

New Aspects of 1,3-Diphosphacyclobutane-2,4-diyls

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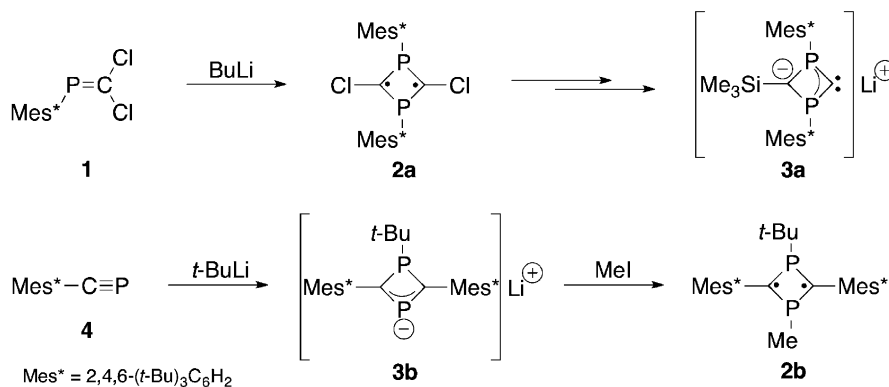
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Dedicated to Prof. Dr. Dieter Seebach on the occasion of his 75th birthday

1,3-Di(*tert*-butyl)-2,4-bis[2,4,6-tri(*tert*-butyl)phenyl]-1,3-diphosphacyclobutane-2,4-diyl was formed from [2,4,6-tri(*tert*-butyl)phenyl]phosphaacetylene and *t*-BuLi. In addition, the X-ray diffraction analysis was carried out, together with theoretical calculations of the structure and NMR data.

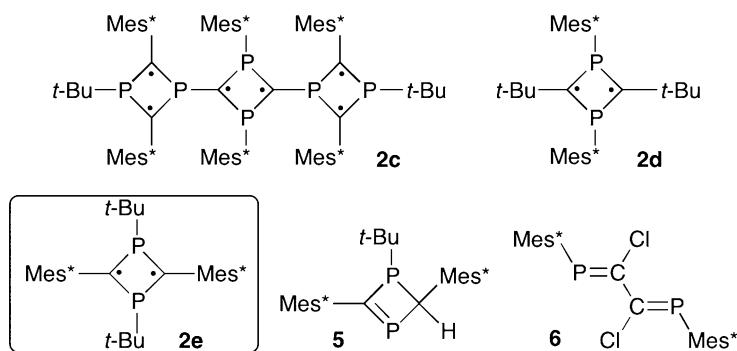
Introduction. – In recent years, 1,3-diphosphacyclobutane-2,4-diyls **2a** [1] and **2b** [2] have become available as stable species by using phospho-alkene **1** or phospho-alkyne **4** with the 2,4,6-tri(*tert*-butyl)phenyl (abbreviated as Mes*) as a sterically bulky substituent. Compounds **2** are of interest in terms of bonding, physical properties, and chemical reactivity. Anionic systems **3a** [3] and **3b** [4] – derived from **2a** or being precursor of **2b** – (Scheme 1) have been established as well and shall be used as building blocks.

Scheme 1



To gain better understanding of the bonding and properties of biradicals, the first attempt was made to prepare a multi-biradical system such as **2c** (*Scheme 2*) via reaction of 1,3-diphosphacyclobutenyl anion **3b** with **2a**. Multi-biradicals, for which interesting chemical and physicochemical features might be expected, are different from the individual **2a** and/or **2b** units that possess singlet ground states. Oligomeric (or polymeric) biradicals might serve as chemicals for hydrogen storage [5][6], oxidation/reduction [7], and UV/VIS and CV-featured substance [8]. Accumulation of these characters in one molecule [8–10] may lead to interesting materials in view of electrochemical, electromagnetic, and optophysical properties.

