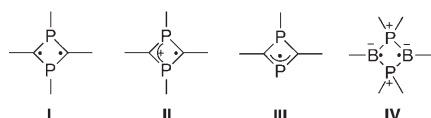


# Poly(Biradicals): Oligomers of 1,3-Diphosphacyclobutane-2,4-diyl Units\*\*

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Studies on stable organic biradicals have been of great interest from the perspective of fundamental molecular science and exploration of innovative materials.<sup>[1]</sup> The 1,3-diphosphacyclobutane-2,4-diyl **I** is a remarkable biradical and

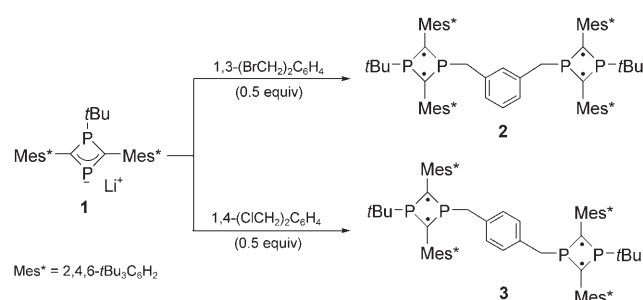


occupies a special place as a product of low-coordinated organophosphorus chemistry.<sup>[2]</sup> This biradical has a range of potential applications owing to its considerable stability, as described by Niecke et al.<sup>[3,4]</sup> and our group.<sup>[5]</sup> Some of our air-stable 1,3-diphosphacyclobutane-2,4-diyls of type **I** are quite electron-rich and are easily oxidized to the corresponding P-heterocyclic cation radicals (**II**).<sup>[6]</sup> The 1,3-diphosphacyclobutane-2,4-diyl moiety may thereby serve as a module for redox-functionalized molecular systems. In addition to the biradical derivatives, we succeeded in preparing a neutral monoradical **III** by use of a synthetic intermediate for **I** (**1**).<sup>[7]</sup>

Covalent assembly of redox-active biradical units derived from **I** is an attractive strategy to develop new materials for molecular electronics and spintronics applications.<sup>[8]</sup> As an example of double catenation of stable biradical units, Bertrand and co-workers succeeded in binding two 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl moieties (**IV**) with the *m*- or *p*-phenylene unit to build  $\pi$ -conjugative communication between the  $P_2B_2$  biradical centers.<sup>[9]</sup> We are interested in distinct “multi-biradical” systems in which each biradical unit experiences a static interaction through a nonconjugative covalent spacer. Such nonconjugative cate-

nation will lead to stable polyradical systems without strong or shared interaction between individual biradical components.

Therefore, on the basis of our synthetic method for 1,3-diphosphacyclobutane-2,4-diyls,<sup>[5a]</sup> we demonstrate multi-biradical derivatives in which the P-heterocyclic biradical moieties are catenated with di- or trimethylenephenyl groups. According to our previous report<sup>[5a]</sup> (Scheme 1), anion **1** was prepared from phosphalkyne  $Mes^*C\equiv P$



**Scheme 1.** Preparation of bis(biradical) derivatives **2** and **3** from P-heterocyclic anion **1**.

( $Mes^* = 2,4,6-tBu_3C_6H_2$ ) and one half of an equivalent of *tert*-butyllithium. Subsequently, **1** was allowed to react with  $\alpha,\alpha'$ -dibromo-*m*-xylene to afford the corresponding bis(biradical) derivative **2** in moderate yield. Similarly, **3** was obtained from **1** and  $\alpha,\alpha'$ -dichloro-*p*-xylene. The bis(biradical) derivatives **2** and **3** are stable blue solids and showed no decomposition in air at room temperature over six months. However, **3** is only sparingly soluble in common solvents, and no useful spectroscopic data were obtained in solution. It should be noted that, in contrast to the successful preparation of **2** and **3**, the reaction of **1** with  $\alpha,\alpha'$ -dibromo-*o*-xylene failed to give the desired bis(biradical) compound, probably owing to steric congestion.

The successful catenation of two 1,3-diphosphacyclobutane-2,4-diyl moieties prompted us to combine three P-heterocyclic units (Scheme 2). Since a one-pot synthesis as in Scheme 1 was unsuccessful, we employed a stepwise procedure. Initially, anion **1** was allowed to react with 0.5 equivalents 1,3,5-tris(bromomethyl)benzene to obtain bis(biradical) **4**, and subsequently **4** was treated with another equivalent of **1** to give the desired tris(biradical) **5** as an air-stable deep blue solid. As observed for the bis(biradical)s **2** and **3**, tris(biradical) **5** possesses extremely high tolerance to air.

