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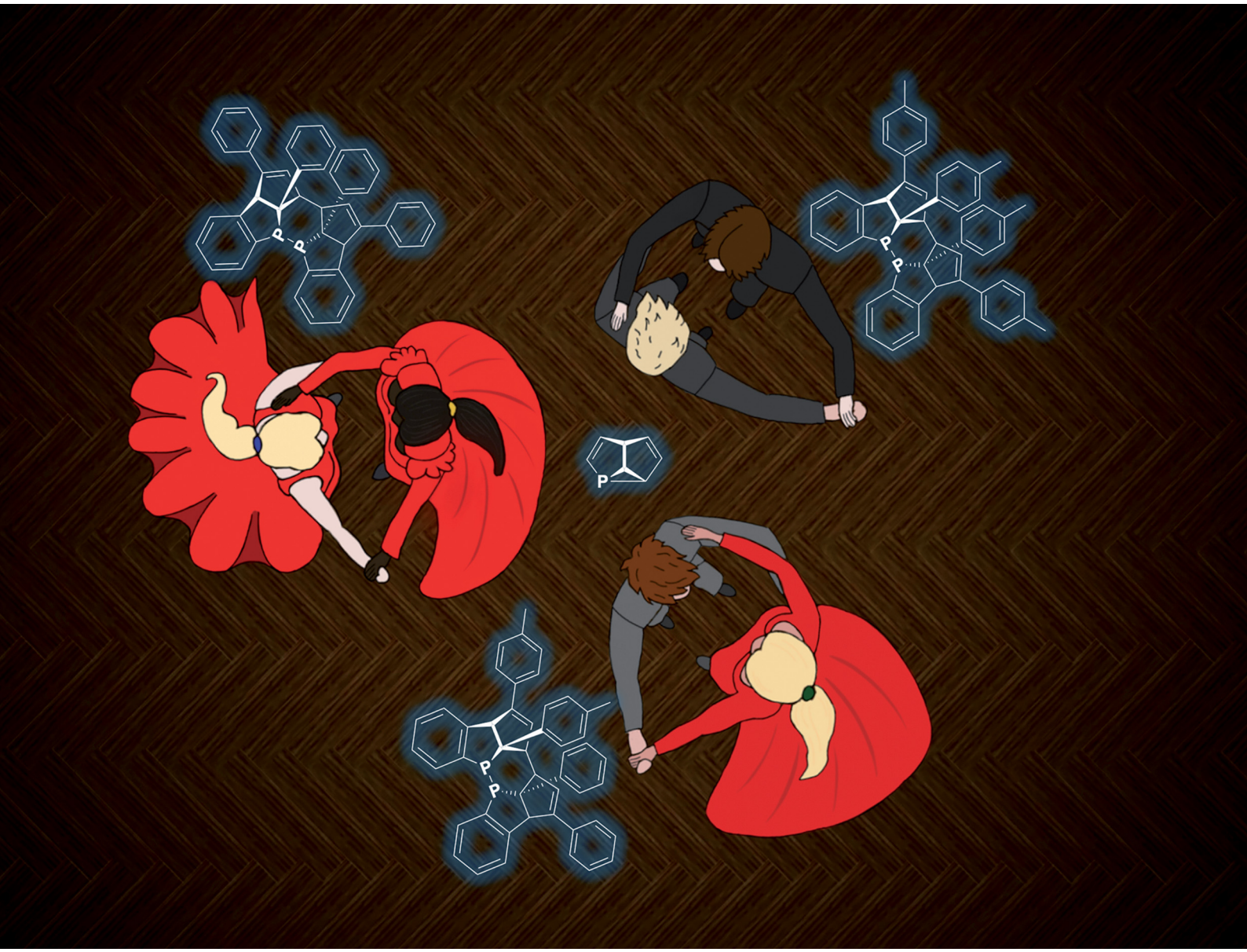

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Di-π-methane rearrangement in 1-phosphabarrelenes: formation and reactivity of an unprecedented 2-phosphasemibullvalene

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The photolysis of 1-phosphabarrelenes, generated from 3,5-diarylphosphinines and benzyne in a [4 + 2] cycloaddition reaction, affords hitherto unknown 2-phosphasemibullvalenes *via* di-π-methane rearrangement reaction. These compounds occur only as intermediates, while subsequent and rapid dimerization to 6-membered, cyclic diphosphanes with a P–P bond was observed. The results are in stark contrast to the photochemical conversion of 1-phosphabarrelenes, obtained from 2,4,6-triarylphosphinines and a strong dienophile. In this case, the corresponding 5-phosphasemibullvalenes are formed selectively and exclusively. Our results nicely demonstrate the strong impact of the substitution pattern of the starting material on the outcome of the di-π-methane rearrangement reaction.