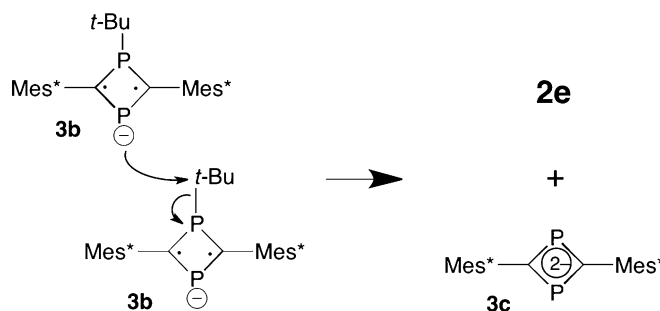
Scheme 2



Results and Discussion. – Biradical **2a** was reacted with **3b** to afford a blue crystalline product. Based on preliminary spectroscopic analysis of this product, including NMR, UV/VIS, and CV, **2d** was assumed to be formed instead of the desired mixed multi-biradical system **2c**, mainly due to the ^1H -NMR spectrum, in which the Me signals appeared as a *triplet* that was reasonably assigned to an AX_2 spin system for **2d**. However, X-ray crystallographic analysis of the compound unambiguously confirmed that the product was **2e** [4], revealing that the desired framework of compound **2a** was not incorporated. Furthermore, in an attempt to get further insight into the assumed structure of **3b**, a deep colored crystal from the concentrated solution of **3b** in Et_2O in the presence of 12-crown-4 was submitted to X-ray analysis, but again the structure turned out to be that of **2e**. Observation of a small amount of **4** in the ^{31}P -NMR spectrum indicated an equilibrium between **3b** and the starting material, although the equilibrium might be far right-shifted and product-oriented. A solution of the anion formed under the same conditions in the presence of the crown ether followed by quenching the reaction with MeI, gave the expected product **2b**. Based on the finding that no evidence was available for the source of an electrophilic *t*-Bu group in the **2e** formation besides **3b** itself (even if *t*-BuLi remained in a slight excess, it was supposed to serve as a nucleophile), transformation might occur during the isolation process of **3b** involving concentration. *Scheme 3* displays a proposed reaction mechanism: **3b** can serve as a nucleophile and an electrophile to give **2e** and a cyclic dianion **3c**. It should be noted that **2e** was alternatively obtained from anion **3b** with *t*-BuI in good yield [4]. In

addition to the formation of **2e**, **5** [11] was also obtained in a small amount as a result of protonation product of **3b** based on the ^{31}P -NMR analysis. Although attempts to isolate **3c** have failed so far, probably due to the thermal instability, concentration of a THF solution of **2e** generated a thermally unstable compound exhibiting a ^{31}P resonance at 175 ppm together with **4**, **5**, and phospho-alkenes ($\text{Mes}^*\text{C}(\text{H})=\text{P}(t\text{-Bu})$, $\delta(\text{P})$ 281 and 292 ppm). The peak at $\delta(\text{P})$ 175 ppm might be responsible to that of the DFT-optimized **3c**¹.

Scheme 3



Attempts to achieve a ‘simple’ halogen/metal exchange on the ring of **2a** did not seem to take place. In fact, **2a** gave diphosphabutadiene **6** after reaction with $t\text{-BuLi}$, followed by MeI quenching, suggesting that the process includes the C_2P_2 ring cleavage during the reaction, and no incorporation with MeI was observed.

X-Ray Analysis. The structure of compound **2e** was unambiguously confirmed by X-ray crystallography (Fig. 1)². It is thus confirmed that the two $t\text{-Bu}$ groups are attached to the P-atoms and not to the C-atoms of the four-membered ring.