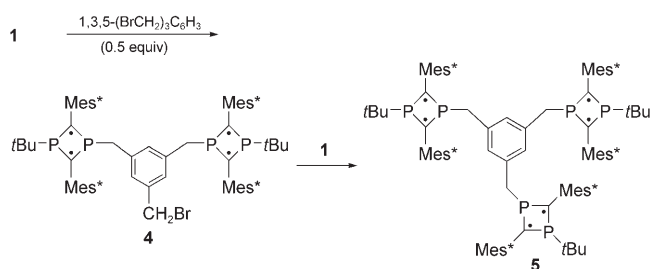
Table 1 summarizes selected spectroscopic data for **2** and **5** together with those of their elementary model **6**. Each

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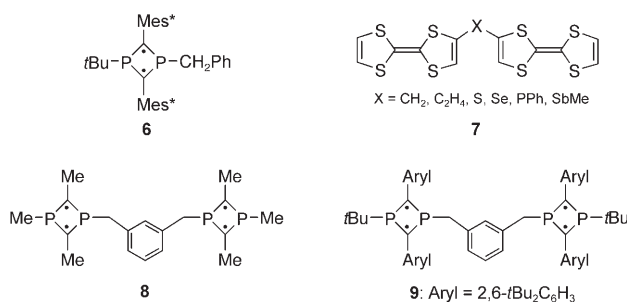


**Scheme 2.** Synthesis of tris(biradical) **5** by a stepwise procedure from **1**.

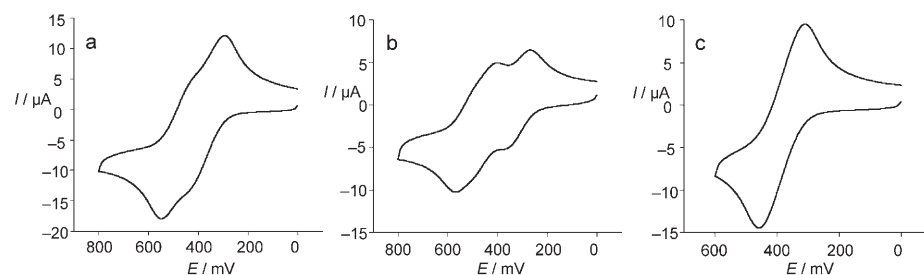
biradical unit in **2** and **5** is identical, and one AB pattern and one resonance for C(sp<sup>2</sup>) carbon atoms were observed in the <sup>31</sup>P and <sup>13</sup>C NMR spectra, respectively. No significant differences were observed in the NMR spectra of **2**, **5**, and **6**. On the other hand, the UV/Vis data (Table 1) indicate nonconjugative covalent interactions between the biradical units in **2** and **5**.

**Table 1:** Spectroscopic data for **2**, **5**, and **6**.

	$\delta_P$ [ppm]	$^2J_{PP}$ [Hz]	$\delta_C$ (sp <sup>2</sup> ) [ppm]	$^1J_{PC}$ [Hz]	$\lambda_{max}$ [nm]	$\epsilon$ [10 <sup>3</sup> M <sup>-1</sup> cm <sup>-1</sup> ]
<b>2</b>	57.7, 1.0	335.2	109.1	15.5	616	2.1
<b>5</b>	63.5, -0.7	327.2	110.0	15.5	626	4.4
<b>6</b> <sup>[5c,d]</sup>	58.1, 0.6	334.8	108.6	16.8, 15.8	610	1.6



Electrochemical investigation by cyclic voltammetry (CV) for the multi-biradicals revealed another intriguing property arising from intramolecular interaction between the biradical units (Figure 1, Table 2). Model compound **6**, containing one



**Figure 1.** Cyclic voltammograms for a) **2**, b) **5**, and c) **6**. 1 mM in CH<sub>2</sub>Cl<sub>2</sub>; supporting electrolyte: 0.1 M tetrabutylammonium perchlorate (TBAP); working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgCl ( $E_{1/2} = +0.60$  V vs. ferrocene/ferricinium) at 20 °C; scan rate: 50 mV s<sup>-1</sup>.

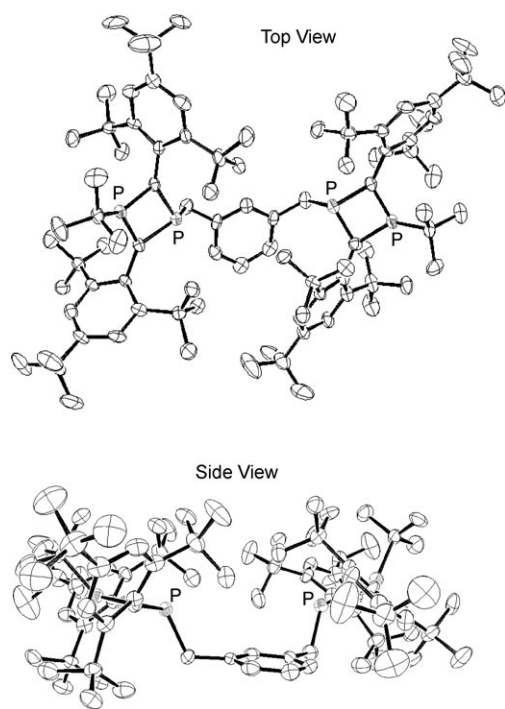
**Table 2:** Redox potentials (V vs. Ag/AgCl) for **2**, **5**, and **6**.

