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Synthesis and Properties of Oligo(biradicals) Composed of 1,3-Diphosphacyclobutane-2,4-diyl Units and Benzyl-type Linkers

Shigekazu Ito,[1] Joji Miura,[2] Noboru Morita,[2] Masaaki Yoshifuji,[3] and Anthony J. Arduengo, III[3]

[1]*Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8552, Japan*

[2]*Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan*

[3]*Department of Chemistry, the University of Alabama, Tuscaloosa, Alabama 35487-0336, USA*

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ABSTRACT: *We have succeeded in catenating two sterically encumbered 1,3-di-t-butyl-2,4-bis(2,4,6-tri-t-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyl units with a spacer 1,2-*$(CH_2)_2C_6H_4$ *to obtain bis(biradicals) as considerably stable compounds. We have discussed physicochemical properties of the dimer, together with DFT calculations of model compounds. Spectroscopic data, redox properties, and X-ray structures of the oligo(biradicals) derivatives including other spacers like 1,3-*$(CH_2)_2C_6H_4$*, 1,4-*$(CH_2)_2C_6H_4$*, and 1,3,5-*$(CH_2)_3C_6H_3$*, reveal that the P-heterocyclic biradical moieties interact through nonconjugative pathways. These properties of oligo(biradicals) will facilitate to design novel molecular systems for electronics.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:404–411, 2010; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20625

INTRODUCTION

Cyclobutane-1,3-diyl **A** (Fig. 1) is a prototypical cyclic biradical system and has been studied from the perspectives of molecular science and application for electronic and magnetic materials [1,2]. However, the cyclic biradical moiety is inherently unstable, and it is necessary to carry out studies on such biradicals by using cryogenic and inert conditions. On the other hand, in 1995 Niecke and co-workers reported room-temperature stable 1,3-diphosphacyclobutane-2,4-diyl **B** by utilizing reactivity of kinetically stabilized phosphaalkenes [3]. The successful isolation of **B** indicated that phosphorus atom can facilitate the synthesis of stable organic biradical derivatives. In fact, in 2002, Bertrand and co-workers also succeeded in the synthesis of an isolable cyclic biradical composed of phosphorus and boron involving an apparently different stabilization mode at phosphorus (**C**) [4]. So far, several isolable cyclic biradicals have been developed by utilizing heavier main group elements such as germanium, tin, and aluminum [5–7]. A 1,3-diphosphacyclobutane-2,4-diyl species possesses properties of a singlet biradical and exhibits a number of intriguing characteristics because of the low-energetic difference between HOMO and LUMO and the unique open-shell electronic structure (alternatively named as biradicaloid) [3–7].

In the course of our research on chemistry of low-coordinated phosphorus compounds originating from a sterically stabilized phosphaalkyne **1**, we found an efficient synthetic method for 1,3-diphosphacyclobutane-2,4-diyl **3** from the cyclic

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Correspondence to: Shigekazu Ito; e-mail: ito.s.ao@m.titech.ac.jp.

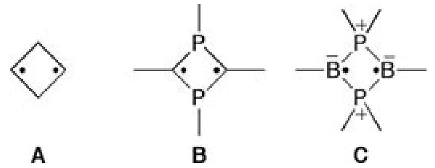


FIGURE 1 Structure of cyclic biradicals **A–C**.

phosphaallyl anion **2** [8,9] (Fig. 2). The P-heterocyclic biradicals (**3**) thus obtained showed sufficiently high stability to enable handling even in air at room temperature. Effective protection of the biradical moiety by electronic perturbation of phosphorus atoms and steric protection of the Mes* (2,4,6-tri-*t*-butylphenyl) groups on carbon atoms is believed responsible for this enhanced stability. This high stability of **3** is advantageous for exploration of chemical properties of the P-heterocyclic biradicals such as redox properties under ambient conditions. We found that the P-heterocyclic biradical shows a considerable electron-donating ability, resulting in a stable radical cation species [8,9]. We have successfully observed the corresponding radical cation via chemical oxidation [10]. These findings indicate that the P-heterocyclic biradicals are suitable candidates for exploration of novel electro-functional materials.