The sample turned out to be non-merohedrally twinned. The twin fractions (0.67:0.33) are connected *via* the refined twin law $(-10.19394 \ 0.00064 \ -1.19452 \ 0.002000 \ -1.00000 \ -0.00393 \ -0.80567 \ -0.00044 \ 0.19394)$. Furthermore, a slight disorder of the P-atoms could be found and solved. The main orientation (‘P’ and ‘P#’; 85%) is depicted in non-transparent purple color, whereas the side occupation (‘Ps’, ‘Ps#’; 15%) is displayed in faded pink.

The twinning and disorder problems could be solved, thus the outcome is a good and publishable structure. The Table lists selected bond lengths and angles. In spite of the disorder of the compound, it is confirmed that C_2P_2 ring is almost coplanar, and that

¹) A GIAO calculation for **3c**, optimized by DFT method [B3PW91/6-31 + G(d)], was performed at the wB97XD/6-31 + + G(2d,p) level to estimate ^{31}P chemical shifts, $\delta(\text{P})$, of 152.00 and 152.07 ppm.

²) **Crystallographic data of 2e:** $\text{C}_{46}\text{H}_{76}\text{P}_2$; M_r 691.91, orthorhombic, *Pccn* (#56), $a = 14.2075(9)$, $b = 25.6989(16)$, $c = 11.6699(8)$ Å, $V = 4260.9(5)$ Å³, $Z = 4$, $T = 100(2)$ K, $\rho_{\text{calc}} = 1.077$ g cm⁻³, $\mu(\text{MoK}\alpha) = 0.131$ mm⁻¹, $2\theta_{\text{max}} = 50.5^\circ$, $F_{000} = 1528$, 4450 observed reflections, 3766 unique reflections ($R_{\text{int}} = 0.086$), $R1 = 0.062$ ($I > 2\sigma(I)$)/0.074 (all data), $wR = 0.157$ ($I > 2\sigma(I)$)/0.172 (all data), $S = 1.132$. CCDC-878538 contains the supplementary crystallographic data for this work. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

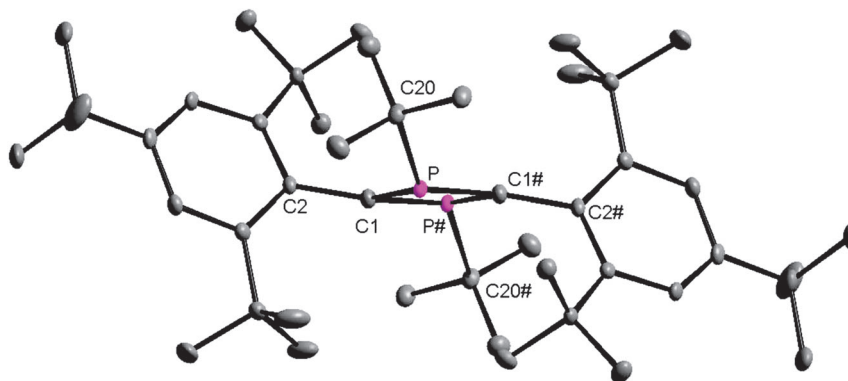


Fig. 1. Molecular structure of **2e** by X-ray analysis (only the major structure is depicted)

the two P-atoms have a pyramidal configuration, which is a typical structure for diphosphacyclobutanediyls.

Table. Selected Bond Lengths [Å] and Angles [°] of **2e**

Bond	DFT Calculation	X-Ray Analysis	Angle	DFT Calculation	X-Ray Analysis
P1–C1	1.7568	1.751(3)	C1–P1–C2	91.63	91.4(1)
P1–C2	1.7633	1.766(3)	C1–P2–C2	91.67	91.4(1)
P2–C1	1.7623	1.766(3)	P1–C1–P2	88.36	88.6(1)
P2–C2	1.7565	1.751(3)	P1–C2–P2	88.34	88.6(1)
P1–C3	1.9016	1.918(4)	$\Sigma_{\text{angles}}(\text{P1})$	332.63	334.6
P2–C4	1.9022	1.918(4)	$\Sigma_{\text{angles}}(\text{P2})$	332.70	334.6
C1–C5	1.4830	1.490(4)	$\Sigma_{\text{angles}}(\text{C1})$	357.38	357.8
C2–C6	1.4831	1.490(4)	$\Sigma_{\text{angles}}(\text{C2})$	357.35	357.8