The synthesis of barrelene (C_8H_8) with the systematic name bicyclo[2.2.2]octa-2,5,7-triene was first reported by Zimmerman and Paufler in 1960 (**A**, Fig. 1).[1] One of the most notable features of barrelene is its photochemical reactivity, particularly the di-π-methane rearrangement. Upon UV irradiation, barrelene undergoes a light-induced 1,2-shift of one π-system, forming semibullvalene **B**.[2] This reaction proceeds through a biradical intermediate formed upon excitation, which then undergoes a series of bond breaking and bond formation steps. Semibullvalene itself exhibits a rapid, degenerate Cope rearrangement (Fig. 1).[2,3]

Replacing one CH-group of barrelene by an isolobal, trivalent phosphorus atom leads to phosphabarrelenes. Among the series of known derivatives, the 1-phosphabarrelene (**C**) has first been described by Märkl and Lieb in 1968.[4] **C** was prepared by [4 + 2] cycloaddition reaction of 2,4,6-triphenylphosphinine with the strong dienophile hexafluoro-2-butyne. Later on, a series of benzophosphabarrelenes (**D**) have been prepared using *in situ* generated benzyne as highly reactive dienophile.[5] 1-Phosphabarrelenes have emerged as fascinating stereorigid phosphines (PR_3), which are used as powerful ligands in several catalytic reactions.[6–11] As an example, the enantiomerically pure pyridyl-functionalized 1-phosphabarrelene (**E**) was recently used as chiral P,N-hybrid ligands in Rh- and Ir-catalyzed hydrogenation reactions, leading to ee's of up to 95%.[12]

As we could demonstrate for the first time, also 2,4,6-triphenyl-benzophosphabarrelene **F** undergoes a photochemical di-π-methane rearrangement upon UV irradiation.[13] The light-induced reaction is highly selective and the 5-phosphasemibullvalene derivative **G**, along with its enantiomer, is formed quantitatively. Most importantly, it turned out, that

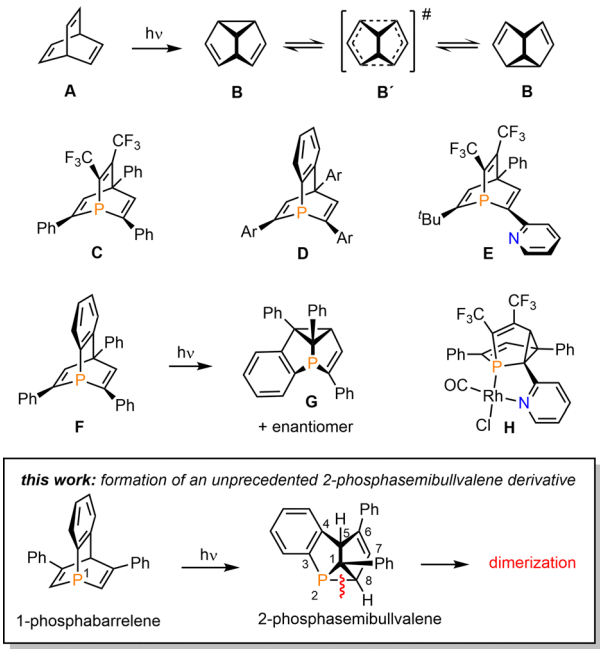

Fig. 1 Photolytic di-π-methane rearrangement of barrelene **A** to semibullvalene **B** and degenerate Cope-rearrangement to give enantiomer **B″**. Achiral (**C**) and (**D**) and chiral (**E**) 1-phosphabarrelenes, photochemical di-π-methane rearrangement of 2,4,6-triphenyl-benzophosphabarrelene **F** to 5-phosphasemibullvalene **G**, pyridyl-functionalized phosphasemibullvalene-Rh-complex **H** and brief summary of this work.

