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Expanding the phosphorus–carbon analogy: formation of an unprecedented 5-phosphasemibullvalene derivative†

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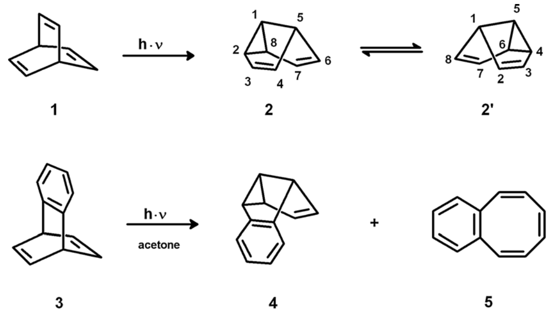
We could access for the first time a 5-phosphasemibullvalene derivative *via* quantitative and selective photochemical di-π-methane rearrangement from the corresponding phosphabarrelene. Due to the striking analogy between phosphorus and carbon, this hitherto unknown transformation of vinyl-phosphorus species provides the possibility to prepare novel, chiral and conformationally rigid organophosphorus cage compounds in a straightforward manner.

For several decades, many main-group-chemists endeavor the often very challenging and tedious preparation of phosphorus analogues of extraordinary hydrocarbon or nitrogen-containing molecules.[1] Fascinating compounds have been synthesized and, in particular, the chemistry of compounds containing P═C double and P≡C triple bonds has been investigated to quite some extent.[1,2] This also includes the access to phosphorus heterocycles and polycyclic cages.[1–3] The inspiration to this field is mainly based on the diagonal relationship between phosphorus and carbon and is justified by the isovalency between a phosphorus atom and a CH-moiety. In fact, some of these species have received tremendous interest due to their particular stereoelectronic properties, which can differ significantly from their related carbon- or nitrogen-containing counterparts.[4]

During the course of our investigations on low-coordinate phosphorus heterocycles, we came across the remarkable semibullvalene(tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**2**, **2′**)).[5,6] This compound has been the subject of intensive studies both from an experimental and theoretical point of view.[7] Semibullvalene was first synthesized by Zimmerman *et al.* *via* the photosensitized di-π-methane rearrangement of barrelene (**1**) and shows rapid degenerate Cope rearrangement (Scheme 1).[6,8,9] Substituted barrelenes, such as benzobarrelene **3**, undergo similar interconversions upon irradiation with UV-light. These transformations, however, are usually not selective and the formation of byproducts is observed in many cases.[10]



Scheme 1 Photoinduced rearrangement of barrelenes to semibullvalenes.

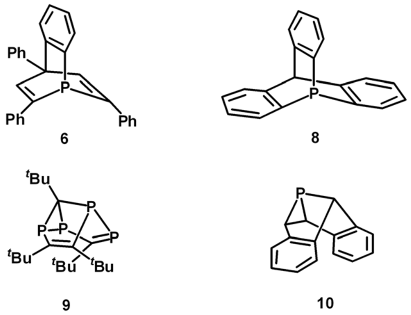


Fig. 1 Literature-known phosphabarrelene and semibullvalene derivatives.

Phosphorus derivatives of **1** and **2** are also known (Fig. 1). Phosphabarrelene **6** has first been synthesized by Märkl and coworkers through a [4+2] cycloaddition reaction of the aromatic 2,4,6-triphenylphosphinine (**7**) with *in situ* generated benzyne.[11] Derivatives of **6** were later applied very successfully by Breit *et al.* as monodentate phosphorus–ligands in the Rh-catalyzed hydroformylation of internal alkenes.[12] Related to **6** is phosphatriptycene **8**, reported by Bickelhaupt and co-workers in 1974.[13]

The formation of tetraphosphasemibullvalene **9** was observed by Regitz *et al.* during thermal cyclotetramerization of the

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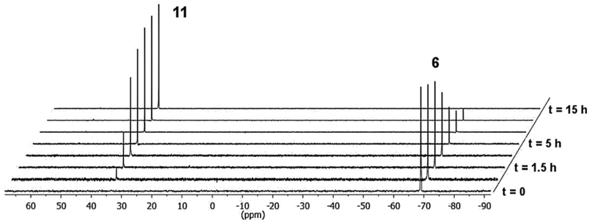


