

# Tunable Cyclopentane-1,3-diyls Generated by Insertion of Isonitriles into Diphosphadiazanediyls

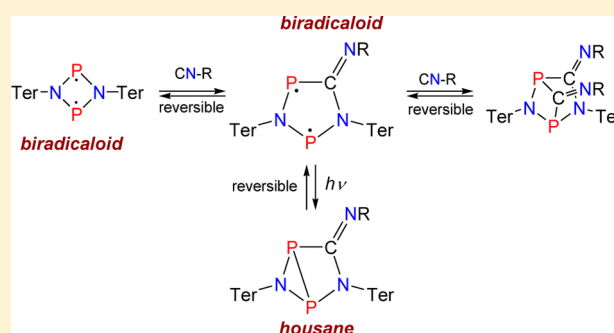
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**S** Supporting Information

**ABSTRACT:** Diphosphadiazanediyl ( $[P(\mu\text{-N}Ter)]_2$ , **1**) is known to readily react with small molecules bearing multiple bonds to give [2.1.1]bicyclic species. On the contrary, in the reaction of isonitriles with **1**, planar five-membered heterocycles (**3**) with biradical character are formed by insertion of the carbon atom into one P–N bond. Under irradiation, heterocyclic biradicaloids **3** are shown to generate housane-type [2.1.0]-bicyclopentanes by transannular bond formation. However, these housane species thermally equilibrate, reforming the open-shell singlet cyclopentenediyl. The biradical character of **3** indicates high reactivity which is further demonstrated in the activation of small molecules bearing multiple bonds leading to [2.2.1]bicyclic heterocycles. Depending on the substituent of the isonitrile, the reaction with a second equivalent of isonitrile is also observed for smaller substituents. By employing suitable diisonitriles, even the catenation of two open-shell singlet cyclopentane-1,3-diyls is achieved. CASSCF(6,6) computations revealed biradical character for **3** ranging between 26 and 27%.

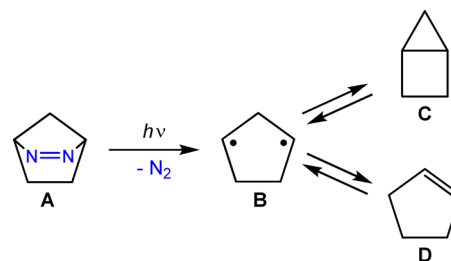


## INTRODUCTION

As early as 1915, Schlenk and Brauns described the first paramagnetic biradical obtained in the reaction of tetraphenyl-*m*-xylenedichloride with metals such as copper alloys or silver.<sup>1</sup> They clearly stated that the product of this dehalogenating process contains two trivalent carbon atoms and called this species a divalent radical. Since biradicals are putative intermediates in the processes of bond formation and bond breaking, their characterization and isolation are of great interest.<sup>2–4</sup> In cycloadditions, biradicals were identified as obligatory intermediates.<sup>5</sup> Implicitly, biradicals are highly reactive species, which allows a rich follow-up chemistry.<sup>6–11</sup> The term biradicaloids used throughout this paper refers to a subset of biradicals with two radical centers interacting significantly.<sup>12</sup>

Cyclopentane-1,3-diyls have been targeted frequently in recent research (species **B** in Scheme 1).<sup>2,13–18</sup> These species can be conveniently generated by photolytic denitrogenation of the corresponding azoalkanes (species **A** in Scheme 1). After the first observation of the parent cyclopentane-1,3-diyl in 1975 by Buchwalter and Closs,<sup>19</sup> pioneering work in this area with substituted cyclopentane-1,3-diyls has been carried out by the groups of Adam, Abe, and Borden who observed singlet as well as triplet cyclopentane-1,3-diyls.<sup>2,13–18</sup> Cyclopentane-1,3-diyls were determined to have a very small singlet–triplet gap of only <3 kcal mol<sup>−1</sup> as shown by Roth et al.<sup>20</sup> But usually, cyclopentenediyls are very short-lived and could be mostly observed as transient species (selected examples are shown in

Scheme 1. Generation of Cyclopentane-1,3-diyl (species **B**)



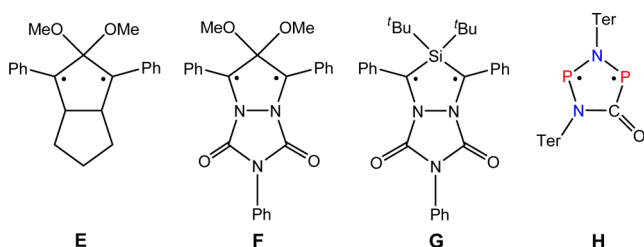
Scheme 2; E, F, and G). Isolable substances within the class of cyclopentenediyls are either trapping products,<sup>13,16,21,22</sup> or isomeric species such as [2.1.0]bicyclopentanes<sup>14,15,23–30</sup> and cyclopentenes if group migration is possible (species **C** and **D** in Scheme 1, or species **I**, **J**, and **K** in Scheme 3).<sup>31,32</sup> Abe et al. carried out computational studies on the lifetime of cyclopentenediyls, which is strongly influenced by stretch and cooperative effects.<sup>33,34</sup> An important contribution to the understanding of the chemistry of cyclopentane-1,3-diyl was made by Carpenter, utilizing labeling experiments and theoretical methods.<sup>35</sup>

Our group recently reported on the activation of CO by cyclophosphadiazanediyl (**1**),  $[P(\mu\text{-N}Ter)]_2$ , that lead to the isolation of the first stable cyclopentane-1,3-diyl derivative with

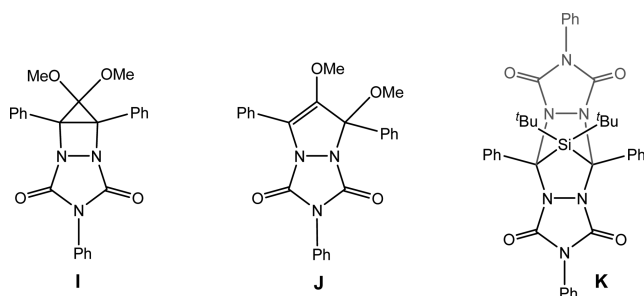
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**Scheme 2. Selected Observed CyclopentanediyIs with Different Heteroatom-Substitution Patterns (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl)**

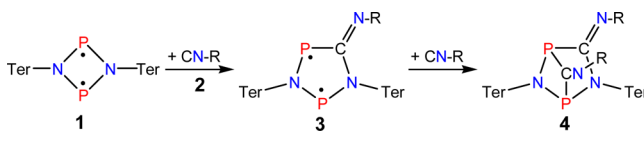


**Scheme 3. Selected Known Isomerization Products (I and J) and Trapping Products (K) of CyclopentanediyIs**



a  $P_2N_2C$  five-membered heterocycle and an exocyclic CO functionality (Scheme 2, species H).<sup>36,37</sup> Since isonitriles (2) show similar electronic properties to CO but allow tuning of the electronic properties by different substitution, we were intrigued by the idea to study the activation of isonitriles by cyclodiphosphadiazanediyls (1, Scheme 4). In this contribution,

**Scheme 4. Activation of Isonitriles with 1**



we present our results with respect to the activation of isonitriles, which depends on the steric influence of its organic substituent. By employing bifunctional isonitriles in the reaction with 1, catenated cyclopentane-1,3-diyls could be obtained featuring four radical centers. The reactivity of the 1,3-diphospha-2,4-diazacyclopentane-1,3-diyls (3) is still high and was studied in the activation of small molecules.

## RESULTS

### Synthesis and Reactivity of Cyclopentane-1,3-diyls: Influence of the Substituent.

In a series of experiments we investigated the reaction of 1 with isonitriles CN-R (2R), in the hope to yield the novel five-membered heterocyclic biradicaloids 3R (Scheme 4). To study steric and electronic effects, four differently substituted isonitriles CN-R with R = N(SiMe<sub>3</sub>)<sub>2</sub>, <sup>t</sup>Bu, 2,6-dimethylphenyl (Dmp), and 2,6-bis(2,4,6-trimethylphenyl)-phenyl (Ter) were utilized. It should be noted that the steric strain (maximal cone angle for  $d_{cov}(R-NC) = 1.45 \text{ \AA}$ <sup>38,39</sup> in 2R decreases along the series R = <sup>t</sup>Bu (160°) < Dmp (199°) < N(SiMe<sub>3</sub>)<sub>2</sub> (218°) < Ter (232°), while the positive partial charge at the carbon atom increases along R = N(SiMe<sub>3</sub>)<sub>2</sub> < <sup>t</sup>Bu < Dmp < Ter (Table S1). Consequently,

biradicaloids of the type 3R could only be observed for R = <sup>t</sup>Bu, Dmp, and N(SiMe<sub>3</sub>)<sub>2</sub> but not for the bulky terphenyl substituent, for which no reaction was detected. Obviously, both the steric congestion and the electronic situation for 2Ter/3Ter are not favorable to allow insertion into the four-membered P<sub>2</sub>N<sub>2</sub> ring of 1.