Taking previous attempts to utilize biradical moieties for electronically functionalized compounds into account, binding several biradical units together in the same molecules would facilitate the exploration of novel and unique properties. In an attempt to construct high-spin organic molecules, Dougherty and co-workers reported generation of ferromagnetic molecular species by binding two cyclic biradicals with a 1,3-dimethylenecyclobutane spacer (**4**) [11]. Bertrand and co-workers succeeded in binding their cyclic biradical units composed of phosphorus and boron with *p*- and *m*-phenylene groups (**5**), indicating that the amplitude of the communication is influenced by the structure of the catenating unit (P_2B_2 four-membered ring) [12], specifically where biradical units are, through π-electron systems in the linking groups (Fig. 3). On the other hand, the catenation of biradical units with nonconjugative spacers is an alternative approach to explore novel characteristics of biradical species in terms to electronic functionality. In fact, dual catenation of tetrathiafulvalene (TTF) moieties with an alkyl chain induced through-space interaction between the TTF chromophores [13].

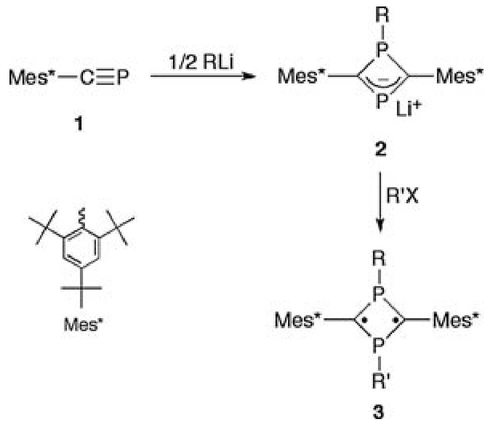


FIGURE 2 Preparation of biradicals **3** from phosphaalkyne **1**.

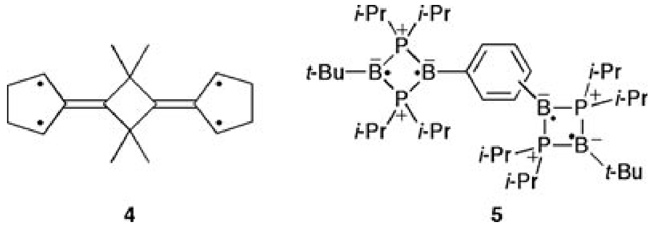


FIGURE 3 Structure of bis(biradicals) **4** and **5**.

In this work, we examined catenation of two and three P-heterocyclic biradical units with nonconjugative 1,2-, 1,3-, and 1,4-dimethylene- and 1,3,5-trimethylenebenzene spacers because such catenation would derive characteristics from the P-heterocyclic biradicals [14,15]. Studies of a simple series of oligo(biradicals) provide key information about through-space interaction between the biradical units. Additionally, substituents at the terminal phosphorus of the P_2C_2 four-membered oligomers affect the conformation of chains. As indicated in the examples of dual TTF catenation [13], such catenation of 1,3-diphosphacyclobutane-2,4-diyl units without π-conjugative bridges between the biradical chromophores is expected to be suitable to propagate characteristics from the electron-donating P-heterocyclic biradicals. Furthermore, the benzyl-type substituents are expected to raise stability of the biradical structure [9], which is advantageous to explore novel functional materials.

RESULTS AND DISCUSSION

Catenation of Two P-Heterocyclic Biradical Units

Following to our previous results [8], cyclic phosphaallyl anion **2a** was prepared from **1** and *t*-butyllithium, and allowed to react with bis(halomethyl)benzenes to afford the corresponding bis(biradicals) **6a–8a** [14] (Fig. 4). Several renewed attempts to obtain bis(biradicals) **6a** (whose

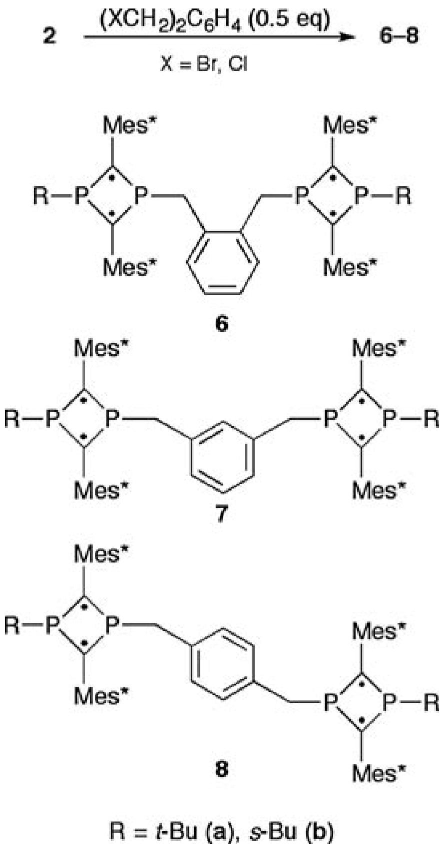


FIGURE 4 Structure of *o*-, *m*-, *p*-bis(biradicals) **6–8**.