Optimum Structure. A theoretical calculation was carried out for **2e** to indicate that the optimum structure for the compound is almost identical to that of the real compound, as shown in Fig. 2 and in the Table [12][13]. TD-DFT Calculation [M06-2X/6-31G(d)] characterized HOMO to LUMO (593.77 nm, $f=0.0476$), HOMO to LUMO + 1 (344.90 nm, $f=0.2475$), and HOMO–1 to LUMO (324.21 nm, $f=0.1896$) transitions, which is comparable to the experimentally observed UV/VIS spectrum.

NMR Calculation. NMR Parameters were calculated using the GIAO program [14][15] at the B3LYP/6-31G(2d,p)//M06-2X/6-31G(d) level of theory. ^{31}P -NMR Chemical shifts of the compound were calculated as 38.06 and 38.08 ppm, and ^{13}C -NMR shifts for the ring C-atoms were both as 120.7 ppm. Although the coupling constants between H- and P-atoms are not calculated for a molecule with free rotation, in some cases 3J values are smaller than those of 5J , which might be due to the appearance of a pseudo-triplet signal of H-atoms of *t*-Bu moiety directly bound to the P-atom for **2e**.

Conclusions. – We have been successful in obtaining further important insights into the biradical system **2**, including the features of anion **3b** and the X-ray structure

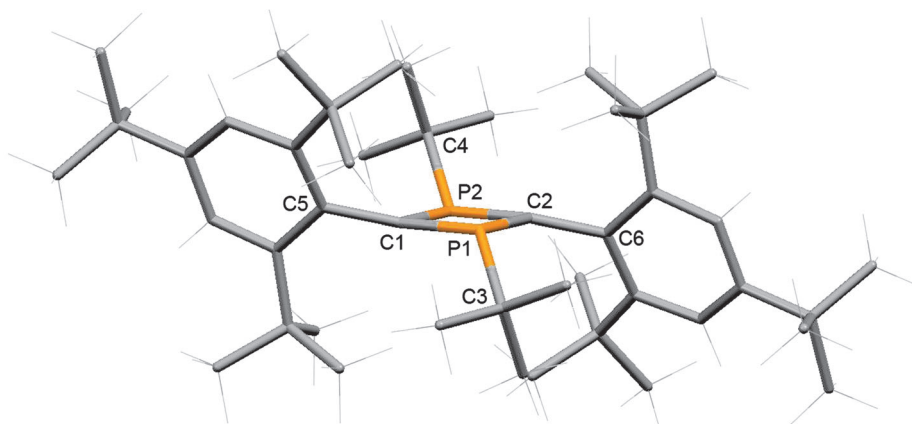


Fig. 2. Optimum structure of **2e** by calculation [M06-2X] on the basis of 6-31G(d)

analysis of **2e** as a biradical di(*tert*-butyl)bis[2,4,6-tri(*tert*-butyl)phenyl] derivative. These findings will not only provide basic and useful information to the R&D community in main-group element chemistry, but will also enable us to pursue some of the proposed lines of research.

Financial support from the *Alexander von Humboldt Foundation* is gratefully acknowledged providing *M. Y.* and *Y. H.* for their research stay in Bonn (August to October 2011). *R. S.* is also grateful to the *COST* action cm0802 'PhoSciNet'.