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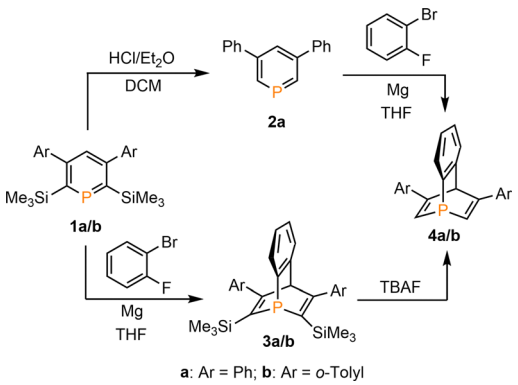
the adjacent phenyl-groups in 2- and 6-position of the phosphorus-heterocycle are important for the stabilization of one of the radicals, formed upon excitation. This leads to the exclusive formation of the observed product **G**, which is formed as a racemate. Later, we could demonstrate that the photochemical di-π-methane rearrangement can also occur in transition metal complexes based on pyridyl-functionalized 1-phosphabarrelenes. In this way, coordination compounds, such as **H**, could be obtained in up to 90% yield.[14]

Inspired by this highly selective di-π-methane rearrangement of 1-phosphabarrelenes to 5-phosphasemibullvalenes and the influence of additional phenyl-groups on the product formation, we anticipated that aryl groups located in the 3,5-position of the phosphorus heterocycle should lead to yet unknown 2-phosphasemibullvalenes. In this isomer, the phosphorus atom is incorporated in the three-membered ring of the semibullvalene core. We envisaged two possible routes towards 3,5-diaryl-benzophosphabarrelenes **4a/b** (**a**: Ar = Ph, **b**: Ar = *para*-tolyl), both starting from phosphinines **1a/b**. These aromatic phosphorus heterocycles can easily be synthesized from the corresponding diazaphosphinine (Scheme 1).[15]

First, protodesilylation of **1a** with HCl/Et_2O in dichloromethane affords the literature-known 3,5-diarylphosphinine **2a**, which shows a triplet in the ^{31}P NMR spectrum at δ(ppm) = 205,7 ($^2J_{H-P}$ = 37.0 Hz).[16] Phosphinine **2a** was further characterized crystallographically, and the molecular structure of this compound, along with selected bond lengths and angles, is depicted in Fig. 2. It turned, however, out that the [4 + 2] cycloaddition of **2a** with *in situ* generated benzyne towards the target compounds **4a** is not very selective, as several by-products could be observed in the corresponding $^{31}P\{^1H\}$ NMR spectrum, which could not be separated by conventional methods from the 1-phosphabarrelene. We therefore reacted phosphinines **1a/b** first with *in situ* prepared benzyne. In this case, 1-phosphabarrelenes **3a/b** could be obtained in reasonable yields as colorless compounds after recrystallization.[17] Both compounds show a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ(ppm) = −58.5 (**3a**)[17] and δ(ppm) = −58.2 (**3b**),



a: Ar = Ph; **b**: Ar = *o*-Tolyl

Scheme 1 Desilylation of **1a** with HCl/Et_2O to yield phosphinine **2a**, which can be converted with 1-bromo-4-fluorobenzene/Mg to 1-phosphabarrelene **4a**. Alternative conversion of **1a/b** with 1-bromo-4-fluorobenzene/Mg to yield the barrelenes **3a/b** and subsequent desilylation using TBAF·nH_2O.

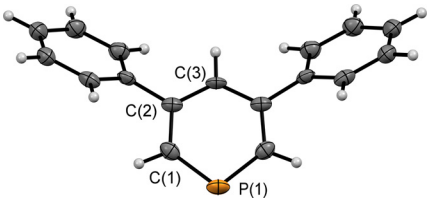


Fig. 2 Molecular structure of **2a** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–C(1): 1.712(6), C(1)–C(2): 1.410(8), C(2)–C(3): 1.406(6). C(1)–P(1)–C(1′): 101.0 (4)°.

respectively. The TMS-substituted 1-phosphabarrelene **3b** was additionally characterized crystallographically (see SI). Subsequently, desilylation of **3a/b** was achieved with tetrabutylammonium fluoride (TBAF·nH_2O) in THF. After workup and filtration of the reaction mixture over a silica plug with of *n*-pentane/toluene (see SI) the desired 1-phosphabarrelenes **4a/b** could be obtained in yields of 76% (**4a**) and 46.7% (**4b**), respectively.