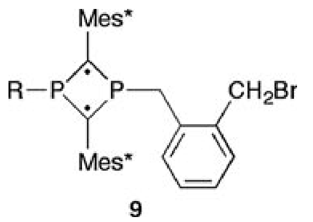


FIGURE 5 Structure of mono(biradicals) **9**.

synthesis was unsuccessful in the previous studies) [14] were made and we found conditions appropriate to prepare **6a** (namely, utilization of a chelating diamine to increase nucleophilicity of the phosphaallyl moiety). Furthermore, slow addition of a solution of 1,2-bis(bromomethyl)benzene into a reaction mixture containing **2** was required to avoid the puzzling formation of a byproduct containing one biradical unit (**9a**) because **9a** only reluctantly reacts with **2a** to give **6a**. Probably due to excessive steric hindrance, **6a** showed relatively low stability and decomposed within a few days in air in the crystalline state. Nevertheless, it is essential to obtain pure **6a** for understanding the through-space interaction in the bis(biradicals) series as described below. By contrast to the *ortho*-substitution in **6a, 7a** (bearing a 1,3-dimethylenebenzene spacer) showed high stability in air over 1 year in solid state. The molecular structure for **7a** was unambiguously confirmed (vide infra) by its spectra and a solid-state structural determination [14]. The *p*-linked bis(biradicals) **8a** shows low solubility in any common solvents and could not be employed for analyzing physicochemical properties in solution. Similarly to **6a–8a**, bis(biradicals) bearing *s*-BuP moieties **6b–8b** were obtained from **2b** [15]. In the case of the stepwise synthesis of **6b** from a combination of **2b** and 1,2-bis(bromomethyl)benzene through **9b**, an inseparable mixture of **6b** and 1,3-di-*s*-butyl-2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyl was obtained [15] (Fig. 5). Unlike **8a**, compound **8b** was soluble enough in common organic solvents for spectroscopic analyses in solution. Due to reduction of steric encumbrance around phosphorus atoms, however, **6b–8b** show somewhat inferior stability to **6a–8a** and decomposed within a few days in air [15].

Catenation of Three P-Heterocyclic Biradical Units

As reported earlier, the reaction of **2** with 1,3,5-tris(bromomethyl)benzene afforded the corresponding tris(biradicals) **10** [14,15] (Fig. 6). In the

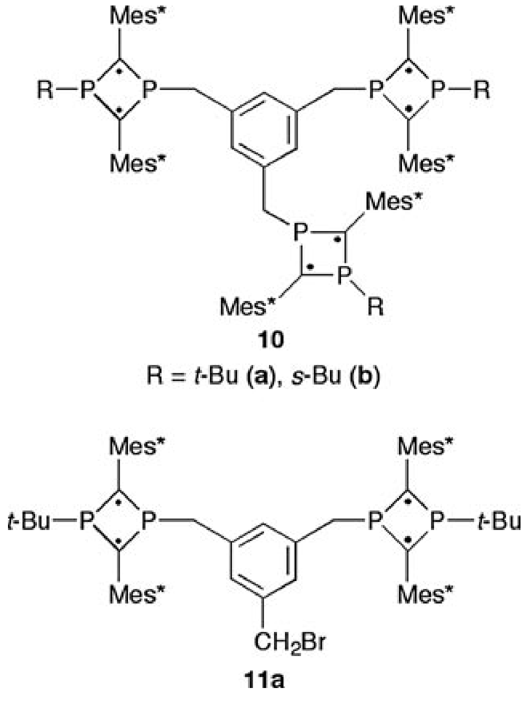


FIGURE 6 Structure of tris(biradicals) **10** and bis(biradicals) **11a**.