A completely different situation is found for the highly reactive isonitrile 2N(SiMe<sub>3</sub>)<sub>2</sub> which was readily activated by diphosphadiazanediyl 1, and in a 1:1 stoichiometric reaction full conversion of the isonitrile was observed within minutes, finally yielding a dark green solution. However, <sup>31</sup>P NMR spectra revealed a mixture of several species in solution, among which even the starting material 1 was identified (+276.4 ppm). Utilizing an excess of the isonitrile 4N(SiMe<sub>3</sub>)<sub>2</sub> did not lead to a “controlled” reaction with exclusive formation of either 3N(SiMe<sub>3</sub>)<sub>2</sub> and/or 4N(SiMe<sub>3</sub>)<sub>2</sub>. According to <sup>31</sup>P NMR studies, this reaction resulted in the formation of the targeted biradicaloid 3N(SiMe<sub>3</sub>)<sub>2</sub> (18%, Scheme 4, cf. Table 1), double

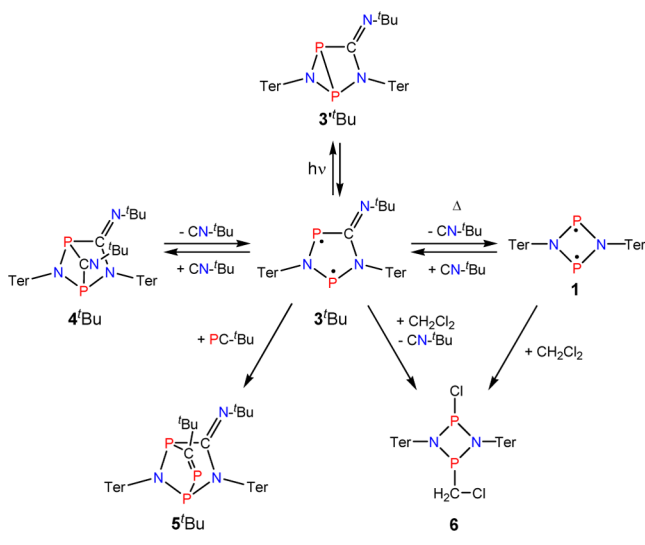
**Table 1. Selected NMR Spectroscopic Data<sup>a</sup>**

	$\delta(^{31}\text{P})$ , ppm	$ J_{\text{pp}} $ , Hz
CyclopentanediyIs		
3N(SiMe <sub>3</sub> ) <sub>2</sub>	+274.5, +228.5	151
3 <sup>t</sup> Bu	+260.6, +196.6	146
3Dmp	+258.4, +222.3	136
10 (Z,Z isomer)	+259.3, +223.4	141
Housane Isomers		
3 <sup>t</sup> Bu	-60.7, -106.4	57
3 <sup>t</sup> Dmp	-63.6, -129.4	60
10 <sup>o</sup> (main isomer) <sup>b</sup>	-62.9, -125.9	67
[2.1.1]Bicyclic Species		
4N(SiMe <sub>3</sub> ) <sub>2</sub>	+240.8, +146.9	26
4 <sup>t</sup> Bu	+210.8, +166.7	31
[2.2.1]Bicyclic Species		
5 <sup>t</sup> Bu <sup>c</sup>	+368.5, +127.1, +58.2	224, n.r., 16 <sup>d</sup>
5Dmp <sup>c</sup>	+345.5, +146.2, +80.4	244, 13, 15
7	+107.7, +61.1	22
11 <sup>o</sup> ([2.2.1] part) <sup>c</sup>	+344.9, +146.3, +80.8	242, 10, 14
11 <sup>o</sup> (biradicaloid part) <sup>c</sup>	+258.4, +221.4	136
11 <sup>o</sup> (main isomer) <sup>b,c</sup>	+344.9, +146.0, +80.2	240, n.r., n.r. <sup>d</sup>

<sup>a</sup>Depicted <sup>31</sup>P NMR spectra can be found in the SI. <sup>b</sup>three different isomers were observed, here only the dominant signal is presented. <sup>c</sup>AMX spin systems, given in the order:  $\delta(A)$ ,  $\delta(M)$ ,  $\delta(X)$ ; couplings  $J_{AM}$ ,  $J_{AX}$ ,  $J_{MX}$ ; <sup>d</sup>n.r. = not resolved.

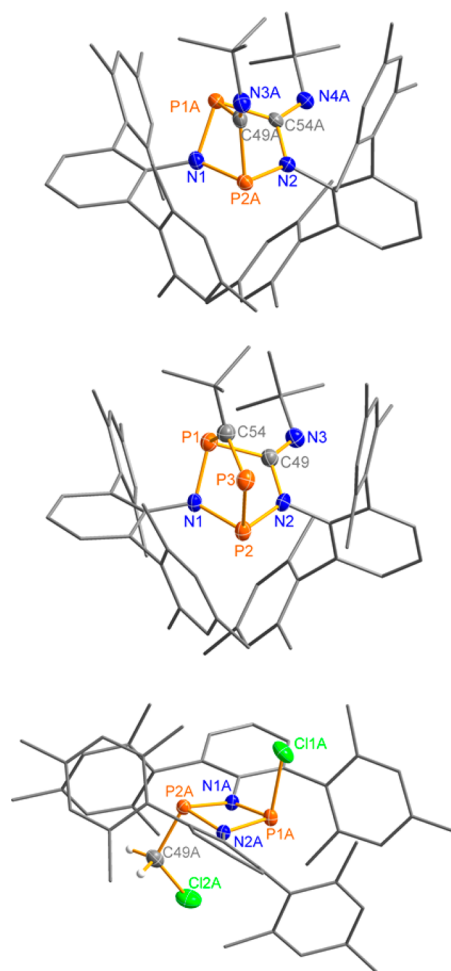
addition product 4N(SiMe<sub>3</sub>)<sub>2</sub> (34%), and dicyano-cyclodiphosphadiazane [(NC)P( $\mu$ -N<sup>Ter</sup>)<sub>2</sub>] (15%, *cis*-[(NC)P( $\mu$ -N<sup>Ter</sup>)<sub>2</sub>] + 159.3, *trans*-[(NC)P( $\mu$ -N<sup>Ter</sup>)<sub>2</sub>] + 174.4 ppm) and further unidentified products (33%, cf. Figure S1). All attempts to isolate 3N(SiMe<sub>3</sub>)<sub>2</sub> and 4N(SiMe<sub>3</sub>)<sub>2</sub> failed, so there was a need to employ less reactive and more stable isonitriles in the reaction with 1.

Conversion of orange 1 with 1 equiv of colorless 2<sup>t</sup>Bu again afforded a green solution within minutes. <sup>31</sup>P NMR spectra indicated the presence of the cyclopentanediyI derivative 3<sup>t</sup>Bu (13%), [2.1.1]bicyclic 4<sup>t</sup>Bu (50%), and even housane-type 3<sup>t</sup>Bu (6%) and the starting material 1 (31%, Table 1, Scheme 5, Figure S2). With an excess of the isonitrile, pure colorless 4<sup>t</sup>Bu could be isolated in good yield (53%) and fully characterized (Table 1, Figure 1 top). Interestingly, upon redissolution of 4<sup>t</sup>Bu, the solution unexpectedly turned green again indicating partial formation of biradicaloid 3<sup>t</sup>Bu. Indeed,

Scheme 5. Equilibrium Chemistry of  $4^t\text{Bu}$  in Solution along with Trapping Reactions of  $3^t\text{Bu}$  with  $\text{CH}_2\text{Cl}_2$  and  $\text{PC}^t\text{Bu}$ 

