ORGANIC LETTERS

2013
Vol. 15, No. 13
3404–3407

Through-space Electrostatic Interaction between the Electron-donating 1,3-Diphosphacyclobutane-2,4-diyl Units

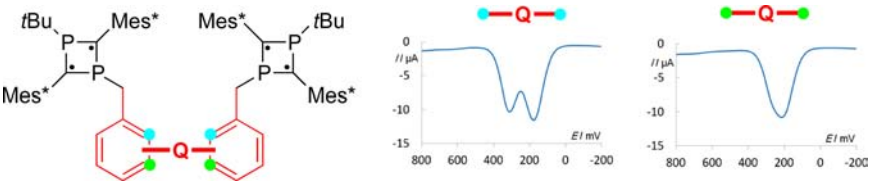
Shigekazu Ito,* Makoto Kobayashi, and Koichi Mikami

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

ito.s.ao@m.titech.ac.jp

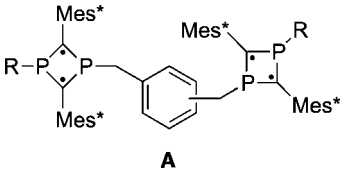
Received May 23, 2013

ABSTRACT



Catenation of stable 1,3-diphopsphacyclobutane-2,4-diyl units with biphenyl-, diphenyl ether-, and diphenylmethane-based bridging groups were utilized for evaluation of the distinct through-space interaction between the electron-donating P-heterocyclic biradical chromophores. Structural properties of the oligo(biradicals), characterized by X-ray crystallography and DFT calculation, suggest a possible distance between the biradical units for the through-space interaction.

The air-tolerant 1,3-diphosphacyclobutane-2,4-diyl unit can be utilized as a good electron-donating molecular unit,[1] which is expected to be available for development of electro-functional materials based on the chemistry of phosphorus heterocycles.[2,3] We previously reported that catenation of such electron-rich P-heterocyclic biradical units using xylyl spacers (**A**) induces a through-space interaction even in the absence of a π-conjugative structure between the biradical units, and stepwise electron-releasing processes would generate the corresponding mixed-valence intermediates (Figure 1).[4,5] Such a nonconjugative through-space interaction would be based on the particular properties of a singlet biradical,[6] and further molecular designs for accumulation of the redox-active P-heterocyclic biradicals will provide novel useful compounds for such organic electronics. On the other hand, synthesis of novel oligo(biradicals) is desirable to discuss the through-space interaction in detail, because the previous catenation using the xylyl-type spacing groups[4] might contain the possibility of a homoconjugative interaction between the biradical units via P−CH_2 sigma bonds.



A

Figure 1. Previous examples of dually catenated 1,3-diphosphacyclobutane-2,4-diyl units with xylyl spacers. Mes* = 2,4,6-tBu$_3$C$_6$H$_2$.

In this paper we demonstrate dual catenation of the P-heterocyclic biradical units using biphenyl-, diphenyl ether-, and diphenylmethane-based spacing groups in which the possible homoconjugative effect would be

(1) Yoshifuiji, M.; Arduengo, A. J., III; Kobovalova, T. A.; Kispert, L. D.; Kikuchi, M.; Ito, S. *Chem. Lett.* **2006**, *35*, 1136–1137.
(2) Baumgartner, B.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681–4727.
(3) Niecke, E.; Fuchs, A.; Baumeister, F.; Nieger, M.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 555–557.
(4) Ito, S.; Miura, J.; Morita, N.; Yoshifuji, M.; Arduengo, A. J., III *Angew. Chem., Int. Ed.* **2008**, *47*, 6418–6421. See also: Rodriguez, A.; Tham, F. S.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 4876–4880.
(5) (a) Ito, S.; Miura, J.; Morita, N.; Yoshifuji, M.; Arduengo, A. J., III *Z. Anorg. Allg. Chem.* **2009**, *635*, 488–495. (b) Ito, S.; Miura, J.; Morita, N.; Yoshifuji, M.; Arduengo, A. J., III *Heteroat. Chem* **2010**, *21*, 404–411.
(6) (a) Breher, F. *Coord. Chem. Rev.* **2007**, *251*, 1007–1043. (b) Power, P. P. *Nature* **2010**, *463*, 171–177. (c) Grützmacher, H.; Breher, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4006–4011.