TABLE 1 Spectroscopic Data for **6–8**, **10**, and **12**

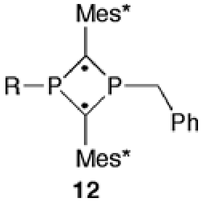
		NMR			*UV-Vis*	
R		δ_P	$^2J_{PP}$/Hz	δ_C	λ_{max}/nm	log ε
t-Bu	**6a**	54.9, −0.8	337.8	107.3	614	3.1
t-Bu	**7a**[a]	57.7, 1.0	335.2	109.1	616	3.3
t-Bu	**10a**[a]	63.5, −0.7	327.2	110.0	626	3.6
t-Bu	**12a**[b]	58.1, 0.6	334.8	108.6	610	3.2
s-Bu	**6b**[c]	27.2, 0.31 27.0, 0.28	374.4 373.5	nd	nd	nd
s-Bu	**7b**[c]	27.7, 1.3	377.9	109.2, 109.9	610	3.4
s-Bu	**8b**[c]	25.8, 2.1 25.9, 2.1	380.2 380.2	nd	608	3.3
s-Bu	**10b**[c]	36.1, −2.1	365.6	110.6, 111.5	620	3.5
s-Bu	**12b**[c]	26.6, 1.5	379.1	109.0, 109.6	606	3.1

nd = not determined.
[a] Ref [14].
[b] Ref [9].
[c] Ref [15].

synthesis of **10a**, it was impossible to introduce three biradical units in a single step due to excess steric bulk. Thus, stepwise procedures were employed to accomplish threefold introduction of **2a** [14]. Two equivalents of phosphaallyl anion **2a** were allowed to react with 1,3,5-tris(bromomethyl)benzene to afford the corresponding bis(biradicals) **11a** and subsequently **11a** was treated with **2a** to afford the corresponding tris(biradicals) **10a** in a separate step. However, **10b** could be successfully synthesized from **2b** and 1,3,5-tris(bromomethyl)benzene in a one-pot manner [15].

NMR and UV-Vis Spectroscopic Data of Oligo(biradicals)

Table 1 summarizes the available NMR and UV-Vis data of **6–9** together with **12a** and **12b** [14,15] (Fig. 7). In the ^{31}P NMR spectra, the expected signals of a typical AB pattern were observed. Compound **6a** showed almost the same ^{31}P NMR data as **3a**, indicating that the geometry around the phosphorus atoms remains undistorted, although its stability is considerably reduced as compared to **3a** (vide supra). The chemical shifts of the RP (R = *t*- or *s*-Bu) phosphorus in tris(biradicals) **10** show lower-field shifts compared with the other compounds, suggesting that the RP phosphorus atoms may exhibit slightly less pyramidalized geometries (possibly due to steric bulk of the three biradical units). The extent of pyramidalization also correlates with the difference of ^{31}P chemical shifts between the *t*-butyl (**a**) and the *s*-butyl (**b**) derivatives [15]. The $^2J_{PP}$ constants also seem to be affected by the pyramidalization determining interaction between the two ^{31}P nuclei. The sp^2 carbon atoms, on which an unpaired electron is formally located, are observed around δ_C = 110 ppm. UV-Vis spectra showed that the absorption maxima are dependent on number of biradical units. Compound **6a** showed slightly smaller red shift in comparison with **7a**, indicating that the nonconjugative, shorter distance between the biradical units hardly affects the photo-absorption properties. Thus, in spite of the absence of obvious and direct conjugating structures, the P-heterocyclic biradical units appear to experience an intramolecular interaction.



12

FIGURE 7 Structure of mono(biradicals) **12**.

Electrochemical Properties

Redox properties of oligo(biradicals) **6–8** and **10** were examined by voltammetric analysis to confirm that, in spite of the absence of conjugative structures through the spacer, the biradical units interact each other showing the expected stepwise releases of electrons [14,15]. As shown in a cyclic voltammogram of **6a** (Fig. 8), two reversible oxidation potentials were characterized due to presence of intramolecular interaction between the redox-active biradical

