating of the adduct **6** in d_6-benzene solution at 85 °C (6 h) resulted in a cleavage of the P/B Lewis pair from the organic framework. Admixed with some pentane, from which it was hard to separate due to its marked volatility, we isolated a hydrocarbon product in low yield (*ca.* 35%) which we tentatively assign the structure of the 6,6-dimethylfulvene [6 + 4] dimer isomer **7**. This is likely formed from the dimer **4** by means of a rapidly proceeding thermally induced 1,5-hydrogen migration inside the cyclopentadiene moiety of the dimer framework. Compound **7** features a total of four olefinic ^1H NMR signals at δ 6.13 (3-H), 6.02 (4-H), 5.96 (8-H), and 5.76 (10-H). Then there are the $^1H/^{13}C$ NMR signals of four CH_3 substituents. The 9-H/H′ resonances were found at δ 2.69/2.68.

The mechanism of the formation of the formal frustrated Lewis pair adduct **6** of the 6,6-dimethylpentafulvene [6 + 4] dimer still needs to be elucidated. It is well conceivable that the formation of the dimeric framework might have been induced by the strong boron Lewis acid part of **5**, following a cationic reaction sequence with an eventual cooperative trapping by the intramolecular phosphorus Lewis base. Alternatively, it is conceivable that the frustrated P/B Lewis pair has effectively added to the fulvene dimer **4** from an unfavorable dimer/monomer equilibrium situation.[11] Whatever the detailed mechanism might be, the remarkable formation of product **6** from the Lewis pair **5** and 6,6-dimethylfulvene, indicates that frustrated Lewis pair chemistry might actually have a much wider implication and application potential than previously thought.

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[11] Secondary orbital interactions should favor the formation of the *exo*-[6 + 4] fulvene dimer. However, the *endo*-[6 + 4] product is found to be the major product observed in the *iso*-benzofulvene dimerization reaction (see ref. 5).