10.1021/ol401456h
Published on Web 06/13/2013

effectively reduced. Structural aspects of the novel bis(biradicals) are studied using X-ray crystallographic analysis and DFT calculation. Electrochemical measurements are utilized for evaluation of the through-space interaction. Furthermore, linear-triple catenation of the biradical units is also performed.

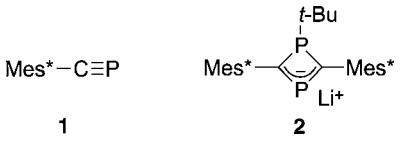


Figure 2. Precursors for synthesis of the air-stable P-heterocyclic biradical derivatives.

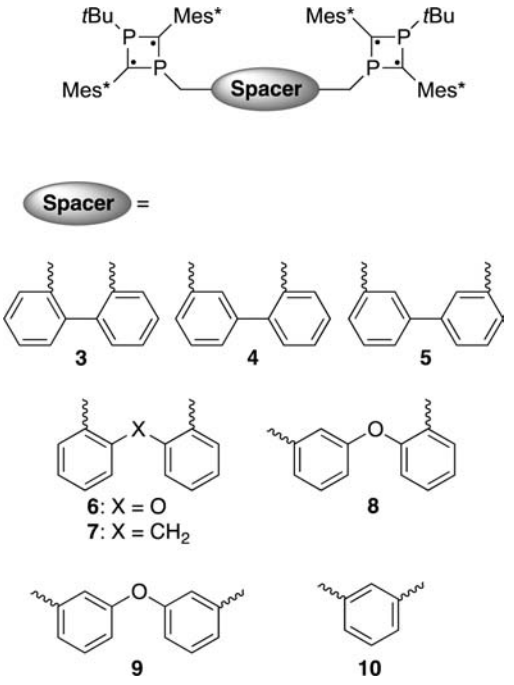


Figure 3. Novel bis(biradicals) **3**–**9** and the related known compound **10**.

One of the structural modifications of **A** for minimizing the possible homoconjugative interaction is to employ nonconjugative skeletons as the spacing group. In this study we first employed biphenyl skeleton for the spacers because biphenyl inherently displays twisted conformations.[7] Next, as an attempt to the minimization of the homoconjugative interaction, we also examined catenation of the biradical units with bis(methylenephenyl)ether and bis(methylphenyl)methane spacers.

According to our established procedures, phosphaalkyne **1** was allowed to react with 0.5 equiv of *t*-butyllithium to generate cyclic anion **2** (Figure 2)[8] and subsequently treated with bis(bromomethyl)biphenyls to afford air-tolerant crystalline bis(biradicals) **3**–**5**. Isolated yields of **3** and **4** were relatively low in comparison with that of **5**, indicating effects of the steric encumbrance. Furthermore, di(methylphenyl)ether and di(2-methylphenyl)methane moieties were also nonproblematic to combine the biradical units, and air-stable **6**–**9** were isolated in moderate to good yields (Figure 3).