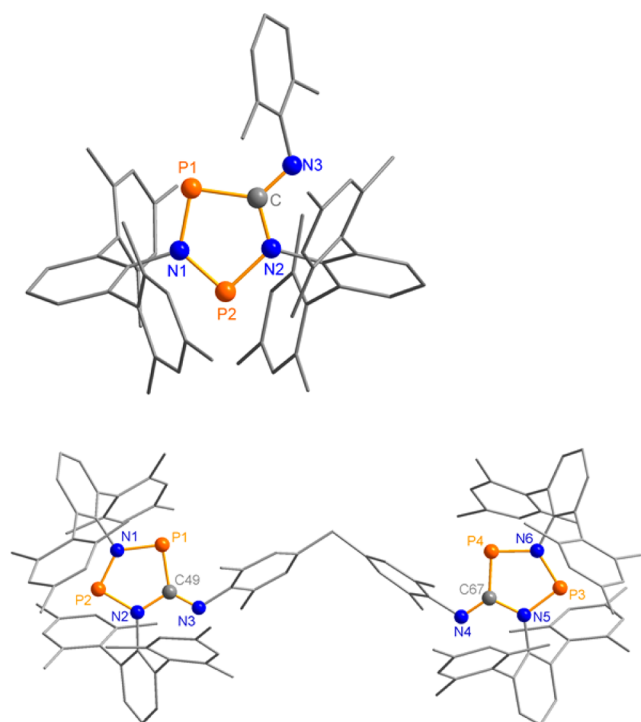
variable-temperature  $^{31}\text{P}$  NMR studies revealed again equilibrium chemistry between  $4^t\text{Bu}$ ,  $3^t\text{Bu}$ ,  $3'^t\text{Bu}$  and upon heating even **1** as depicted in Scheme 5. Obviously,  $4^t\text{Bu}$  is labile in solution releasing easily 1 or 2 equiv of the isonitrile depending on the temperature. This equilibrium chemistry raised the question if it is possible to trap intermediately formed cyclopentenediyl  $3^t\text{Bu}$  at ambient temperature with the phosphalkyne  $\text{PC}^t\text{Bu}$ , affording [2.2.1]bicyclic  $5^t\text{Bu}$  (Scheme 5). For this purpose,  $4^t\text{Bu}$  was dissolved in benzene, and  $\text{PC}^t\text{Bu}$  was added. Volatiles were removed in vacuo, and after recrystallization yellow crystals of neat  $5^t\text{Bu}$ , which could be fully characterized (Table 1, Figures 1 and S4), were obtained in good isolated yields (53%). The  $^{31}\text{P}$  NMR spectrum revealed an AMX pattern with three distinct resonances (+368.5  $\text{PC}=\text{PP}$ , +127.1  $\text{PC}=\text{PP}$ ; +58.2 ppm  $\text{PC}=\text{PP}$ , Table 1, Figure S4). Another experimental indication for the intermediate formation of biradicaloid  $3^t\text{Bu}$  was observed, when  $4^t\text{Bu}$  was dissolved in  $\text{CH}_2\text{Cl}_2$ . From this reaction 1-chloro-3-chloromethylene-cyclopentane-1,3-diphospha-2,4-diazane **6** could be isolated in 83% yield. It should be noted that also **1** reacts with  $\text{CH}_2\text{Cl}_2$  affording **6**.

Since the steric influence of the  $^t\text{Bu}$  substituent was apparently too small to prevent a second isonitrile from reacting with the cyclopentane-1,3-diyl, the bulkiness was increased to be capable of exclusively isolating the cyclopentane-1,3-diyl species. For this reason, we tried isonitrile **2Ter**, which showed no reaction, but **2Dmp** enabled a stoichiometric reaction with **1** to exclusively afford blue open-shell singlet biradicaloid **3Dmp** (Scheme 4). Even when an excess of the isonitrile was used, no formation of **4Dmp** or any other product was observed. Complete transformation of **1** with **2Dmp** in benzene was achieved within 2 h at ambient temperatures yielding dark blue block-shaped crystals of **3Dmp** (86% yield). The  $^{31}\text{P}$  NMR spectrum of **3Dmp** displayed the expected two doublet resonances at +258 and +222 ppm with a  $^2J_{\text{PP}}$  coupling constant of 136 Hz (Table 1, Figure S3). X-ray crystal analysis unequivocally revealed the existence of biradicaloid **3Dmp** (see below, Figure 2), which can be prepared in bulk and decomposes at 260 °C. These properties allow follow-up chemistry, and thus render this species a valuable starting material for the activation of small molecules.



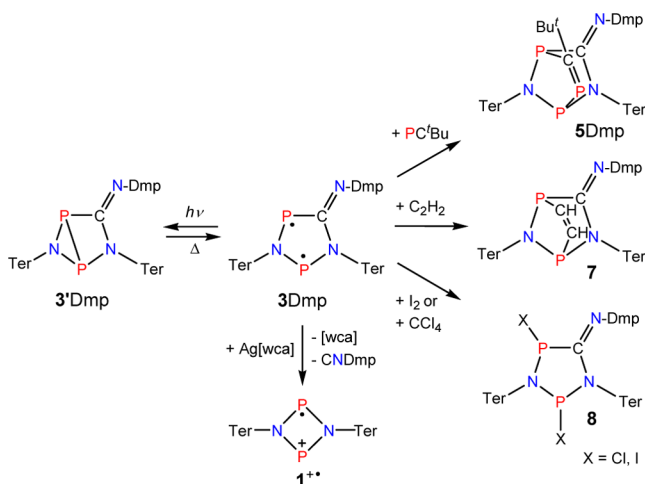
**Figure 1.** Molecular structure of  $4^t\text{Bu}$  (top),  $5^t\text{Bu}$  (middle), and **6** in the crystal. Thermal ellipsoids set to 50% probability at 173 K. Selected bond lengths [Å] and angles [°] (disorder found in  $4^t\text{Bu}$  and **6**, data for main part):  $4^t\text{Bu}$ : P1–N1 1.742(2), P1–C54 1.884(3), P1–C49 1.934(2), P1–P2 2.6280(7), P2–N2 1.731(2), P2–N1 1.770(2), P2–C49 1.887(2), N3–C49 1.249(2), N3–C50 1.494(3), N4–C54 1.276(3), N4–C55 1.482(2);  $5^t\text{Bu}$ : P1–N1 1.750(3), P1–C54 1.868(3), P1–C49 1.885(3), P2–N2 1.709(3), P2–N1 1.737(3), P2–P3 2.272(1), P3–C54 1.674(4), C49–N3 1.272(4), C49–N2 1.418(4), N1–C1 1.444(4), N2–C25 1.454(4), N3–C50 1.487(5), C54–P3–P2 94.7(1), P3–C54–P1 118.0(2); **6**: Cl1–P1 2.1872(8), Cl2–C49 1.770(2), N1–C1 1.426(2), N1–P1 1.709(2), N1–P2 1.763(2), N2–C25 1.415(2), N2–P1 1.707(2), N2–P2 1.747(2), P1–P2 2.6001(7), P2–C49 1.845(2), Cl2–C49–P2 116.85(1).

The reactivity of **3Dmp** was investigated in the activation of small molecules bearing single, double, and triple bonds. Reaction with the triple bonds of  $\text{PC}^t\text{Bu}$  and  $\text{C}_2\text{H}_2$  led to the isolation of the addition products **5Dmp** and **7**, respectively (Scheme 6), which were isolated and fully characterized (Figure 3). Again the  $^{31}\text{P}$  spectrum of **5Dmp** features the expected AMX pattern (Figure S5) with three resonances at +345.5 ( $\text{PC}=\text{PP}$ ), +146.2 ( $\text{PC}=\text{PP}$ ), and +80.4 ppm ( $\text{PC}=\text{PP}$ ) in accord with the values observed for  $5^t\text{Bu}$  (vide supra, Table 1). Halogenation was possible with elemental iodine as well as with  $\text{CCl}_4$  leading to the formation of **8I** and **8Cl** as indicated by mass spectroscopic and NMR experiments (see SI). It is noteworthy to mention that the formation of several isomers aggravated crystallization, so the isolation of larger amounts of pure substances failed. Finally, we tried to oxidize **3Dmp**



**Figure 2.** Molecular structure of 3Dmp (top) and 10 (bottom) in the crystal. Listed below are selected computed bond lengths [Å] and angles [°] which are in good agreement with the poor X-ray data: 3Dmp: P1–P2 2.958, P1–C 1.803, P1–N1 1.739, P2–N1 1.664, P2–N2 1.695, N2–C 1.422; N1–P1–C 92.6, N1–P2–N2 94.5; 10: P1–P2 2.979, P3–P4 2.979, P1–C49 1.816, P4–C67 1.816, P1–N1 1.669, P2–N2 1.738, P3–N6 1.670, P4–N6 1.738, P2–N2 1.693, P3–N5 1.693, N2–C49 1.417, N5–C67 1.417; N1–P1–C49 91.7, N6–P4–C67 91.7, N1–P2–N2 93.5, N6–P3–N5 93.5.