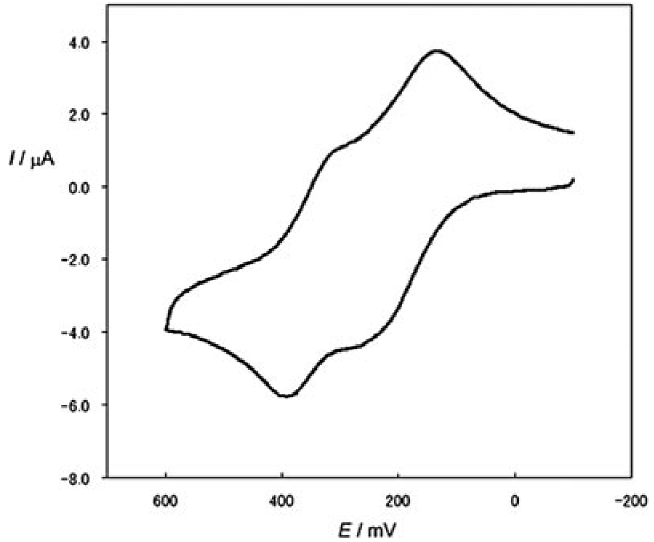


FIGURE 8 Cyclic voltammogram of **6a**. *Conditions*: 1 mM in CH_2Cl_2; supporting electrolyte: 0.1 M tetrabutylammonium perchlorate (TBAP); working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgCl ($E_{1/2} = +0.49$ V vs. ferrocene/ferricinium) at 20°C; scan rate: 50 mVs^{-1}.

units. Table 2 summarizes reversible oxidation potentials for oligo(biradicals) **6–8** and **10**. Separations of the oxidation potentials ($\Delta E^{\mathrm{ox1-ox2}}$) for **6a** are similar to those of **7a** and **8b**, indicating that the extent of intramolecular interaction between the biradical units is independent of π-conjugation structure of the benzyl-type spacer. In other words, the magnitude of the intramolecular interaction is almost constant in bis(biradicals) **6–8**. As for tris(biradicals), the $\Delta E^{\mathrm{ox1-ox2}}$ value of **10** reflects the same structural characteristics as **7** (utilizing the same spacer component), whereas the $\Delta E^{\mathrm{ox2-ox3}}$ split indicates smaller subsequent interaction [14]. It should be noted that oxidation potentials of the *s*-butyl derivatives **7b, 8b,** and **10b** are higher than those for the *t*-butyl derivatives by 0.1 V, consistent with a reduced electron-donating property of *s*-butyl group relative to *t*-butyl. The differences of oxidation potentials enable estimation of stabilization energy of the radical cation and the dication species by using the relationship: $-RT\ln K = -\Delta EF$, where F is the Faraday constant. Thus the stabilization energies for **6a**$^{\cdot+}$, **7a**$^{\cdot+}$, **7b**$^{\cdot+}$, **8b**$^{\cdot+}$, and **10a**$^{\cdot+}$ were calculated as 3.5, 3.0, 1.8, 2.5, and 3.2 kcal·mol^{-1}, respectively, and similarly 1.6 kcal·mol^{-1} for **10a**$^{2+}$. On the other hand, the fact that $E_{1/2}{}^{\mathrm{ox3}}$ was not observed for **10b** likely reflects a low stability of **10b**$^{\cdot+}$ and **10b**$^{2+}$ [15].

Molecular Structures of Oligo(biradicals)

We obtained crystals of **7a** suitable for X-ray analysis by recrystallization from dichloromethane [14]. Although the quality of the crystals was rather poor due to the inclusion of solvent molecules and the disorders that are often problematic in these highly *t*-butylated systems, it is obvious that two bulky biradical units are positioned on the same side of the central C_6H_4 aromatic ring in a *syn*-fashion. In the crystalline state, the edge of the C_6H_4 aromatic plane (1,2-position) of the catenating bridge faces the other C_6H_4 edge of a second bis(biradical) molecule with a nonbonded C···C distance of 3.87 Å (see Fig. 9).

Figure 10 displays two optimized structures for **13** as a model compound for **6a** [B3LYP/6–31G(d)] [16], where *t*-Bu and Mes* groups are replaced by methyl (Fig. 11). Intramolecular P···P distances of 3.92 Å (*syn*) and 4.95 Å (*anti*) are shorter than the corresponding data of model compounds for **7** and **8** [14,15]. In spite of the theoretically predicted short intramolecular P···P distance of **13**, the splitting of oxidation potentials ($\Delta E^{\mathrm{ox1-ox2}}$) of **6a** was almost the same as **7a** and **8b** (see Table 2). Therefore, the magnitude of the putative through-space interaction between the 1,3-diphiosphacyclobutane-2,4-diyl units may be almost constant in bis(biradicals) **6–8**.