The successful desilylation is apparent from the occurrence of a triplet resonance at δ(ppm) = −78.1 (both for **4a** and **4b**) in the proton-coupled ^{31}P NMR spectra. Moreover, we could further characterize the desilylated 3,5-diaryl-benzophosphabarrelene **4b** by means of single crystal X-ray diffraction (Fig. 3). Structural information of **4a** was obtained by single crystal X-ray diffraction of the corresponding 1-phosphabarrelene-selenide **4a** = Se (see SI).

J. Young NMR tube samples of **4a/b** in THF were subsequently irradiated with UV-light (λ = 365 nm) for up to 16 h and the reactions were monitored by means of NMR spectroscopy. Fig. 4 shows the ^{31}P NMR spectra for the photolysis of **4a** in THF over a time interval of 16 h. The 1-phosphabarrelene **4a** (δ(ppm) = −78.1) is gradually consumed upon irradiation with UV light. Moreover, a transient intermediate (**5a**) of low signal intensity is observed during the course of the reaction, which shows a doublet of doublet at δ(ppm) = −111.1.

This species, however, disappears with prolonged reaction time. Additionally, a new species (**6a**) is formed, which shows a single resonance at δ(ppm) = −11.6. This compound is at the same time the only species that remains in the reaction mixture after full consumption of **4a**. A similar product distribution was

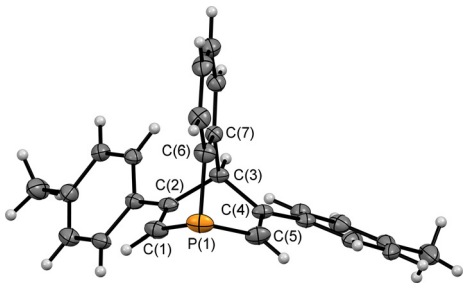


Fig. 3 Molecular structure of **4b** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–C(1): 1.837(3), P(1)–C(5): 1.829(3), P(1)–C(6): 1.849(3), C(1)–C(2): 1.341(4), C(2)–C(3): 1.535(4), C(3)–C(4): 1.535(4), C(4)–C(5): 1.334(4), C(3)–C(7): 1.528(4). Σ∢(C–P–C): 282.81°.

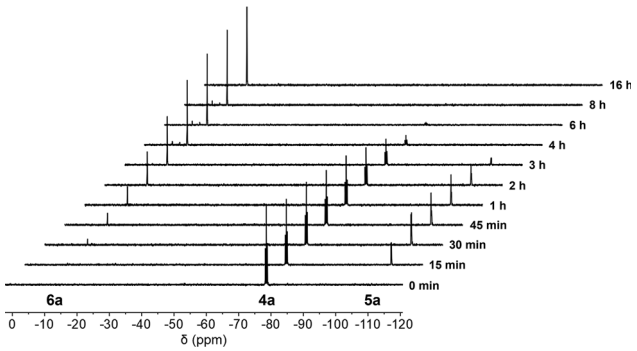
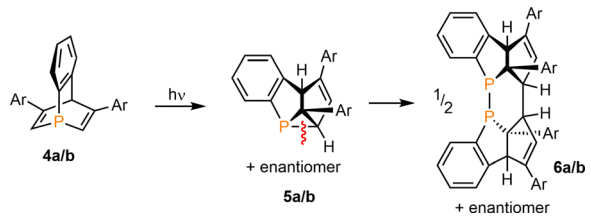


Fig. 4 ^{31}P NMR spectra of the photolysis of **4a** in THF. Time interval: 16 h.



Scheme 2 Irradiation of the 3,5-diaryl-benzophosphabarrelenes **4a/b** with UV-light yielding 2-phosphasemibullvalenes **5a/b**, which dimerize to the cyclic diphosphane **6a/b**.

also observed for the photochemical conversion of **4b** to **6b**, with **5b** as the transient intermediate (Scheme 2).