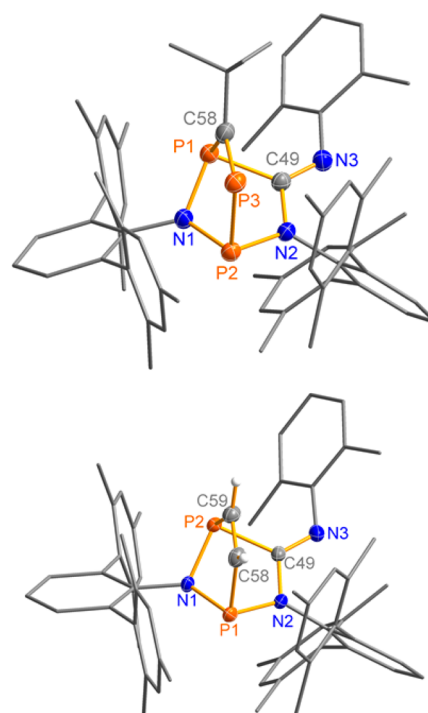
**Scheme 6. Activation of Small Molecules with 3Dmp Affording 5Dmp, 7, and 8<sup>+</sup>**



<sup>a</sup>Oxidation with Ag[wca] yielding radical cation 1<sup>+</sup>.

utilizing an Ag[wca] salt [wca] = tetrakis-pentafluorophenylborate) which resulted in an immediate change of color from blue to orange due to the expulsion of the isonitrile and formation of the known radical salt [(P(μ-NTer))<sub>2</sub>(B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)] (species 1<sup>+</sup> in Scheme 6).<sup>40</sup>

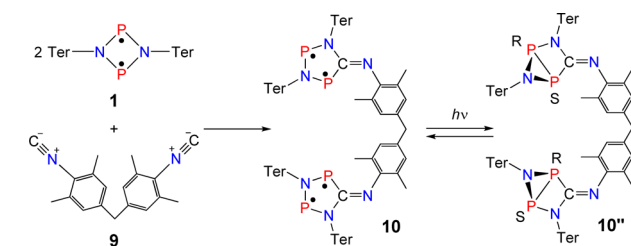
**Synthesis of a Tetradicaloid by Catenation of Two Cyclopentane-1,3-diyls.** In a last series of experiments, we



**Figure 3.** Molecular structure of 5Dmp (top) and 7 (bottom) in the crystal. Thermal ellipsoids set to 50% probability at 173 K. Selected bond lengths [Å] and angles [°]: 5Dmp: P1–N1 1.740(2), P1–C58 1.866(2), P1–C49 1.887(2), P2–N1 1.735(2), P2–N2 1.739(2), P2–P3 2.2664(9), P3–C58 1.674(2), N2–C49 1.401(2), N3–C49 1.276(2), N3–C50 1.416(2); C58–P3–P2 94.32(7), P3–C58–P1 118.4(1). 7: P1–N1 1.743(1), P1–N2 1.756(1), P1–C58 1.857(1), N1–P2 1.748(1), P2–C59 1.852(1), P2–C49 1.883(1), N3–C49 1.274(2), N3–C50 1.421(2), C58–C59 1.332(2); C58–C59–P2 113.00(9), C59–C58–P1 112.69(9).

attempted the catenation of cyclopentane-1,3-diyls by employing a bifunctional isonitrile in the reaction with [P(μ-NTer)]<sub>2</sub> (1). To ensure a similar reactivity compared to 2Dmp, a diisonitrile, 4,4'-methylenebis(2,6-dimethylphenyl-isonitrile) (9), featuring comparable structural and electronic properties was chosen (Scheme 7). Both starting materials 1 and 9

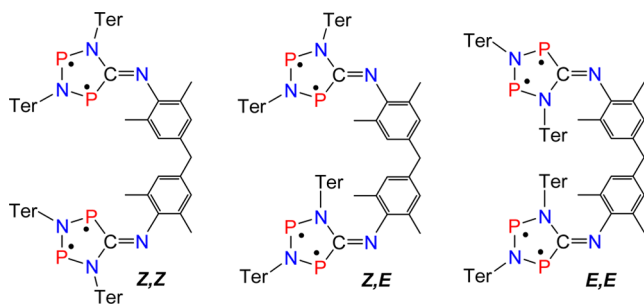
**Scheme 7. Catenation of Two Cyclopentane-1,3-diyls**



combined as solids, and benzene was added as solvent at ambient temperatures, resulting in the formation of a blue solution after <30 min. From this reaction mixture dark blue black-shaped crystals could be isolated in good yields (78%). X-ray elucidation unequivocally revealed the existence of the desired tetradicaloid as illustrated in Figure 2 (Scheme 7). Interestingly, with respect to the C=N double bond of the inserted isonitrile group there are three isomers of 10 possible (Z,Z; Z,E; E,E; Scheme 8). In solution only two, namely the Z,Z and Z,E isomers were detected in the ration 9:1 as



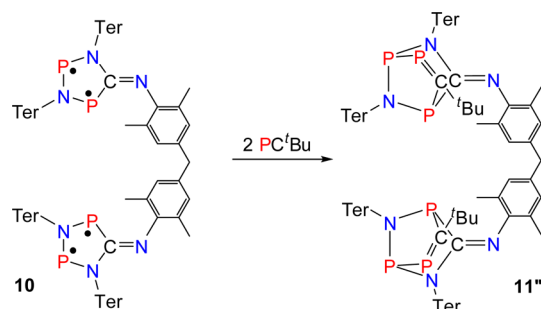
Scheme 8. Isomers of 10



indicated by two sets of doublets at +259/+223 and +258/+221 ppm, respectively, in the  $^{31}\text{P}$  NMR spectrum (Table 1, Figure S7). These values are in accord with those found for the other biradicaloids 3R (R = N(SiMe<sub>3</sub>)<sub>2</sub>: +274/+228; <sup>t</sup>Bu: +261/+197 ppm) and almost identical compared to 3Dmp (+258/+222 ppm) indicating two independent five-membered biradicaloid rings in 10. The observed P–P coupling constants ( $^2J_{\text{PP}}$ ) of 141/138 Hz are also in the expected range (cf. 3R, R = N(SiMe<sub>3</sub>)<sub>2</sub>: 151, <sup>t</sup>Bu: 146, Dmp: 136 Hz). Upon crystallization only crystalline material of the Z,Z isomer was obtained as proven by X-ray structure elucidation (Figure 2).

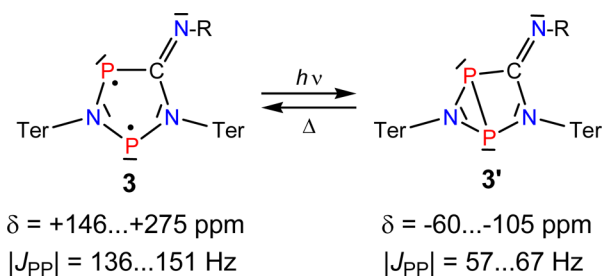
The activation of small molecules bearing triple bonds by tetradicaloid 10 was again studied in the reaction with phosphalkyne PC<sup>t</sup>Bu. After addition of PC<sup>t</sup>Bu to the dark blue solution of 10, the color turned yellow within minutes, and three isomers could be distinguished in the ratio 7:2:1 in the  $^{31}\text{P}$  NMR spectrum, even though the AMX patterns of each of the isomers are superimposed (cf. Figure S10). The reaction is regioselective, and the <sup>t</sup>Bu group is always aligned toward the isonitrile of the cyclopentenediyl. However, there is no preferred direction for the approach of the phosphalkyne with respect to the approach from above and from below the five-membered ring. Hence, there are initially four possible binding sites at both of the isomers of 10. The addition of PC<sup>t</sup>Bu occurs stepwise: Initially, the monoaddition product 11' is formed, in which one biradicaloid moiety is still intact, while the other is incorporated in a [2.2.1]bicyclus (Figure S9, cf. Table 1). In principle, there are three isomers of 10, which can react with 2 equiv of PC<sup>t</sup>Bu each, which leads to 12 possible isomers as illustrated in Figure S11. After addition of two phosphalkynes, several stereogenic centers are present in the structure. Thus, the isomers can display the configurations (R,S,S,R), (R,S,R,S), (S,R,S,R), and (S,R,R,S) on the P atoms, out of which the two pairs of (R,S,R,S)/(S,R,S,R) and (S,R,R,S)/(R,S,S,R), respectively, are enantiomers and therefore cannot be distinguished in the  $^{31}\text{P}$  NMR spectrum. Assuming that only the Z,Z and Z,E isomers of starting material 10 are present in solution, the formation of only eight isomers is possible out of which enantiomers exhibit identical NMR patterns. Therefore, four sets of signals (representing four different diastereomers of 11'') might be expected of which only three were detected (Figure S10).