TABLE 2 Redox Properties of Oligo(biradicals) (V vs. Ag/AgCl)[a]

R		$E_{1/2}^{ox1}$	$E_{1/2}^{ox2}$	$E_{1/2}^{ox3}$	$\Delta E^{ox1-ox2}$	$\Delta E^{ox2-ox3}$
t-Bu	**6a**	+ 0.35	+ 0.50		0.15	
t-Bu	**7a**[b]	+ 0.35	+ 0.48		0.13	
t-Bu	**10a**[b]	+ 0.31	+ 0.45	+ 0.52	0.14	0.07
s-Bu	**7b**[c]	+ 0.45	+ 0.53		0.08	
s-Bu	**8b**[c]	+ 0.47	+ 0.56		0.11	
s-Bu	**10b**[c]	+ 0.43	+ 0.59	nd	0.16	nd

nd = not determined.
[a] Ferrocene/ferricinium = +0.60 V.
[b] Ref [14].
[c] Ref [15].

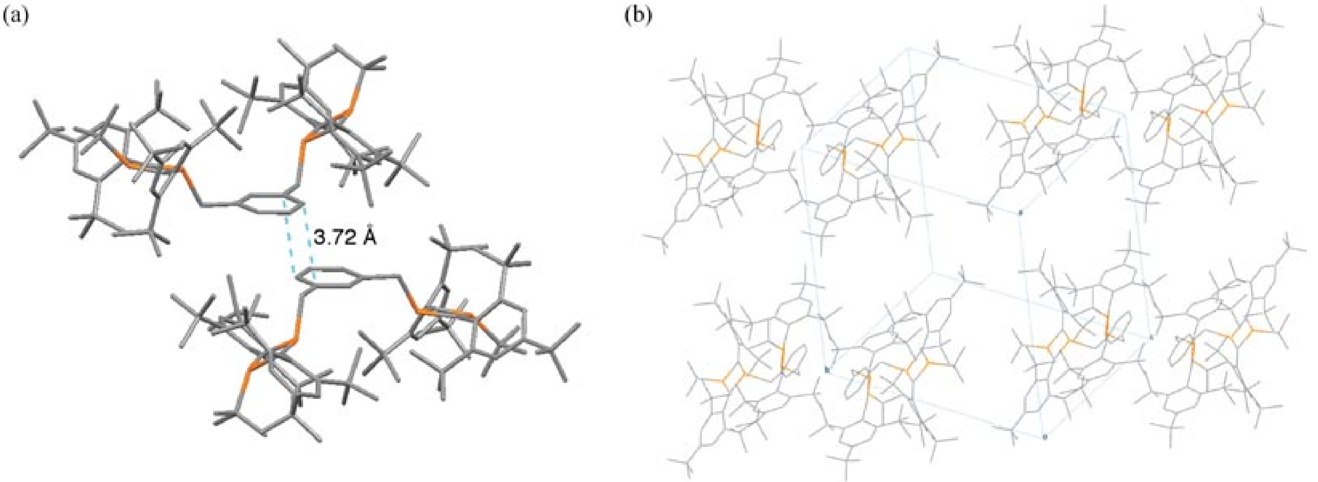


FIGURE 9 (a) A pair of **7a** in solid state. Hydrogen atoms and solvent molecules are omitted for clarity. (b) Crystal packing in **7a**.

AM1 calculations for **14** as a "near-experimental" molecule bearing 2,6-*t*-$Bu_2C_6H_3$ and *t*-butyl groups characterized energetic preference of the anticonformation by 5.98 kcal·mol^{-1}. [Electronic supplementary material is available on request from the authors: DFT calculations for **13** and **15**, and AM1 calculations for **14** and **16**.]

In an attempt to obtain structural aspects of the triply catenated derivatives **10**, DFT calculations for **15** as a model compound were undertaken (Fig. 12). Two types of structures (*alternate*-type and *cone*-type) were characterized revealing only small energetic differences. In taking the presence of six Mes* groups in **10** into account, the *alternate*-type structure might predominate in the experimentally characterized tris(biradicals). Similar to the discussions for **7a** [14], AM1 calculation for **16** with 2,6-di-*t*-butylphenyl groups showed that the *alternate*-type is energetically preferable to the *cone*-type by 2.05 kcal·mol^{-1}.