	$E_{1/2}^{ox_1}$	$E_{1/2}^{ox_2}$	$E_{1/2}^{ox_3}$	$E_p^{ox}$	$E_p^{red}$
<b>2</b>	+0.35	+0.48		+1.76	-0.71
<b>5</b>	+0.31	+0.45	+0.52	+1.78	-0.82
<b>6</b>	+0.38			+1.69	-0.76

biradical unit, shows a reversible oxidation potential around +0.4 V vs. Ag/AgCl (Figure 1c). Bis(biradical) **2** appears to show two oxidation potentials around +0.4 V vs. Ag/AgCl (Figure 1a), and tris(biradical) **5** possesses three oxidation potentials around +0.4 V vs. Ag/AgCl (Figure 1b, see also the Supporting Information). Thus, the number of reversible oxidation potentials corresponds to the number of biradical units. Similar oxidation waves of bis(tetrathiafulvalenyl) derivatives such as **7** are reported to be the result of the interaction between the tetrathiafulvalene units through a Coulombic force.<sup>[10]</sup> The separation between the first and second oxidation potentials in **5** is almost the same as the corresponding separation in **2**, whereas the separation between the second and third oxidation of **5** is considerably smaller. The larger separations of the reversible oxidation potentials observed in **2** and **5** may indicate structural similarities (especially P<sub>2</sub>C<sub>2</sub> conformations). Furthermore, the lowest oxidation potentials of **2** and **5** are lower than that of **6**, possibly owing to interaction between the biradical units analogous to that reported for **7**.<sup>[10]</sup> The irreversible oxidation potentials of **2** and **5** around 1.7 V are higher than that for **6**, probably indicating a Coulombic effect on multiple oxidations. However, the reductions of **2** and **5** relative to **6** show no obvious cumulative effect.

Figure 2 displays an ORTEP drawing of the molecular structure of **2**.<sup>[11]</sup> Disordered substituent groups and the presence of numerous solvent molecules in the crystals limit the quality of structural data that can be obtained from single crystal X-ray diffraction measurements. Nonetheless, it is possible to discuss gross conformational features of the molecule. Each four-membered biradical unit displays a structure similar to the known 1,3-diphosphacyclobutane-2,4-diyls<sup>[5a,c,d]</sup> with a distortion in the sterically encumbered Mes\* groups, as we have reported.<sup>[12]</sup> Interestingly, in spite of the steric congestion, two bulky biradical units are positioned on the same side of the xylyl moiety in a *syn*-type conformation; the shortest P...P separation is 6.5 Å.

Model calculations were conducted on **8** in which the Mes\* and *tert*-butyl groups of **2** were replaced with methyl groups. In contrast to the X-ray analysis, and as predicted from the steric effects, the *anti* conformation is calculated as slightly more stable than the *syn* form, but only by 0.13 kcal mol<sup>-1</sup> (B3LYP/6-31G(d),<sup>[13]</sup> see the Supporting Information). Also, semiempirical calculations for the *anti* conforma-



**Figure 2.** ORTEP drawings for the molecular structure of **2**; thermal ellipsoids are set at the 40% probability level, and hydrogen atoms are omitted for clarity. The solvent molecules ( $\text{CH}_2\text{Cl}_2$ ) in the crystal are omitted. The central  $\text{C}_6\text{H}_4$  aryl ring is disordered, and the minor structure is omitted. Two *p*-*tert*-butyl groups in the  $\text{Mes}^*$  groups are disordered, and the atoms with the predominant occupancy factors (0.58, 0.69) are displayed.

tion on another model compound **9**, in which the  $\text{Mes}^*$  groups of **2** were replaced with 2,6-di-*tert*-butylphenyl groups, turned out to be slightly more stable than the *syn* conformation by  $3.93 \text{ kcal mol}^{-1}$  (AM1),<sup>[14]</sup> suggesting that steric congestion raises the energetic difference between these two model conformations (see the Supporting Information). However, it could be concluded that both the *anti* and *syn* forms of **8** and **9** possess similar stability, and the *syn* geometry found in the X-ray structure of **2** need not be energetically disfavored. Multiple explanations are possible for the *syn* conformation of the structure of **2**. There might be  $\text{CH}/\pi$  interactions<sup>[15]</sup> between the alkyl groups and aromatic rings in the biradical units, or crystal packing forces could provide sufficient stabilization to overcome the slight energetic disadvantage suggested by the preliminary model calculation. Furthermore, this observed *syn* conformation of **2** may cause sharing of the  $\pi$  electrons upon oxidation because of the proximal positioning of the biradical subunits, which might lower the first reversible oxidation potentials while reducing the highest occupied molecular orbital (HOMO) levels.<sup>[10,16]</sup> Furthermore, the two different separations of the reversible oxidation potentials of **5** indicate the presence of both *syn* and *anti* conformations.