Fig. 2 Time-dependent $^{31}P\{^{1}H\}$ NMR spectra for the irradiation of **6** in THF.

corresponding phosphaalkyne and its constitution was determined by means of NMR spectroscopy.[14] The only existing mono-phosphorus containing semibullvalene derivative known until now is dibenzo-1-phosphasemibullvalene **10**, reported by Grützmacher and co-workers.[15] **10** was synthesized *via* a multistep procedure, starting from 5-chloro-5*H*-dibenzo[*a*,*d*]cycloheptene and tris(trimethylsilyl)phosphine ($P(SiMe_3)_3$). This compound turned out to be thermally unstable and its coordination chemistry has not been investigated any further.

Although phosphabarrelenes of type **6** have been known for several decades (*vide supra*), we were very surprised that no investigations on photosensitized di-π-methane rearrangements of these compounds to phosphasemibullvalene-derivatives have been described in the literature so far. As $^{31}P\{^{1}H\}$ NMR spectroscopy would provide a perfect tool for following this rearrangement reaction, we started to investigate the irradiation of a solution of **6** in THF with UV-light and the course of the reaction is depicted in Fig. 2.

Most strikingly, phosphabarrelene **6** is indeed gradually consumed upon irradiation and a new single species (**11**) is formed quantitatively within 15 h of reaction time. Compound **11** shows a resonance peak at δ (ppm) = 33.1 in the $^{31}P\{^{1}H\}$ NMR spectrum, which is almost 105 ppm downfield of the signal of the starting material (δ (ppm) = −71.8). In the $^{13}C\{^{1}H\}$ NMR spectrum of **11**, three resonance peaks can be detected in the aliphatic region at δ = 47.82, 60.43 and 63.68 ppm. These signals can be attributed to three sp^3-hybridized carbon atoms of a cyclopropane ring, integrated in a semibullvalene derivative. In contrast, starting material **6** contains only one sp^3-hybridized carbon atom, which shows a single resonance peak in the aliphatic region of the $^{13}C\{^{1}H\}$ NMR spectrum. Likewise, a new resonance peak, which integrates for one proton, can be detected at δ = 4.20 ppm in the ^{1}H NMR spectrum of the product, suggesting the successful photochemical di-π-methane rearrangement of a phosphabarrelene to a phosphasemibullvalene derivative. Moreover, the identical molecular weights of **6** and **11** were confirmed by means of mass spectrometry.

Compound **11** was obtained as a pale yellow solid but, unfortunately, no single crystals could be grown for structural characterization. We therefore attempted to convert **6** with grey selenium into the corresponding selenide **12**, hoping for a structural proof of this compound. The product could be prepared as an off-white solid in 97% isolated yield and the presence of a phosphorus–selenium species was confirmed by the presence of a ^{31}P–^{77}Se coupling constant (^{1}J = 824.9 Hz) in the $^{31}P\{^{1}H\}$ NMR spectrum of **12**.[16]

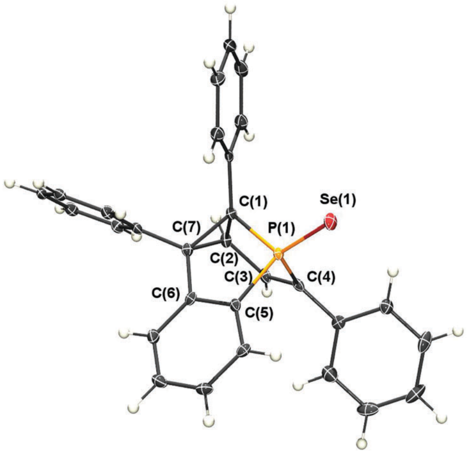
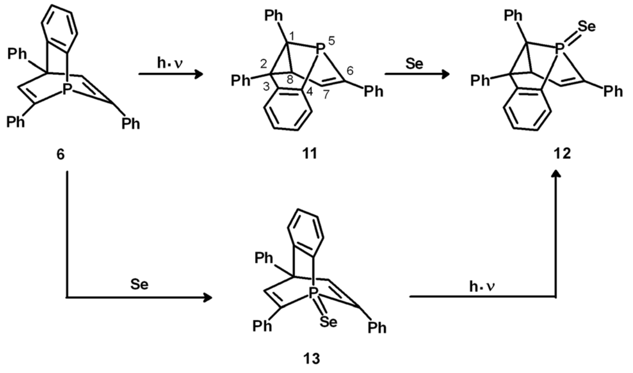