**Photoinduced Housane Formation.** As illustrated in Scheme 1, cyclopentadiyls are prone to form the [2.1.0]bicyclic isomer, the housane (species C), and in case of biradicaloid H (Scheme 2), we could demonstrate that it can be transformed into a housane by UV irradiation (Scheme 10, medium pressure mercury lamp in quartz vessel).<sup>36</sup> Thus, we studied the influence of irradiation on biradicaloids 3 and tetradicaloid 10 by means of  $^{31}\text{P}$  NMR experiments. 3<sup>t</sup>Bu already formed the

Scheme 9. Addition of 2<sup>t</sup>Bu to 10 affording 11''<sup>a</sup>

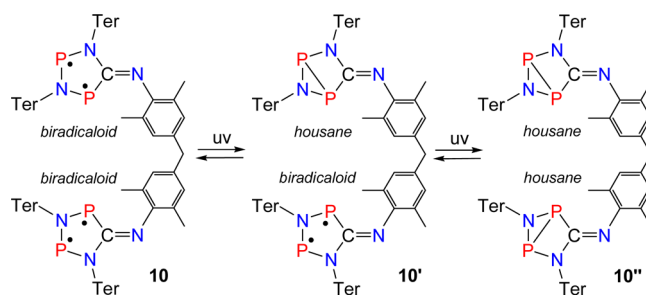
<sup>a</sup>Only one isomer is shown.

Scheme 10. Housane Formation Under UV Irradiation



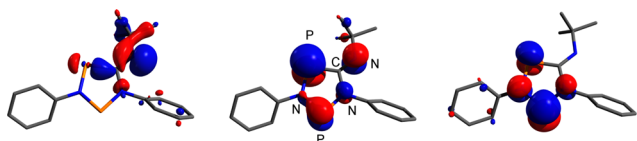
housane species 3'<sup>t</sup>Bu in small amounts under daylight, while dark blue 3Dmp revealed the formation of colorless 3'Dmp only under UV irradiation (Scheme 10). This transformation is easily followed by  $^{31}\text{P}$  NMR studies, as a dramatic high-field shift ( $\Delta\delta > 250$  ppm) occurs upon housane formation (3: two doublets in the range  $\delta(^{31}\text{P}) = +275 - +146$ ; 3':  $-60 - -105$  ppm) and a decrease of the P–P coupling constants ( $|J_{\text{PP}}|$  3: 136–151; 3': 57–67 Hz). Such  $^{31}\text{P}$  shifts and relatively small  $^1J_{\text{PP}}$  coupling constants are characteristic for  $\lambda^3\lambda^3$ -azadiphosphiridines<sup>41–43</sup> clearly indicating the formation of a housane-type product. The rather small  $|J_{\text{PP}}|$  coupling constants (<60 Hz) are typical for such strained three-membered ring species owing to the existence of a strongly bent  $\sigma(\text{p})$  P–P bond. Isolation of the colorless products 3' failed due to intrinsic back-transformation of housane 3' into biradicaloid 3 (Scheme 10) within 1 h at ambient temperature in benzene solution (3Dmp → 3'Dmp,  $\Delta G^{298} = +5.1$  kcal mol<sup>-1</sup>, Scheme 10).<sup>44</sup> In case of the blue tetradicaloid 10, mono (10') and even double housane formation (10'', Scheme 11) was detected after UV irradiation now with either one or two  $\lambda^3\lambda^3$ -azadiphosphiridine rings. Similar to the reaction of 10 with PC<sup>t</sup>Bu, each isomer of 10 can lead to two distinguishable isomers of 10'',

Scheme 11. Mono and Double Housane Formation in Tetradicaloid 10



since the folding of the P<sub>2</sub>N<sub>2</sub>C heterocycles can afford either (R,S) or (S,R) configuration for both of the cyclopentanediyli moieties (Figures S13 and S14). <sup>31</sup>P NMR data indicate the existence of mainly two isomers of double housane (**10''**), which feature a similarly small <sup>1</sup>J<sub>PP</sub> coupling constant (<sup>1</sup>J<sub>PP</sub> = 67 Hz, vide supra), and a third set of resonances, which can be assigned to the mixed catenated species with one housane and one biradicaloid moiety (**10'**, Scheme 11). Similarly to the situation for **3** and **3'**, the housane formation is endergonic (**10** → **10''**, ΔG<sup>298</sup> = +9.9 kcal mol<sup>-1</sup>; cf. ΔG<sup>298</sup> = +5.1 kcal mol<sup>-1</sup> for **3** → **3'**).

All here considered open-shell singlet biradicaloids **3** feature a characteristic deep blue color (λ<sub>max</sub>; **3**<sup>Bu</sup>: 494, 675; **3**<sup>Dmp</sup>: 411, 647; **10**: 422, 645 nm), with absorptions mainly caused by π → π\* transitions according to time-dependent density functional theory (TD-DFT) computations.<sup>44</sup> The highest occupied molecular orbital (HOMO) → lowest unoccupied molecular orbital (LUMO) excitation (>600 nm) promotes an electron from the formally P...P transannularly antibonding π-type HOMO into the P...P transannularly bonding π-type LUMO (Figure 4). The second observed excitation between



**Figure 4.** Molecular orbitals of **3**<sup>Bu</sup>-M (left: HOMO-1, middle: π-HOMO, right: π-LUMO, M = model species with phenyl instead of terphenyl groups).

400 and 500 nm can be assigned to the HOMO-1 → LUMO transition, again populating the transannular P...P bond. This nicely explains the transformation of the cyclopentane-1,3-diyls into the housane upon irradiation, because the excitations increase the population of the LUMO with the transannular P...P bond and therefore the formation of a housane-type bicyclus. Once irradiation is switched off, thermal equilibration affords the cyclopentane-1,3-diyl with no observable decomposition. Such behavior can be referred to as a photochromic molecular switch.<sup>45,46</sup> Interestingly, both the HOMO and LUMO are

mainly localized at the P<sub>2</sub>N<sub>2</sub> moiety of the five-membered heterocycle; there are only very small contributions from the C atom, hence the electronic situation of **10** is very similar to that of the starting material, biradicaloid **1**. It is noteworthy to mention that there is a bathochromic shift of the lowest lying transition compared to the UV-vis data of [Ter<sub>2</sub>N<sub>2</sub>P<sub>2</sub>CO] (cf. λ<sub>max</sub> = 531 nm), indicating a considerably smaller HOMO-LUMO gap. The photoinduced isomerization of **3** to **3'** and the thermal regeneration of the biradicaloid were further studied by DFT calculations. The transition state of the minimal trajectory for the regeneration of the biradicaloid on the singlet hypersurface requires a moderate activation energy (20 kcal mol<sup>-1</sup>),<sup>44</sup> and consequently the cyclopentanediyli **3** is quickly reformed at ambient temperature, as it was observed for [Ter<sub>2</sub>N<sub>2</sub>P<sub>2</sub>CO] as well. In contrast to the previously known [Ter<sub>2</sub>N<sub>2</sub>P<sub>2</sub>CO], for **3** and **10** the housane-biradicaloid isomerization cycle is fully reversible according to <sup>31</sup>P NMR studies, and no formation of decomposition products was observed, thus allowing application as molecular switch.