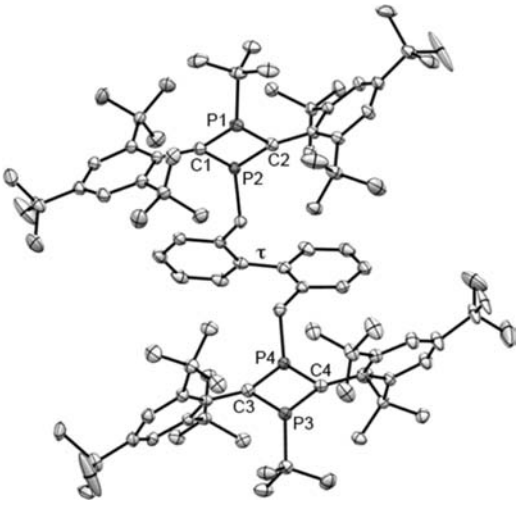


Figure 4. An ORTEP drawing of X-ray structure of **3** (20% probability ellipsoids). Hydrogen atoms and solvent molecules (dichloromethane) are omitted for clarity. Three *p*-*t*-butyl groups are disordered and the atoms with predominant occupancy factors (0.72, 0.57, 0.55) are displayed. Bond lengths (Å): P1−C1 1.722(4), P1−C2 1.713(4), P2−C1 1.773(4), P2−C2 1.778(4), P1−*t*Bu 1.875(5), P2−CH_2 1.848(4), C1−Mes* 1.503(5), C2−Mes* 1.484(5), P3−C3 1.713(4), P3−C4 1.714(3), P4−C3 1.789(3), P4−C4 1.794(4), P3−*t*Bu 1.885(4), P4−CH_2 1.858(4), C3−Mes* 1.490(5), C4−Mes* 1.497(5). Sums of angles (deg): P1 342.3(2), P2 317.9(2), C1 359.5(3), C2 357.6(3), P3 346.9(2), P4 317.4(2), C3 358.3(3), C4 358.6(3). Torsion angle (τ) = 64.0(5)°.

Compounds **3**–**9** were characterized by the spectroscopic data. In the ^{13}C NMR spectra of **3**, due to the helical conformation of the bridging biayl skeleton, two signals for the diastereotopic skeletal sp^2-C atoms were observed. Furthermore, we examined X-ray crystallographic analysis of the single crystals of **3** (Figure 4, $P2_1/n$ space group). Probably due to unsolved disordered structures, quality of the structure refinement was slightly insufficient, and was not improved even in analysis with lower-symmetrical space group such as $P2_1$. However, the data seemed to be reasonable enough to confirm the skeletal parameters. The gross structure of **3** indicates that the two biradical units cannot interact through any rigid π-conjugated skeleton.[9] The metric parameters around the four-membered cycles are comparable to those of the previously reported air-stable

(7) Vonlanthen, D.; Rotzler, J.; Neuburger, M.; Mayor, M. *Eur. J. Org. Chem.* **2010**, 120–133.

(8) Sugiyama, H.; Ito, S.; Yoshifuji, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3802–3804.

1,3-diphosphacyclobutane-2,4-diyls.[8,10] On the other hand, interestingly, in spite of the remarkable steric hindrance, torsion angle of the biaryl linker (64°) is not perpendicular completely in the crystalline state. The conformation of the spacer indicates the presence of an attractive interaction between the biradical units probably due to electrostatic effects. The distance between the skeletal centroids of **3** (8.494 Å) is comparable or rather shorter in comparison with that of **10** (8.847 Å).[4] The Mes* aryl groups are considerably distorted due to the steric encumbrance,[11] whereas the dihedral angles between the 4-membered planar heterocycles and Mes* aryl planes are 68−70°.

Such structural characters of **3** were supported by DFT calculations (Figure S1, Supporting Information) [M06−2X/6-31G(d); as the enantiomeric form].[12,13] The typical metric parameters around the P-heterocyclic skeletons, including the sp^2-type planar skeletal carbons and the sp^3-type pyramidalized phosphorus atoms, are characterized.[10] The distance between the centroids of the P_2C_2 four-membered rings is within 1 nm (DFT: 8.175 Å), which would enable the through-space communication.[14]

In order to evaluate the through-space interaction, we examined electrochemical measurements of the novel bis(biradicals). Figure 5 displays the cyclic voltammograms and DPV (differential pulse votammetry) data of **3**−**5**. Compounds **3** and **4** exhibit two-step reversible electron-releases, indicating that the electron-donating biradical units electrostatically interact each other. On the other hand, quite small separation of oxidation potentials exhibiting almost single-step electron release was observed in the votammetric measurements of **5**. Therefore, it is plausible that the through-space interaction between the biradical chromophores can be operable by the bridging structures. The DFT-optimized structure of **3** characterized the HOMO and HOMO-1 orbitals with the quite small energetic difference (Figure S2, Supporting Information), which might relate to the elecrochemical properties in solution.