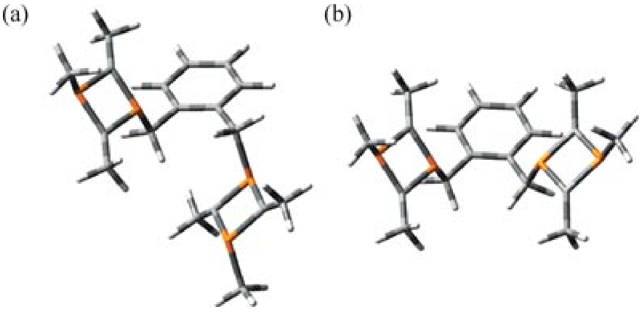
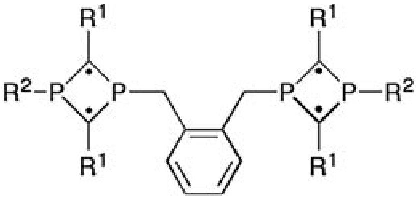


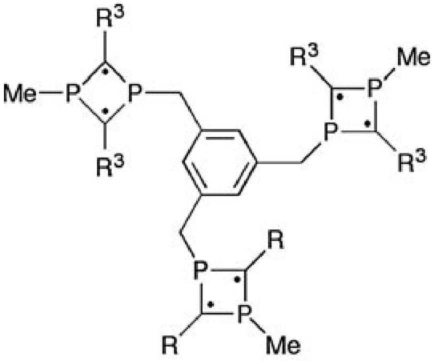
FIGURE 10 Optimized *anti* (a) and *syn* (b) structures of **13** at the B3LYP/6–31G* level. Relative energies are 0.00 and 1.88 kcal·mol^{-1}, respectively.

CONCLUSION

We have succeeded in catenating two and three sterically encumbered 1,3-diphospacyclobutane-2,4-diyl units with benzyl-type spacers to obtain oligo(biradicals) **6–8** and **10** as remarkably stable compounds. Spectroscopic data, redox properties, and molecular structures of the oligo(biradicals) derivatives revealed that the P-heterocyclic biradical



13: $R^1 = R^2 = Me$
14: $R^1 = 2,6\text{-}t\text{-}Bu_2C_6H_3$, $R^2 = t\text{-}Bu$



15: $R^3 = Me$
16: $R^3 = 2,6\text{-}t\text{-}Bu_2C_6H_3$

FIGURE 11 Structure of model compounds **13–16**.

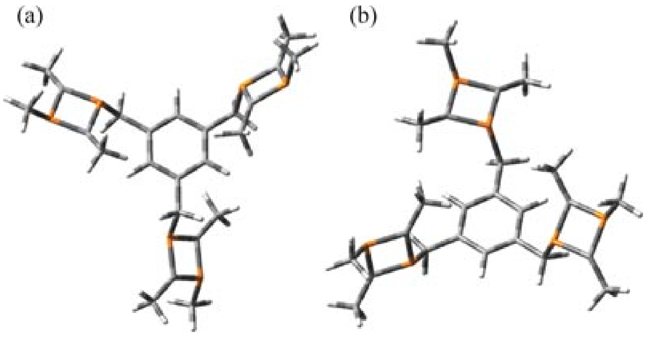


FIGURE 12 Drawings of *alternate*-type (a) and *cone*-type (b) structures of **15** at the B3LYP/6–31G(d) level. Relative energies are 0.00 and 0.38 kcal·mol^{-1}, respectively.

moieties interact through nonconjugative pathways. The properties of oligo(biradicals) hold promise for the design control of spin–spin interactions in novel molecular architectures.

EXPERIMENTAL

All manipulations were carried out under an argon atmosphere by the standard Schlenk technique. All solvents employed were dried by appropriate methods. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker Avance 400 or AMX 300 spectrometer with Me_4Si (^{1}H, ^{13}C) and H_3PO_4 (^{31}P) as internal and external standards. Mass spectra were recorded with a Bruker APEX3 or a JEOL JMS T100LC spectrometer. UV-Vis spectra were recorded with a Hitachi U-3210 spectrometer. Electrochemical analyses were performed with a BAS CV-50W voltammetric analyzer. Phosphaalkyne **1** was prepared according to the method reported previously from 2,2-dibromo-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (Mes*P = CBr_2) [8,9]. Preparation of **7a, 8a, 10a, 6b, 7b, 8b**, and **10b** was described in our previous reports [14,15].