We were able to grow single crystals of the product **6b**, suitable for an X-ray crystal structure determination and the molecular structure of this compound is depicted in Fig. 5, along with selected bond lengths.

Much to our surprise the crystallographic characterization of **6b** unequivocally confirms the presence of a cyclic diphosphane, rather than the anticipated 2-phosphasemibullvalene **5b**. Upon inspection of the molecular structure, however, it is clear that **6b** was formed by cleavage of the P(1)–C(2) (respectively P(2)–C(22)) bond (Fig. 5) and subsequent dimerization, as

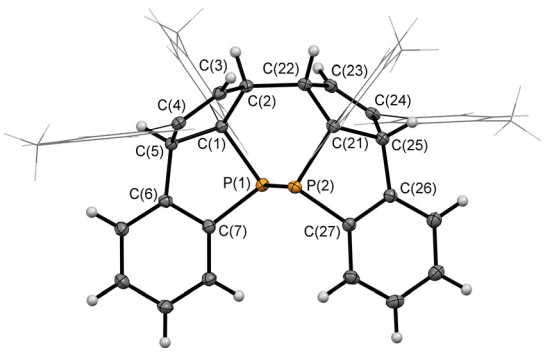
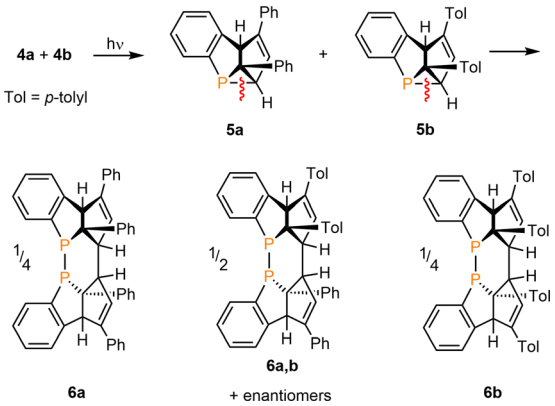


Fig. 5 Molecular structure of **6b** in the crystal, Ar groups are displayed as wireframes. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): P(1)–P(2): 2.2301(4), P(1)–C(1): 1.8867 (11), C(1)–C(2): 1.5648(15), C(2)–C(3): 1.5005(15), C(3)–C(4): 1.3409(15), C(4)–C(5): 1.5296(15), C(5)–C(1): 1.5820(15), C(2)–C(22): 1.5460 (15).

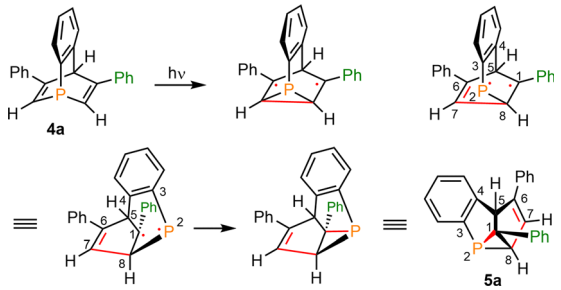


Scheme 3 Irradiation of a 1 : 1 mixture of 1-phosphabarrelenes **4a** and **4b** yielding the 2-phosphasemibullvalenes **5a** and **5b** as intermediates, which dimerize to form the homo-dimerization products **6a** and **6b** as well as the mixed hetero-dimer **6a,b**.

half of the molecule represents an almost complete 2-phosphasemibullvalene. In order to investigate whether the final product has been formed by dimerization of two 2-phosphasemibullvalenes, we irradiated a 1 : 1 mixture of **4a** and **4b** with UV light. If the intact 2-phosphasemibullvalenes **5a** and **5b** are formed by photochemical di-π-methane rearrangement of **4a** and **4b**, the subsequent dimerization should afford a mixture of the homo-dimers **6a** and **6b**, as well as the heterodimer **6a,b** in a ratio that is reasonably close to the statistically expected ratio of 0.25 : 0.5 : 0.25 (along with the corresponding enantiomers, Scheme 3 and SI).