Fig. 3 Molecular structure of **12** in the crystal. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (°): P(1)–C(1): 1.842(2); P(1)–C(4): 1.816(2); P(1)–C(5): 1.801(2); P(1)–Se(1): 2.0814(6); C(1)–C(2): 1.505(3); C(1)–C(7): 1.536(3); C(2)–C(7): 1.559(3); C(2)–C(3): 1.479(3); C(3)–C(4): 1.341(3); C(5)–C(6): 1.403(3); C(6)–C(7): 1.504(3); C(1)–P(1)–C(5): 94.77(9); C(1)–P(1)–C(4): 94.60(10); C(4)–P(1)–C(5): 96.64(9).

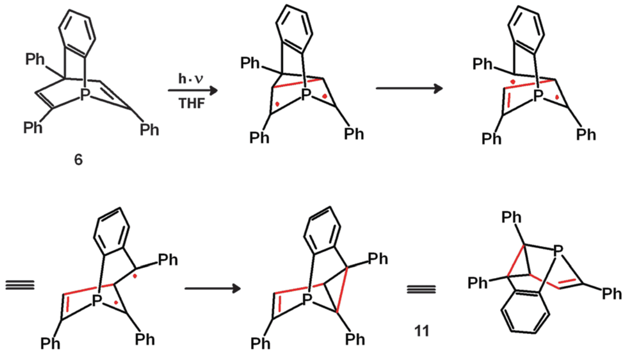
Indeed, we were able to obtain crystals of **12** suitable for single crystal X-ray diffraction *via* slow evaporation of the solvent and the molecular structure along with selected bond lengths and angles is depicted in Fig. 3. The X-ray crystal structure determination confirms that compound **12** is indeed the desired 5-phosphasemibullvalene-selenide. We can therefore assume that the photochemical conversion of phosphabarrelene **6** has led to the exclusive formation of the unprecedented and hitherto unknown 5-phosphasemibullvalene derivative **11**.

Alternatively, we found that **12** can also be obtained quantitatively from the corresponding phosphabarrelene-selenide **13**, as this compound was converted to **12** within 1.5 h upon irradiation with UV light.[17] The transformations described above are summarized in Scheme 2.

We assume that the photochemical conversion of phosphabarrelene **6** to 5-phosphasemibullvalene **11** proceeds in an analogous manner as the acetone-sensitized rearrangement of benzobarrelene **3** to benzosemibullvalene **4**, investigated by Zimmerman *et al.* (Scheme 1, *vide supra*).[10] In the case of **6**,



Scheme 2 Synthetic routes to **12**.



Scheme 3 Proposed mechanism for the di-π-methane rearrangement of phosphabarrelene **6** to 5-phosphasemibullvalene **11**.

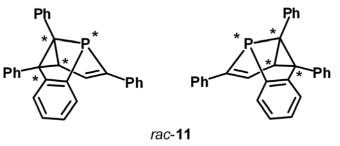


Fig. 4 The two enantiomers of **11**.

the radicals formed during interconversion are most likely stabilized by the phenyl-groups in the α-position of the phosphorus heterocycle (Scheme 3). This substitution pattern would consequently account for the high selectivity observed for the conversion of **6** to **11**, in contrast to the conversion of **3** to **4** (Scheme 3).