In conclusion, two and three stable 1,3-diphosphacyclobutane-2,4-diyl units were concatenated to construct multi-biradical derivatives by utilizing 1,3-di-, 1,4-di-, and 1,3,5-trimethylenephényl moieties as bridging groups. UV/Vis and

CV investigations of the multi-biradicals **2** and **5** indicate nonconjugative covalent interaction between the concatenated biradical units. The X-ray structure of **2** also supports the possible interaction between the bulky biradical units in terms of through-space pathways. Therefore, the results described herein suggest approaches to novel open-shell materials for molecular electronic applications by utilizing the interaction between the biradical subunits, the 1,3-diphosphacyclobutane-2,4-diyl moieties.<sup>[17]</sup>

## Experimental Section

**2:** *tert*-Butyllithium (0.18 mmol, 1.4 M solution in pentane) was added to a solution of 2-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethyne ( $\text{Mes}^*\text{C}\equiv\text{P}$ ,  $\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$ ; 100 mg, 0.35 mmol) in THF (5 mL) at  $-78^\circ\text{C}$  and stirred for 10 min. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The solution containing **1** was mixed with a solution of  $\alpha,\alpha'$ -dibromo-*m*-xylene (0.18 mmol) in THF (1 mL) and subsequently stirred for 1 h. The volatile materials were removed in vacuo, and the residue was extracted with hexane. The hexane extract was concentrated in vacuo, and the residual solid was washed with ethanol to afford **2** as a deep blue solid (51 mg, 43%). Compound **2** was recrystallized from  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$ . M.p.  $164\text{--}165^\circ\text{C}$  (decomp). See the Supporting Information for  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ), UV/Vis ( $\text{CH}_2\text{Cl}_2$ ), and ESI-MS.

**3:** In a similar manner to the preparation of **2**,  $\text{Mes}^*\text{C}\equiv\text{P}$  (0.52 mmol), *tert*-butyllithium (0.27 mmol), and  $\alpha,\alpha'$ -dichloro-*p*-xylene (0.27 mmol) were employed to afford **3** as a deep blue insoluble solid (80 mg, 44% yield). M.p.  $148\text{--}150^\circ\text{C}$  (decomp); ESI-MS calcd for  $\text{C}_{22}\text{H}_{14}\text{P}_4$ ;  $m/z$  1371.0057; found:  $m/z$  1371.0061.

**4:** In a similar manner to the preparation of **2**,  $\text{Mes}^*\text{C}\equiv\text{P}$  (0.35 mmol), *tert*-butyllithium (0.18 mmol), and 1,3,5-tris(bromomethyl)benzene (0.18 mmol) were employed to afford **4** as a deep blue solid (87 mg, 68% yield). See the Supporting Information for  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ).

**5:** A solution of **1** (0.55 mmol) in THF (2 mL) was prepared in a similar manner to **2** and **4** and was allowed to mix with a solution of **4** (0.55 mmol). The mixture was stirred for 1.5 h at room temperature, and the volatile materials were removed in vacuo. The residual solid was extracted with chloroform, and the chloroform extract was concentrated in vacuo. The resulting solid was washed with ethanol to afford **5** as a deep blue solid (67 mg, 72%). M.p.  $140\text{--}141^\circ\text{C}$  (decomp). See the Supporting Information for  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ), UV/Vis ( $\text{CH}_2\text{Cl}_2$ ), and ESI-MS.

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**Keywords:** biradicals · conformational analysis · electrochemistry · phosphorus heterocycles · steric hindrance

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- [11] **2**: C<sub>92</sub>H<sub>142</sub>P<sub>4</sub>·4CH<sub>2</sub>Cl<sub>2</sub>, triclinic, space group *P* $\bar{1}$  (#2), *a* = 16.350(5), *b* = 17.842(5), *c* = 18.111(6) Å,  $\alpha$  = 81.457(9),  $\beta$  = 85.370(10),  $\gamma$  = 78.584(9)°, *V* = 5114(3) Å<sup>3</sup>, *Z* = 2 (see the Supporting Information). CCDC-659925 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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- [17] We recently found that multi-biradicals in which the *t*BuP groups of **2**, **3**, and **5** are replaced with *s*BuP exhibit similar physicochemical properties to the those described herein. Details will be reported elsewhere.