Much to our delight, the analysis of the final product composition by means of ^{31}P NMR spectroscopy as well as mass spectrometry indeed verified the presence of the three dimeric species **6a**, **6a,b** and **6b** (see SI). This confirms, that the 2-phosphasemibullvalenes **5a** and **5b** are formed first by di-π-methane rearrangement of **4a/b**, followed by P–C bond cleavage and dimerization by C–C and P–P bond formation reactions. The P–P bond distance was found to be 2.2301(4) Å, which is similar to the values reported by Russell *et al.* for P_2-cages.[18,19]

Our findings suggest, that the transient species, observed during the photolysis of **4a/b** (Fig. 4) can be assigned to the 2-phosphasemibullvalenes **5a/b**. Since we could not isolate these compounds, we decided to verify the nature of compound **5b** by its calculated phosphorus chemical shift. For the quantum chemical calculations of the ^{31}P NMR shifts, the structures of **4b**, the possible intermediate **5b**, and the product **6b** were optimized with density functional methods as implemented in TURBOMOLE (see SI).[20] Overall, it turned out that the local hybrid CHYF-PBE and the NMR-tailored pcSseg-3 basis set lead to the best agreement with the experiment.[21,22] This results in NMR shifts of −80.9 ppm (**4b**), −109.2 ppm (**5b**), and −26.4 ppm (**6b**). The NMR shifts are sensitive to the molecular structure, *e.g.*, using the structure at the r^{2}SCAN-D4 level leads to NMR shifts of −73.9 ppm (**4b**), −98.5 ppm (**5b**), and −17.7 ppm (**6b**), respectively. For the dimer **6b**, the sterically demanding aryl groups lead to larger effects from dispersion.[23] Optimizations of r^{2}SCAN-D4 *vs.* r^{2}SCAN show that D4 leads to a shorter P–P bond length



Scheme 4 Di-π-methane rearrangement of **4a** to **5a**, based on the generally accepted mechanism for the photochemical conversion of barrelene to semibullvalene.

(223.59 pm *vs.* 224.12 pm), which is in better agreement with the crystallographic analysis. Currently, D4 parameters are not available for CHYF-PBE. Therefore, the structure optimized with r^{2}SCAN-D4 is possibly more accurate than the one optimized with CHYF-PBE for **6b**. This may rationalize the larger deviation towards the experiment. Results are, however, in excellent agreement with the experimental findings of δ(ppm) = −78.1 (**4b**), δ(ppm) = −111.7 ppm (**5b**), and δ(ppm) = −11.6 (**6b**).

We anticipate that the photochemical conversion of 1-phosphabarrelenes **4a/b** to the 2-phosphasemibullvalenes **5a/b** proceeds in an analogous manner as the di-π-methane rearrangement of benzobarrelene to benzosemibullvalene, investigated by Zimmerman and co-worker.[2]

The aryl-groups in 3- and 5-position of the 1-phosphabarrelene play an important role in the stabilization of the intermediate radicals, which leads exclusively to a racemic mixture of the novel 2-phosphasemibullvalenes. The proposed mechanism for the formation of one enantiomer of **5a** from **4a** is shown in Scheme 4.[13] The other enantiomer is formed, when the radical is stabilized by the phenyl-group on the opposite side of the heterocycle.

In conclusion, this study presents the first example of a photochemical di-π-methane rearrangement in 1-phosphabarrelenes, leading to the transient formation of previously unknown 2-phosphasemibullvalene derivatives. These highly reactive species undergo rapid dimerization to form six-membered, cyclic diphosphanes. Crucially, the substitution pattern on the phosphorus heterocycle significantly influences the rearrangement pathway: while 2,4,6-triaryl-substituted 1-phosphabarrelenes yield exclusively 5-phosphasemibullvalenes, the 3,5-substitution directs the process toward the 2-isomer. Although the 2-phosphasemibullvalene intermediates could not be isolated, their presence was confirmed by NMR spectroscopy and supported by quantum chemical calculations of phosphorus chemical shifts. X-ray crystallographic analysis of the final products confirmed the formation of cyclic diphosphanes *via* P–C bond cleavage and subsequent dimerization. These findings highlight how subtle changes in substitution can fundamentally alter photochemical reaction outcomes, offering new opportunities for tuning the reactivity of phosphorus-containing systems.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the SI. See DOI: https://doi.org/10.1039/d5cc04015a

CCDC 2471357–2471361 (**2a**, **3b**, **4b**, **6b**, **4a=Se**) contain the supplementary crystallographic data for this paper.[24a–e]

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