**Structure and Bonding of Cyclopentane-1,3-diyl-Based Biradicaloids and Tetraradicaloids.** Although cyclopentanediyli derivative **3**<sup>Dmp</sup> and the tetraradicaloid **10** can be isolated in good yields and as crystalline material, it was very difficult to determine their experimental structure since both species decomposed under X-ray irradiation. Thus, with progressing measuring time the crystals became slowly colorless indicating decomposition, an effect already known from [Ter<sub>2</sub>N<sub>2</sub>P<sub>2</sub>CO] (species **H**, Scheme 2).<sup>36</sup> This phenomenon always resulted in poor X-ray diffraction data sets, which just allowed the confirmation of the connectivity, but no detailed discussion of the molecular geometry (Figure 1). Interestingly, the computationally optimized structures<sup>44</sup> agree nicely with the (poor) experimental data. According to these data, the five-membered heterocycle in **3**<sup>Dmp</sup> is planar including the exocyclic imino nitrogen atom, with rather short NP (1.664, 1.695, 1.739 Å), PC (1.803 Å) and CN (1.422 Å) bonds indicating some double bond character as expected for dicoordinated phosphorus and tricoordinated carbon atoms (cf. Σr<sub>cov</sub>: PN 1.82, PC 1.86, CN 1.46 Å). The transannular P...P distance between the radical centers in **3**<sup>Dmp</sup> amounts to 2.958 Å, which is, owing to the ring expansion, larger than in

**Table 2.** Computed Electronic Parameters<sup>a</sup> for the Biradicaloids and the Tetraradicaloid

	3N(SiMe <sub>3</sub> ) <sub>2</sub>	<b>3</b> <sup>Bu</sup>	<b>3</b> <sup>Dmp</sup>	<b>10</b> <sup>b</sup>
q(C)	+0.068	+0.120	+0.097	+0.097
q(N <sub>3<sub>exo</sub></sub> )	-0.439	-0.600	-0.586	-0.562
q(N1)	-0.722	-0.739	-0.728	-0.724
q(P1)	+1.067	+1.083	+1.080	+1.019
q(N2)	-0.979	-0.978	-0.981	-0.972
q(P2)	+0.597	+0.532	+0.601	+0.599
NICS(0)	-5.63	-6.37	-6.55	-4.29
NICS(1)	-3.86	-4.43	-4.30	-2.42
c <sub>1</sub> <sup>c</sup>	0.919	0.922	0.913	0.834
c <sub>2</sub> <sup>c</sup>	-0.359	-0.353	-0.367	-0.344/-0.317
β <sup>c</sup>	26%	26%	27%	26%/22% <sup>d</sup>
ΔE <sub>S-T</sub>	19.3	20.1	20.8	19.1
Δ <sub>R</sub> G <sub>(eq 1)</sub> <sup>e</sup>	-29.9	-23.9	-27.9	-36.5 <sup>f</sup>

<sup>a</sup>Ring labels: P1-N1-P2-N2-C(N<sub>3<sub>exo</sub></sub>) according to Figure 2 top for **3**<sup>Dmp</sup>. Energies in kcal mol<sup>-1</sup>, charges in e, NICS in ppm. <sup>b</sup>Phenyl-substituted model compound, which causes slightly smaller values. <sup>c</sup>CI wave function Φ(1A) = c<sub>1</sub>|π<sub>1</sub><sup>2</sup>π<sub>2</sub><sup>2</sup>π<sub>3</sub><sup>2</sup> + c<sub>2</sub>|π<sub>1</sub><sup>2</sup>π<sub>2</sub><sup>2</sup>π<sub>4</sub><sup>2</sup> from CASSCF(6,6) and β = 2c<sub>2</sub><sup>2</sup>/(c<sub>1</sub><sup>2</sup> + c<sub>2</sub><sup>2</sup>). <sup>d</sup>The original formalism is not applicable here, hence β = 2c<sub>2/3</sub><sup>2</sup>/(c<sub>1</sub><sup>2</sup> + c<sub>2</sub><sup>2</sup> + c<sub>3</sub><sup>2</sup>) was used, affording 26% and 22%, respectively, for both excitations; cf. Table S2. <sup>e</sup>Equation 1: 1 + 2R → 3R, see Scheme 4. <sup>f</sup>Averaged value for both rings.

the cyclodiphosphadiazanediyl **1**. The X-ray structure of tetradicaloid **10** revealed the formation of the *Z,Z* isomer (Figure 2) with two catenated cyclopentane-1,3-diyl moieties. The existence of the mono addition product **11'** illustrates that the tetradicaloid is in this case adequately described as bis(biradicaloid), in which the biradical units act independently of each other. It is interesting to note that the metrical parameters of the five-membered rings in **10** are almost identical to those of 3Dmp (cf. P...P 2.924 Å).

Contrary to **3** and **10**, a strongly puckered five-membered ring is observed in all addition products **4<sup>t</sup>Bu**, **5R** and **7** with significantly shorter transannular P...P distances (Figures 1 and 3; **4<sup>t</sup>Bu**: 2.6280(7), **5<sup>t</sup>Bu**: 2.272(1), **5Dmp**: 2.2664(9), **7**: 2.8077(6) Å). This, however, cannot be attributed to transannular P...P interactions but to steric strain upon bridging the ring and forming the cage compounds.

When the housanes **3'**, **10'**, and **10''** are generated, computations display the formation of a covalent P–P single bond (e.g., 2.177 Å in 3Dmp, cf.  $\sum r_{\text{cov}}(\text{P}-\text{P}) = 2.22 \text{ \AA}$ )<sup>47</sup> along with the bending of the nitrogen atom (of the PNP unit) out of the plane in the former five-membered ring. Hence, these housanes exhibit a three-membered ring condensed to an almost perpendicular lying four-membered heterocycle with a bent P–P  $\sigma$ -bond (“banana bond”), P–N single bonds (e.g., **3'Dmp**: P1–N1 1.807, N1–P2 1.765, P2–N2 1.781 Å), and a localized exocyclic C=N–R double bond (C–N 1.269 Å).

Both MO and NBO calculations of **3R** (R = N(SiMe<sub>3</sub>)<sub>3</sub>, <sup>t</sup>Bu, Dmp) display a highly delocalized 6 $\pi$ -electronic system within the five-membered ring. According to natural bond orbital (NBO) analysis the best Lewis structure of **3R** shows localized lone pairs in a p-atomic orbital on both N centers and unpaired electrons on both P atoms in the  $\pi$ -electron system along with a localized exocyclic C=N bond as illustrated in Scheme 10 (left). There are many hyperconjugative interactions within the  $\pi$ -electronic system displaying a high degree of delocalization. The partial charges along the (P1–N1–P2–C–N2) ring are positive for P (P1 + 0.5, P2 + 1.0 *e*) and negative for N atoms (N1–1.1, N2–0.7 *e*), while the C atom is almost neutral (+0.1 *e* Table 2).

The frontier orbitals display the characteristic features of biradicals (Figure 4) with the LUMO strongly localized on both P atoms in a bonding fashion but antibonding around the NPNP moiety and the HOMO antibonding between both P atoms but bonding along PCN and PN. Therefore, increasing the population of the LUMO results in a transannular P...P bonding situation, finally in the formation of a housane, in accord with experiment (vide supra). Delocalization into the CN  $\pi$ -bond of the isonitrile is less pronounced.

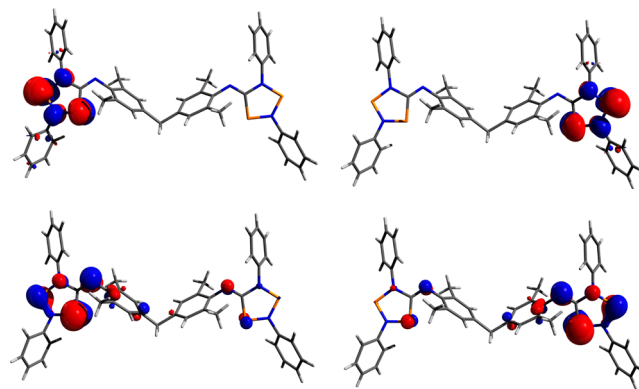
The five-membered heterocycles show aromaticity as judged by nucleus independent chemical shift (NICS) values (NICS(0), NICS(1): **3<sup>t</sup>Bu** –6.4, –4.4; **3Dmp** –6.6, –4.3 ppm), which could provide a hint for the relative stability of the cyclopentane-1,3-diyl and is in accord with other heterocyclic singlet biradicaloids.<sup>37,48,49</sup>