Experimental Part

Preparation of Starting Materials. Diphosphacyclobutanediyl **2a** was prepared from dichlorophospha-alkene **1** according to a method described in [1]. To a soln. of **1** (300 mg, 0.835 mmol) in THF (10 ml) at -100° was added dropwise BuLi (0.29 ml, 0.46 mmol). The soln. was stirred between -100° and -80° for 1 h, and then warmed to r.t. overnight, while the color of the soln. changed from yellow to dark red. After removal of the solvent *in vacuo*, to the crude was added pentane (15 ml $\times$ 4), and the soln. was collected through a filter syringe, then the solvent was removed *in vacuo* to give **2a** (220 mg, 0.343 mmol, 81%). $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): 7.45 (s, 4 H); 1.73 (br. s, 9 H); 1.33 (br. s, 9 H); 1.26 (s, 9 H). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 , 121 MHz): δ 27.8 (s).

Diphosphacyclobutenyl anion **3b** was prepared as described in [2]. To a soln. of **4** (87 mg, 0.30 mmol) in THF (2 ml) at -78° was added dropwise *t*-BuLi (0.10 ml, 0.16 mmol). The mixture was stirred at -78° for 15 min, then at r.t. for 1 h; in the meantime, the color of the soln. changed from yellow to dark blue *via* dark green.

Attempted Reaction of 2a with 3b. To a soln. of **2a** (195 mg, 0.301 mmol) in THF (10 ml) at -78° was added **3b** (0.66 mmol; **3b** was prepared from a soln. of **4** (381 mg, 1.32 mmol) in THF (9 ml) and *t*-BuLi (0.44 ml, 0.70 mmol) as described above). The soln. was stirred at -78° for 1 h, then warmed to r.t. overnight (the color of the soln. changed from red brown to dark red). After recording $^{31}\text{P-NMR}$, removal of the solvent *in vacuo*, and then NMR recordings, CH_2Cl_2 (2 ml) was added to the residue, and the mixture was kept at 0° . After filtration through a filter syringe at 0° , the residue was purified by recrystallization from CH_2Cl_2 (8 ml) at 4° to give blue-purple crystals of **2e**. M.p. $157-158^{\circ}$ (dec.). UV (CH_2Cl_2): λ_{max} (ϵ) 638.5 (932), 524.0 (621), 389.0 (7358), 340.5 (10258), 229.5 (29110). The soln. color of **2e** changed to blue-purple to green (λ_{max} 700; 638.5-nm band disappeared). HR-EI-MS: 690.5417

($C_{46}H_{70}P_2$; calc. 690.5422). CV: $^2E_{1/2}^{ox} = 0.50$ V (looks like irreversible), $^1E_{1/2}^{ox} = 0.15$ V (reversible), $^1E_p^{ox} = -1.0$ V (irreversible).

Attempted Isolation of 3b. To a soln. of **4** (75 mg, 0.26 mmol) and 12-crown-4 (0.030 ml, 0.18 mmol) in Et_2O (2 ml) at -78° was added dropwise *t*-BuLi (0.090 ml, 0.16 mmol). The mixture was stirred at -78° for 15 min, then at r.t. for 1 h. The color of the soln. changed from yellow to dark blue *via* dark green. After removal of the solvent *in vacuo*, to the crude were added pentane (2 ml) and then Et_2O (4 ml). Recrystallization at 4° gave **2e** (blue crystals), the structure of which was confirmed by X-ray structure analysis.

Time-Dependent Change of 3b (^{31}P -NMR Study). To a soln. of **4** (93 mg, 0.32 mmol) in THF (2 ml) at -78° was added dropwise *t*-BuLi (0.11 ml, 0.18 mmol). The mixture was stirred at -78° for 15 min and then at r.t. for 1 h (the color of the soln. started to change from yellow to dark blue *via* dark green). Reaction monitoring was carried out by recording ^{31}P -NMR (0.6 ml of soln., which was taken from the reaction mixture after 1 h into a Young NMR tube); after 1 h, 1 d, and 5 d. From the NMR spectra, the ratio (**3b/2e** 99:1 after 1 h) indicated an equilibrium between **3b** and **2e** (**3b/2e** 93:7 after 1 d) in soln. After 5 d, the ratio did not change.