As obvious from Scheme 3, the conversion of the achiral phosphabarrelene **6** to the 5-phosphasemibullvalene **11** leads to the implementation of a stereogenic phosphorus atom as well as three stereogenic carbon atoms in one single step. However, since all four chiral centers are related to one another, compound **10** is only obtained as a racemic mixture (Fig. 4).

The presence of two enantiomers could indeed be verified by analyzing a sample of *rac*-**12** with the help of a chiral HPLC column. It should be noted here that the introduction of chirality into phosphabarrelenes of type **6** is obviously very difficult. Research in this direction has focused on systems containing chiral auxiliaries or the introduction of axial chirality.[18,19] In phosphasemibullvalenes of type **11**, however, the intrinsic chirality based on four stereogenic centers might lead to very interesting ligand systems based on phosphorus cages for applications in asymmetric homogeneous catalysis in the future. It should be mentioned here that **11** is a very rare example of a configurationally rigid P-chiral compound, as the two enantiomers cannot interconvert without breaking any C–C bond.[20]

In order to evaluate the Tolman electronic parameter χ of **11** and to compare it with related phosphorus-compounds, we investigated the coordination chemistry of **11** as well as of phosphabarrelene **6** and the related 2,4,6-triphenylphosphinine (**7**) towards Ni(0).[21] The phosphorus compounds were reacted with a slight excess of $Ni(CO)_4$ in a Young-NMR tube and the conversion was monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy. After full conversion, all volatiles were removed *in vacuo* and the corresponding $LNi(CO)_3$ complexes **14**, **15** and **16** were obtained quantitatively (Fig. 5).

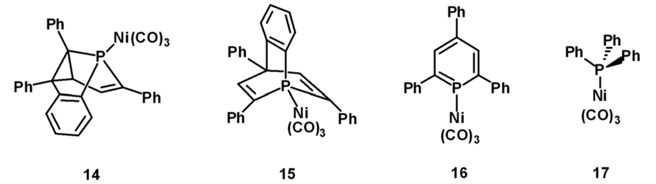


Fig. 5 $Ni(CO)_3$ complexes of 5-phosphasemibullvalene (**14**), phosphabarrelene (**15**), 2,4,6-triphenylphosphinine (**16**) and triphenylphosphine (**17**).

Table 1 Selected spectroscopic data

Compound	$\tilde{\nu}_{(CO)}$ [cm^{-1}] (CH_2Cl_2)	TEP χ (ligand)
16	2079	23
15	2075	19
14	2074	18
17	2069	13

The relevant IR-spectroscopic data ($\tilde{\nu}$ A_1) of this series of Ni(0) complexes are summarized in Table 1, with $Ph_3PNi(CO)_3$ (**17**) as the reference compound. As expected, the aromatic 2,4,6-triphenylphosphinine **7** is the best π-acceptor with the lowest net-donor capability, while phosphabarrelene **6** is a somewhat better σ-donor. Apparently, 5-phosphasemibullvalene **11** can be considered as a slightly stronger net-donor than **6**, while triphenylphosphine is the strongest net-donor within this series.

In summary, we have demonstrated the access to novel, chiral phosphorus cage compounds by photochemical di-π-methane rearrangement of phosphabarrelenes. 8,10,11-Triphenyl-1-phosphatricyclo-[6.2.2.0^{2,7}]dodeca-2(7),3,5,9,11-pentaene (**6**) was quantitatively and selectively converted to the corresponding, hitherto unknown, 5-phosphasemibullvalene derivative (**11**) upon irradiation with UV-light. The product was unambiguously identified by means of single crystal X-ray diffraction of the phosphorus-selenide (**12**). First results on the ligand properties and on the coordination chemistry of **11** have been obtained. The here presented results describe a new approach for the preparation of novel chiral and configurationally stable organophosphorus compounds based on a di-π-methane rearrangement reaction. Although the phosphorus carbon analogy has been well established for many years, it generally refers to compounds with formally sp^2 hybridized atoms. It is thus interesting to note that the here described results apparently demonstrate also a striking analogy between formally sp^3-hybridized phosphorus and carbon centers.

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