To study the biradical character of **3**, the singlet–triplet energy gap ( $\Delta E_{\text{S-T}}$ ) was estimated for **3** and complete active space self-consistent field [CASSCF(6,6)] computations were carried out. Experimentally, biradicaloids **3** display no EPR signal and normal <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P NMR signals at ambient temperature, all species **3** have a singlet ground state in accord with rather large  $\Delta E_{\text{S-T}}$  values (**3R**; R = N(SiMe<sub>3</sub>)<sub>3</sub>: 19.3, <sup>t</sup>Bu: 20.1, Dmp: 20.8 kcal mol<sup>–1</sup>). CASSCF(6,6) computations confirmed the biradicaloid nature of **3**. The dominant

contributions to the configuration interaction (CI) wave function for the <sup>1</sup>A state are  $\Phi(^1\text{A}) = c_1|\pi_1^2\pi_2^2\pi_3^2\rangle + c_2|\pi_1^2\pi_2^2\pi_4^2\rangle$  (CI for *c*<sub>1</sub> and *c*<sub>2</sub> see Table 2). A good measure for the biradical character is  $\beta = 2c_2^2/(c_1^2 + c_2^2)$ , which amounts to 26% (**3N**(SiMe<sub>3</sub>)<sub>3</sub> and **3<sup>t</sup>Bu**) – 27% (**3Dmp**; cf. [( $\mu$ -N<sup>Ter</sup>)P]<sub>2</sub> (**1**) 25%).<sup>37,50–54</sup> Hence, upon insertion of the isonitrile into the four-membered ring of **1**, the biradical character is preserved. Also the natural orbital occupation numbers (HOMO/LUMO; **3Dmp**: 1.37/0.63, **3N**(SiMe<sub>3</sub>)<sub>3</sub>: 1.35/0.65, **3<sup>t</sup>Bu**: 1.34/0.66 *e*) clearly indicate open-shell singlet biradical character.<sup>55</sup>

Finally, we studied the tetradicaloid using a model compound in which the terphenyls are substituted by a phenyl group. MO and NBO analyses clearly show two independent biradical moieties with almost identical features compared to **3Dmp** (e.g., charges,  $\beta$  values, Tables 1 and 2).

For example, as illustrated in Figure 5 the nearly degenerated HOMO/HOMO–1 and LUMO/LUMO+1 describe  $\pi$ -elec-



**Figure 5.** Frontier orbitals of **10-M** (top left: LUMO+1 –0.07136, top right: LUMO –0.07286, bottom left: HOMO –0.16956, bottom right: HOMO–1 –0.17184 au, M = model species with phenyl instead of terphenyl groups).

tronic system either “localized” in the left or right five-membered ring of **10**. The NICS values of both cyclopentanediyli moieties of **10** indicate weak aromaticity (NICS(0) = –4.29, NICS(1) = –2.42 ppm). The slightly lower values compared to **3R** are caused by utilization of the phenyl-substituted model compound (cf. Table 2). Also the CASSCF-(12,12) computation showed either HOMO → LUMO+1 or HOMO–1 → LUMO excitation with  $\beta$  values of 26% and 22%, respectively. The ground state for the tetradicaloid is an open-shell singlet state, which is separated from the respective triplet and quintet state by a large energy gap ( $\Delta E_{\text{S-T}} = 19.1$ ,  $\Delta E_{\text{S-Q}} = 38.3 \text{ kcal mol}^{-1}$ ). Owing to the long bridging unit, which results in quasi-degenerate MOs for the orbitals localized on each of the five-membered rings, and since the delocalized double bond system is fragmented by the methylene group, there is no coupling/communication between the two cyclopentanediyli moieties in **10**, that is, the electron exchange integral is essentially zero. Such behavior was previously observed by S. Ito et al. for oligomers of the diphosphacyclobutanediyl<sup>56,57</sup> and by Y. Ito et al. for a tetradicaloid Ge<sub>9</sub> cluster compound, which comprises two biradicaloid edge-fused Ge<sub>5</sub> clusters.<sup>58</sup> In contrast, the catenated B<sub>2</sub>P<sub>2</sub> moieties investigated by Rodriguez et al. exhibit weak communication between the biradicaloid building blocks,<sup>59</sup> which was supported in a computational study by Bell et al.<sup>60</sup> Furthermore, Schenk et al. reported on a



hexaradicaloid Ge<sub>14</sub> cluster, featuring three communicating biradicaloid Ge<sub>4</sub> units.<sup>61</sup>

## CONCLUSION

Activation of isonitriles utilizing singlet biradicaloid [P( $\mu$ -N<sup>•</sup>Ter)]<sub>2</sub> initially results in the formation of new examples of singlet 1,3-diphospha-2,4-diazacyclopentane-1,3-diyls. In dependence of the bulkiness of the isonitrile, another equivalent of isonitrile can be incorporated, affording [2.1.1]-heterobicycles. The high reactivity of the cyclopentane-1,3-diyls was probed by reactions with molecules bearing multiple bonds, silver salts as oxidants, and halogenating agents. A novel tetraradicaloid was isolated when diisonitriles were reacted with singlet biradicaloid [P( $\mu$ -N<sup>•</sup>Ter)]<sub>2</sub>. Computations as well as the reactivity confirm the biradical character of the cyclopentane-1,3-diyls and the catenated tetraradicaloid. Upon irradiation the reversible formation of housane type species is observed, a behavior which is known from molecular switches. For further studies, singlet biradicaloids featuring different radical centers will be investigated with respect to their reactivity toward isonitriles. Tuned isonitrile-based biradicaloids and tetraradicaloids will be tested in the activation of small molecules such as H<sub>2</sub>, CO, NO, etc. and mixtures of them to see if these biradicaloids might be used even as catalysts.

## EXPERIMENTAL SECTION

All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques. All manipulations were carried out under oxygen- and moisture-free conditions under argon using standard Schlenk or drybox techniques. Additional information can be found in the SI.

**Synthesis of 3Dmp.** [P( $\mu$ -N<sup>•</sup>Ter)]<sub>2</sub> (251 mg, 0.351 mmol, orange) and CNDmp (46 mg, 0.351 mmol, colorless) were combined as solids in the glovebox. After the addition of 5 mL benzene, the solution immediately darkened and had turned green after 15 min. For completion of the reaction, the solution was stirred for further 2 h at ambient temperature and became blue as a result. The solution was concentrated to incipient crystallization (ca. 0.5 mL) and left undisturbed overnight, affording black block-shaped crystals. The supernatant was removed via syringe, and the crystals were dried in vacuo (271 mg, 0.302 mmol, 86%). Mp: 260 °C (dec.). EA for C<sub>57</sub>H<sub>59</sub>N<sub>3</sub>P<sub>2</sub> found (calcd): C 80.13 (80.73), H 6.86 (7.01), N 4.85 (4.95). <sup>31</sup>P NMR (298 K, C<sub>6</sub>D<sub>6</sub>, 121.5 MHz): 258.4 (d, <sup>2</sup>J<sub>PP</sub> = 136.5 Hz), 222.3 (d, <sup>2</sup>J<sub>PP</sub> = 136.5 Hz). UV–vis ( $\lambda_{\text{max}}$ , nm): 320 (br), 420, 646.

**Synthesis of 4<sup>t</sup>Bu.** To a solution of [P( $\mu$ -N<sup>•</sup>Ter)]<sub>2</sub> (275 mg, 0.384 mmol) in benzene (5 mL), an excess of CN<sup>t</sup>Bu was added via microliter syringe (80  $\mu$ L). The solution immediately darkened and became green, but after 30 min it started turning pale yellowish. After 90 min, no further changes could be observed. The solution was concentrated to incipient crystallization (ca. 1 mL) and left overnight at 4 °C, affording pale greenish crystals. The mother liquor was removed via syringe, and the crystals were dried in vacuo (179 mg, 0.203 mmol, 53%). Mp: 164 °C (dec.). EA for C<sub>58</sub>H<sub>68</sub>N<sub>3</sub>P<sub>2</sub> found (calcd): C 78.33 (78.88), H 8.36 (7.76), N 5.36 (6.34). <sup>31</sup>P NMR (298 K, C<sub>6</sub>D<sub>6</sub>, 121.5 MHz): 210.8 (d, <sup>2</sup>J<sub>PP</sub> = 31.2 Hz), 166.7 (d, <sup>2</sup>J<sub>PP</sub> = 31.2 Hz). UV–vis ( $\lambda_{\text{max}}$ , nm): 494, 675.

**Synthesis of 5<sup>t</sup>Bu.** Colorless [Ter<sub>2</sub>N<sub>2</sub>P<sub>2</sub>(CN<sup>t</sup>Bu)<sub>2</sub>] (4<sup>t</sup>Bu, 188 mg, 0.212 mmol) was dissolved in benzene (5 mL). To the resulting green solution, PC<sup>t</sup>Bu (50  $\mu$ L) was added via microliter syringe and the solution was stirred overnight. Within time, the solution turned yellow. Volatiles were removed in vacuo (2 h), and the residue was redissolved in benzene (5 mL). The yellow solution was concentrated to incipient crystallization (ca. 0.5 mL) and left undisturbed overnight, affording yellow crystals. The supernatant was removed via syringe, and the crystals were dried in vacuo (102 mg, 0.113 mmol, 53%). Mp: 193 °C (dec.). EA for C<sub>58</sub>H<sub>68</sub>N<sub>3</sub>P<sub>3</sub> found (calcd): C 77.24 (77.39), H 7.92

(7.61), N 4.76 (4.67). <sup>31</sup>P NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>, 121.5 MHz): 368.5 (d, <sup>1</sup>J<sub>PP</sub> = 224 Hz, PC=PP), 127.1 (d, <sup>1</sup>J<sub>PP</sub> = 224 Hz, PC=PP), 58.2 (s, PC=PP).