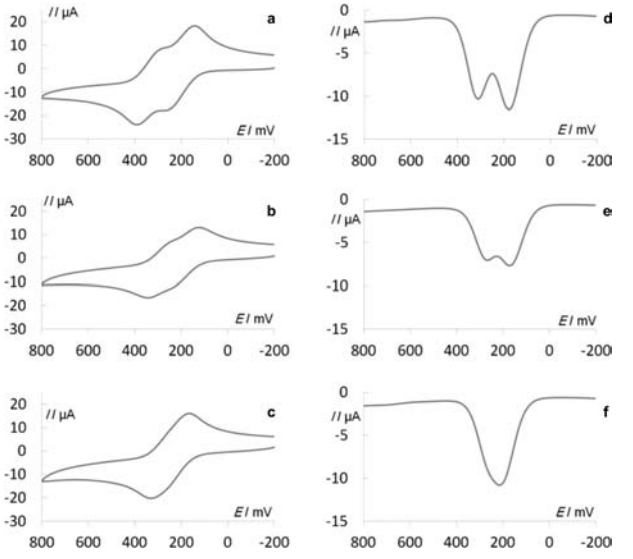


Figure 5. Cyclic voltammograms of (a) **3**, (b) **4**, and (c) **5**, and DPV charts of (d) **3**, (e) **4**, and (f) **5**. Conditions: 1 mM in CH_2Cl_2; 0.1 M tetrabutylammonium perchlorate (TBAP); working electrode, GC; counter electrode, Pt; reference electrode, Ag/AgCl; scan rate 100 mVs^{-1}. T = 298 K. Fc/Fc^+ = 0.52 V.

Table 1 summarizes the voltammetric parameters of **3**−**9**. All the voltammograms indicated reversible oxidation processes (Figures S3, S4, Supporting Information). Compounds **6**−**8** exhibit the through-space interaction between the biradical chromophores inducing the stepwise oxidations. Potential difference between the first and second oxidations considerably depends on the spacer, and the larger distance between the biradical units reduces magnitude of the though-space electrostatic interaction. The similar ΔE_{ox} parameter of **3** to that of **10** (0.13 V)[4] corresponds to the structural characteristics discussed as above. On the other hand, the ΔE_{ox} data of **6** is also close to that of **10**, whereas **7** exhibits smaller ΔE_{ox} data. The DFT-optimized structure of **7** indicated the longer centroid-centroid distance (9.905 Å, see Supporting Information) in comparison with those of **3** and **10**. Although detailed reason for the considerable through-space interaction of **6** is unclear, the diaryl ether structure would be effective to induce the stepwise oxidations. Stabilization energy of the corresponding radical cations is estimated as 1.9−3.1 kcal mol^{-1}.[15] DFT calculations of **4** and **8** indicated the centroid-centroid distances of ca. 1 nm (10.34 and 10.82 Å, respectively), whereas **5** exhibits 1.2 nm (see Supporting Information).

Table 1. Redox Properties of **3**−**9**[a]

compound	$E_{ox1}{}^{1/2}$/mV	$E_{ox2}{}^{1/2}$/mV	ΔE_{ox}/mV	K_c[b]
3	176	312	136	200
4	172	268	96	42
5	214			
6	158	292	134	185
7	192	294	102	53
8	168	252	84	26
9	216			

[a] *Conditions*: 1 mM in CH_2Cl_2; 0.1 M TBAP; working electrode, GC; counter electrode, Pt; reference electrode, Ag/AgCl; scan rate, 100 mVs^{-1}. T = 298 K. Fc/Fc^+ = 0.52 V. [b] Determined by $-RT\ln K_c = -F\Delta E_{ox}$. F = Faraday const.

The redox properties of **5** and **8** correspond to the results of linearly tricatenated biradicals (Figure 6). Taking the

(9) Although the axial bond might be able to rotate, conjugation effect between the biradical units would be considerably reduced.