Preparation of **6a**

t-Butyllithium (0.18 mmol, 1.4 M solution in pentane) was added to a solution of **1** (100 mg, 0.35 mmol) in THF (5 mL) and TMEDA (0.18 mmol) at −78°C and stirred for 10 min. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. To the solution containing **2a** was added a solution of α,α'-dibromo-*o*-xylene (0.088 mmol) in THF (1 mL) over a period of 1 h, 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 **6a** as a deep blue solid (56 mg, 47%). Mp 140–142°C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (d, $^{3}J_{PH} = 14.0$ Hz, 18H, *t*-BuP), 1.28 (s, 36H, *p*-*t*-Bu), 1.33 (s, 36H, *o*-*t*-Bu), 1.63 (s, 36H, *o*-*t*-Bu), 3.65 (pt, $(^{2}J_{PH} + {}^{4}J_{PH})/2 = 4.2$ Hz, 6H, CH_2), 6.60 (t, $^{3}J_{HH} = 6.0$ Hz, 2H, C_6H_4), 6.75 (d, $^{3}J_{HH} = 6.0$ Hz, 2H, C_6H_4), 7.14 (s, 4H, *m*-Mes*), 7.36 (s, 4H, *m*-Mes*); ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2) δ 29.3 (pt, $(^{2}J_{PC} + {}^{4}J_{PC})/2 = 3.8$ Hz, P*CMe*$_3$), 30.8 (dd, $^{1}J_{PC} = 37.0$, $^{1}J_{PC} = 3.0$ Hz, CH_2), 31.1 (s, *p*-C*Me*$_3$), 33.4 (d, $^{5}J_{PC} = 10.6$ Hz, *o*-C*Me*$_3$), 34.4 (s, *p*-*C*Me$_3$), 34.6 (brs, *o*-C*Me*$_3$), 37.5 (s, *o*-*C*Me$_3$), 38.4 (s, *o*-*C*Me$_3$), 47.8 (dd, $^{1}J_{PC} = 52.9$ Hz, $^{3}J_{PC} = 11.3$ Hz, P*C*Me$_3$), 107.3 (pt, $(^{1}J_{PC} + {}^{1}J_{PC})/2 = 7.6$ Hz, CP_2), 121.0 (d, $^{4}J_{PC} = 2.7$ Hz, *m*-Mes*), 122.5 (s, *m*-Mes*), 126.5 (d, $J_{PC} = 2.3$ Hz, C_6H_4), 128.8 (d, $J_{PC} = 1.5$ Hz, C_6H_4), 132.9 (d, $^{3}J_{PC} = 6.0$ Hz, *ipso*-Mes*), 136.0 (d, $J_{PC} = 4.5$ Hz, C_6H_4), 145.3 (s, *p*-Mes*), 148.6 (brs, *o*-Mes*), 150.5 (t, $^{3}J_{PC} = 4.5$ Hz, *o*-Mes*); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 54.9 (d, $^{2}J_{PP} = 337.8$ Hz, *t*-BuP), −0.75 (d, $^{2}J_{PP} = 337.8$ Hz, CH_2P); UV-Vis (CH_2Cl_2) λ_{max} (nm) (log ε): 614 (3.1), 386 (4.0), 339 (4.2); ESI-MS calcd. for $C_{92}H_{142}P_2$ [M^{+}] 1371.0057, found 1371.0078.

Spectroscopic data of **9a**

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (d, $^{3}J_{PH} = 14.1$ Hz, 9H, *t*-BuP), 1.31 (s, 18H, *p*-*t*-Bu), 1.45 (s, 18H, *o*-*t*-Bu), 1.71 (s, 18H, *o*-*t*-Bu), 3.74 (pt, $(^{2}J_{PH} + {}^{4}J_{PH})/2 = 3.0$ Hz, 2H, CH_2), 4.33 (s, 2H, CH_2Br), 6.91–7.05 (m, 4H, C_6H_4), 7.22 (s, 2H, *m*-Mes*), 7.41 (s, 2H, *m*-Mes*); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 56.4 (d, $^{2}J_{PP} = 323.2$ Hz, *t*-BuP), −1.6 (d, $^{2}J_{PP} = 323.2$ Hz, CH_2P); ESI-MS calcd. for $C_{50}H_{75}BrP_2$ [M^{+}] 816.4522, found 816.4516.

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