**Synthesis of 5Dmp.** To a solution of [Ter<sub>2</sub>N<sub>2</sub>P<sub>2</sub>(CNDmp)] (3Dmp, 207 mg, 0.244 mmol) in benzene (5 mL), PC<sup>t</sup>Bu was added via microliter syringe (40  $\mu$ L). Within 10 min, the blue solution turned yellow. Afterward, the solution was concentrated to incipient crystallization (ca. 1 mL) and left undisturbed overnight, resulting in the formation of yellow crystals. The supernatant was removed via syringe, and the crystals were dried in vacuo (120 mg, 0.127 mmol, 52%). Mp: 228 °C (dec.). EA for C<sub>62</sub>H<sub>68</sub>N<sub>3</sub>P<sub>3</sub> found (calcd): C 77.24 (77.39), H 7.92 (7.61), N 4.76 (4.67). <sup>31</sup>P NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>, 121.5 MHz): 368.5 (d, <sup>1</sup>J<sub>PP</sub> = 224 Hz, PC=PP), 127.1 (d, <sup>1</sup>J<sub>PP</sub> = 224 Hz, PC=PP), 58.2 (s, PC=PP).

**Synthesis of 6.** Colorless [Ter<sub>2</sub>N<sub>2</sub>P<sub>2</sub>(CN<sup>t</sup>Bu)<sub>2</sub>] (4<sup>t</sup>Bu, 220 mg, 0.249 mmol) was dissolved in dichloromethane and left at ambient conditions without shielding from light. Within time, the green solution discolored and became pale yellowish. The solution was concentrated to incipient crystallization (ca. 1 mL) and left overnight at 4 °C, resulting in the formation of colorless crystals. The mother liquor was removed via syringe, and the crystals were dried in vacuo (166 mg, 0.207 mmol, 83%). Mp: 256 °C (dec.). EA for C<sub>49</sub>H<sub>52</sub>N<sub>2</sub>P<sub>2</sub>Cl<sub>2</sub> found (calcd): C 72.92 (73.40), H 7.07 (6.54), N 3.88 (3.49). *cis/trans* ratio ~1:5. <sup>31</sup>P NMR (298 K, C<sub>6</sub>D<sub>6</sub>, 121.5 MHz): 243.5 (d, <sup>2</sup>J<sub>PP</sub> = 39.6 Hz, *cis*, PCl), 242.2 (d, <sup>2</sup>J<sub>PP</sub> = 13.2 Hz, *trans*, PCl), 214.8 (d, <sup>2</sup>J<sub>PP</sub> = 13.2 Hz, *trans*, PC), 199.9 (d, <sup>2</sup>J<sub>PP</sub> = 39.6 Hz, *cis*, PC).

**Synthesis of 7.** To a solution of [Ter<sub>2</sub>N<sub>2</sub>P<sub>2</sub>(CNDmp)] (3Dmp, 160 mg, 0.189 mmol) in toluene (2 mL), 3 mL of a solution of acetylene in toluene (saturated at –60 °C) was quickly added at –80 °C via syringe. The initially blue solution immediately turned pale yellow. The solution was stirred for further 30 min at ambient temperature to ensure completion of the reaction. Afterward, it was concentrated to incipient crystallization and left undisturbed overnight, resulting in the formation of colorless crystals. The mother liquor was removed via syringe, and the crystals were dried in vacuo (94 mg, 0.108 mmol, 57%). Mp: 172 °C (dec.). EA for C<sub>59</sub>H<sub>61</sub>N<sub>3</sub>P<sub>2</sub> found (calcd): C 80.92 (81.07), H 7.05 (7.03), N 4.86 (4.81). <sup>31</sup>P NMR (298 K, C<sub>6</sub>D<sub>6</sub>, 121.5 MHz): 61.1 (CPC, J<sub>PP</sub> = 22.0 Hz), 107.7 (NPN, J<sub>PP</sub> = 22.0 Hz).

**Synthesis of 9.** A flask was filled with (H<sub>2</sub>NDmp)<sub>2</sub>CH<sub>2</sub> (750 mg, 2.95 mmol), BnNEt<sub>3</sub>Cl (50 mg, 0.22 mmol), dichloromethane (25 mL), and chloroform (725 mg, 6.07 mmol). An aqueous solution of NaOH (25g NaOH/25g water) was carefully added, and a reflux condenser was connected to the flask. The mixture was stirred vigorously and heated to reflux for 6 h. After cooling of the dark reaction mixture, 250 mL of water were added. The organic phase was separated, and the aqueous phase was extracted three times with 30 mL dichloromethane. The combined organic phases were dried over MgSO<sub>4</sub>. After separation of the solution from the drying agent, volatiles were removed, and the yellowish crude product was recrystallized from 15 mL dichloromethane, yielding colorless crystals. The supernatant was decanted, and the solid was dried in vacuo (320 mg, 1.17 mmol, 40%). Mp: 212 °C (dec.). EA for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub> found (calcd): C 83.22 (83.18), H 7.08 (6.61), N 9.86 (10.21). <sup>1</sup>H NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>, 250.1 MHz): 2.37 (s, 12 H, CH<sub>3</sub>), 3.83 (s, 2 H, CH<sub>2</sub>), 6.92 (s, 4 H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (298 K, CD<sub>2</sub>Cl<sub>2</sub>, 62.9 MHz): 19.06 (s, CH<sub>3</sub>), 41.51 (s, CH<sub>2</sub>), 125.41 (s), 128.59 (s), 135.47 (s), 141.66 (s), 168.56 (s, CN). IR (ATR, cm<sup>-1</sup>): 2111 (vs). Raman (632 nm, cm<sup>-1</sup>): 2084 (1), 2119 (100).

**Synthesis of 10.** 55 mg (0.201 mmol) of the colorless 4,4'-methylene-bis(2,6-dimethyl-isonitrile) (9) and 292 mg (0.407 mmol) orange [P( $\mu$ -N<sup>•</sup>Ter)]<sub>2</sub> were combined as solids. Ten mL benzene was added, and the solution was stirred 2 h at ambient temperature. The solution immediately darkened and became blue after 30 min. The solution was concentrated to approximately 0.5 mL and layered with diethyl ether (8 mL). After standing undisturbed for 3 days, dark blue block-shaped crystals were obtained. The mother liquor was transferred to another flask and stored at –40 °C overnight, affording a second crop of crystals. The supernatant was removed via syringe and discarded. The combined crystalline fractions were dried in vacuo,



yielding 267 mg (0.156 mmol, 78%) of **10**. Mp. 183 °C (dec.). EA for C<sub>115</sub>H<sub>118</sub>N<sub>6</sub>P<sub>4</sub> found (calcd): C 80.39 (80.86), H 7.38 (6.96), N 4.94 (4.92). <sup>31</sup>P NMR (298 K, C<sub>6</sub>D<sub>6</sub>, 121.5 MHz): 223.4 (NPC, d, J<sub>PP</sub> = 141 Hz), 259.3 (NPN, d, J<sub>PP</sub> = 141 Hz).

**Synthesis of 11''.** To a solution of **10** in C<sub>6</sub>D<sub>6</sub> in an NMR tube, an excess of PC<sup>t</sup>Bu (10 μL) was added via microliter syringe. The mixture was shaken thoroughly and turned yellow within minutes. <sup>31</sup>P NMR (298 K, C<sub>6</sub>D<sub>6</sub>, 121.5 MHz): isomer **1**, ca. 70%: 344.9 (d, 240 Hz), 146 (d, 240 Hz), 80 (s); isomer **2**, ca. 20%: 346.5 (d, 240 Hz), 146 (d, 240 Hz), 80 (s); isomer **3**, ca. 10%: 345.3 (d, 240 Hz), 146 (d, 240 Hz), 80 (s).

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05596.

Additional experimental information, computational details, absolute energies of the optimized molecules, investigations of the reaction mechanism (PDF)  
Crystallographic data (CIF)

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### Notes

The authors declare no competing financial interest.

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