Data of 3b. $^{31}P\{^1H\}$ -NMR (THF, 121 MHz): 267.5 (*d*, $J = 87$); 86.8 (*d*, $J = 87$).

Data of 2e. $^{31}P\{^1H\}$ -NMR (THF, 121 MHz): 39.0 (*s*).

Preparation of an Authentic Sample of 2e. To a soln. of **4** (87 mg, 0.30 mmol) in THF (2 ml) at -78° was added dropwise *t*-BuLi (0.18 ml, 0.29 mmol). The mixture was stirred at -78° for 15 min and then at r.t. for 1 h. The color change of the soln. was observed as described above. To the soln. was added *t*-BuI (0.040 ml, 0.34 mmol) at r.t., and the mixture was stirred for 2 min. After removal of the solvent *in vacuo*, to the crude was added pentane (10 ml), and the soln. was filtered through a filter syringe. The solvent was removed *in vacuo*, and the residue was recrystallized from CH_2Cl_2 (4 ml) at 4° to give **2e** (22 mg, 0.031 mmol, 12%). Blue crystals. 1H -NMR ($CDCl_3$, 300 MHz): 7.24 (*s*, 4 H); 1.57 (*s*, 36 H); 1.22 (*s*, 18 H); 0.88 (*t*, $J = 7$, 18 H). $^{31}P\{^1H\}$ -NMR ($CDCl_3$, 121 MHz): 38.7 (*s*).

REFERENCES

- [1] E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W. W. Schoeller, *Angew. Chem., Int. Ed.* **1995**, *34*, 555.
- [2] H. Sugiyama, S. Ito, M. Yoshifuji, *Angew. Chem., Int. Ed.* **2003**, *42*, 3802.
- [3] E. Niecke, A. Fuchs, M. Nieger, O. Schmidt, W. W. Schoeller, *Angew. Chem., Int. Ed.* **1999**, *38*, 3031.
- [4] S. Ito, M. Kikuchi, H. Sugiyama, M. Yoshifuji, *J. Organomet. Chem.* **2007**, *692*, 2761.
- [5] S. Ito, J. Miura, N. Morita, M. Yoshifuji, A. J. Arduengo III, *Inorg. Chem.* **2009**, *48*, 8063.
- [6] S. Ito, J. Miura, N. Morita, M. Yoshifuji, A. J. Arduengo III, *Dalton Trans.* **2010**, *39*, 8281.
- [7] M. Yoshifuji, A. J. Arduengo III, T. A. Konovalova, L. D. Kispert, M. Kikuchi, S. Ito, *Chem. Lett.* **2006**, *35*, 1136.
- [8] S. Ito, J. Miura, N. Morita, M. Yoshifuji, A. J. Arduengo III, *Heteroat. Chem.* **2010**, *21*, 404.
- [9] S. Ito, J. Miura, N. Morita, M. Yoshifuji, A. J. Arduengo III, *Angew. Chem., Int. Ed.* **2008**, *47*, 6418.
- [10] G. Märkl, H. Sejpka, *Tetrahedron Lett.* **1986**, *27*, 171.
- [11] S. Ito, H. Sugiyama, M. Yoshifuji, *Chem. Commun.* **2002**, 1744.
- [12] Y. Zhao, D. G. Truhler, *Theor. Chem. Acc.* **2008**, *120*, 215.
- [13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich,

- A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, *Gaussian, Inc.*, Wallingford CT, 2010.
- [14] A. B. Rozhenko, W. W. Schoeller, M. I. Povolotskii, *Magn. Res. Chem.* **1999**, 37, 551.
- [15] K. Sugimori, H. Kawabe, H. Nagao, K. Nishikawa, *Int. J. Quant. Chem.* **2009**, 109, 3685.

Received August 10, 2012