(10) Yoshifuji, M.; Sugiyama, H.; Ito, S. *J. Organomet. Chem.* **2005**, *690*, 2515–2520.

(11) Ito, S.; Miyake, H.; Yoshifuji, M. *Phosphorus, Sulfur, Silicon* **2009**, *184*, 917–927.

(12) Frisch, M. J. et al. *Gaussian 09*, Revision B.01, Gaussian, Inc.: Wallingford, CT, 2010. See Supporting Information for full reference.

(13) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215–241.

(14) (a) Miller, J. R.; Calcaterra, L. T.; Class, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047–3049. (b) Johnson, M. D.; Miller, J. R.; Green, N. S.; Closs, G. L. *J. Phys. Chem.* **1989**, *93*, 1173–1176.

(15) Richardson, D. E.; Taube, E. *Inorg. Chem.* **1981**, *20*, 1278–1285.

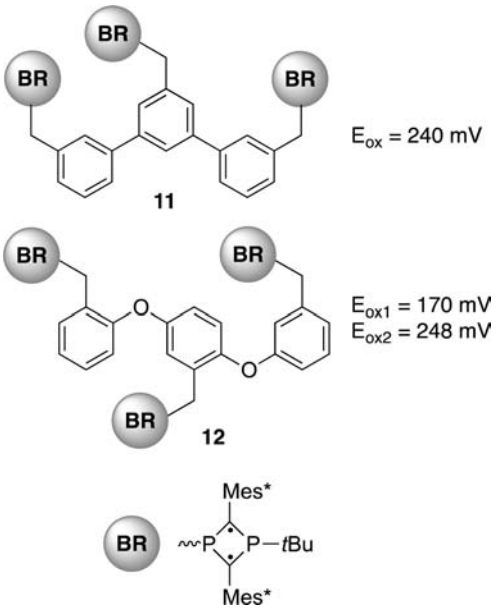


Figure 6. Tris(biradicals) bearing linear bridging groups.

predicted synthetic accessibility based on the dual catenation into account, here we employed 3,3″,5′-trimethyl-1,1′:3′,1″-terphenyl and 2-methyl-1-(*m*-tolyloxy)-4-(*o*-tolyloxy)-benzene skeletons as the linear-type spacers. Voltammetric measurements of **11** and **12**, successfully synthesized according to the established procedures, displayed neglecting and substantial through-space interactions, respectively (Figure S5, Supporting Information). In contrast to our previous results of tris(biradicals) bearing 1,3,5-tris(methylene)benzene spacer, the linearly catenated **12** exhibited only two observable oxidation potentials, putatively due to one centroid chromophore and two almost identical terminal biradical units. Separation of the oxidation potentials of **12** (ΔE_{ox} 78 mV) is comparable to that of **8**.[16]

In conclusion, the scope of the through-space interaction between the electron-donative P-heterocyclic biradical units is evaluated by the biphenyl-, diphenyl ether-, and diphenylmethane-type spacing groups, and it has been obvious that positioning of the biradical units within ca. 1 nm approximately enables generation of the corresponding mixed-valent radical cation intermediates. Attempts to analyze the mixed-valent chemical species and application to electro-functional materials are in progress.

Acknowledgment. This work was supported in part by Grants-in-Aid for Scientific Research (Nos. 22350058 and 23655173) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, Sumitomo Chemical Co., Ltd., and Nissan Chemical Industries, Ltd. We thank Prof. Hiroharu Suzuki and Dr. Masataka Oishi of Tokyo Institute of Technology for supports of X-ray crystallographic analyses. Prof. Yuji Wada and Dr. Masato Maitani of Tokyo Institute of Technology supported UV−vis spectroscopic measurements.

Supporting Information Available. Experimental details, characterization data, X-ray crystallography of **3**, DFT calculations of **3**–**5**, **7** and **9**, and voltammograms of **6**–**9**, **11** and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

(16) The second oxidation step did not indicate simultaneous two-electron release from the two terminal biradical units. This property might be due to effect of the putative Coulombic repulsion.

The authors declare no competing financial interest.