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

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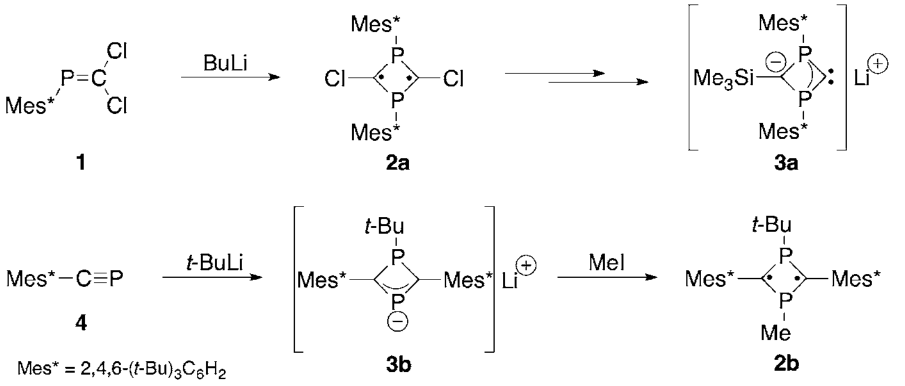
Dedicated to Prof. Dr. *Dieter Seebach* on the occasion of his 75th birthday

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.

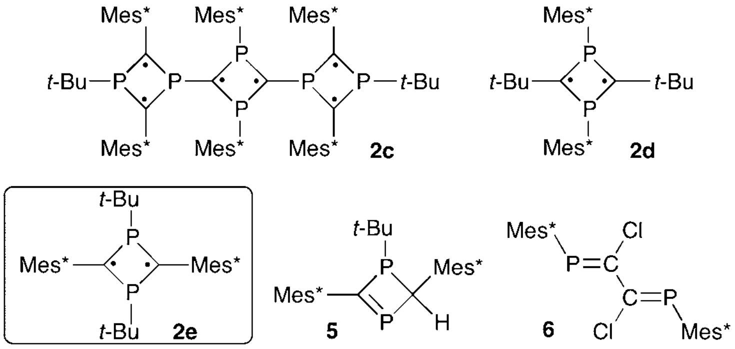
Introduction. – In recent years, 1,3-diphosphacyclobutane-2,4-diyls **2a** [1] and **2b** [2] have become available as stable species by using phospha-alkene **1** or phospha-alkyne **4** with the 2,4,6-tri(*tert*-butyl)phenyl (abbreviated as Mes*) as a sterically bulky substituent. Compounds **2** are 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



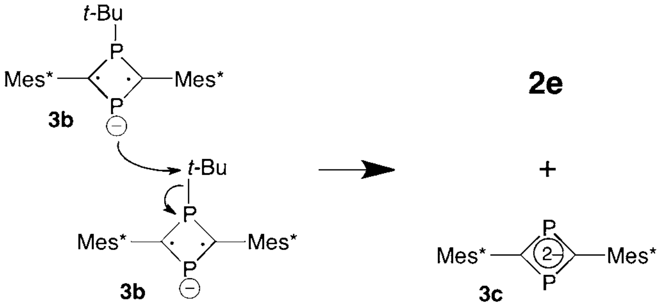
To gain better understanding of the bonding and properties of biradicals, the first attempt was made to prepare a multi-biradical system such as **2c** (*Scheme 2*) *via* reaction of 1,3-diphosphacyclobutenyl anion **3b** with **2a**. Multi-biradicals, for which interesting chemical and physicochemical 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 ^{1}H-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 phospha-alkenes (Mes*C(H)=P(*t*-Bu), δ(P) 281 and 292 ppm). The peak at δ(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*-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*-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

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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, δ(P), of 152.00 and 152.07 ppm.

²) *Crystallographic data of* **2e**: $C_{46}H_{76}P_2$: M_r 691.91, orthorhombic, *Pccn* (#56), $a = 14.2075(9)$, $b = 25.6989(16)$, $c = 11.6699(8)$ Å, $V = 4260.9(5)$ Å^3, $Z = 4$, $T = 100(2)$ K, $\varrho_{calc} = 1.077$ g cm^{-3}, $\mu(\mathrm{Mo}K_{\alpha}) = 0.131$ mm^{-1}, $2\,\theta_{max} = 50.5°$, $F_{000} = 1528$, 4450 observed reflections, 3766 unique reflections ($R_{int} = 0.086$), $R1 = 0.062$ ($I > 2\sigma(I)$)/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.

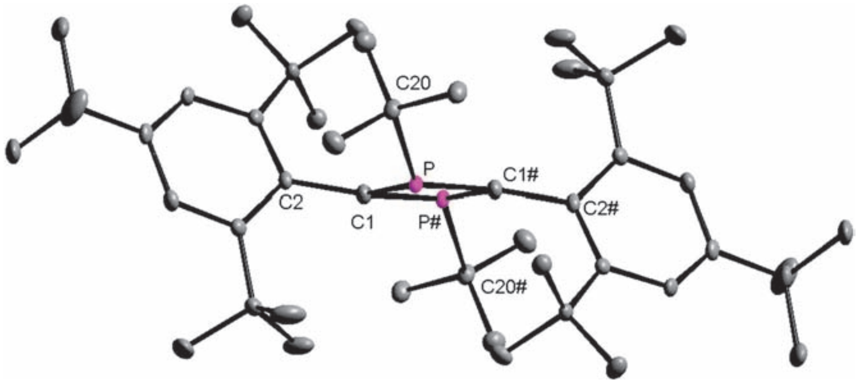

Fig. 1. *Molecular structure of* **2e** *by X-ray analysis* (only the major structure is depicted)

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)	Σ_{angles}(P1)	332.63	334.6
P2–C4	1.9022	1.918(4)	Σ_{angles}(P2)	332.70	334.6
C1–C5	1.4830	1.490(4)	Σ_{angles}(C1)	357.38	357.8
C2–C6	1.4831	1.490(4)	Σ_{angles}(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 ^{3}J values are smaller than those of ^{5}J, which might be due to the appearance of a pseud*o-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

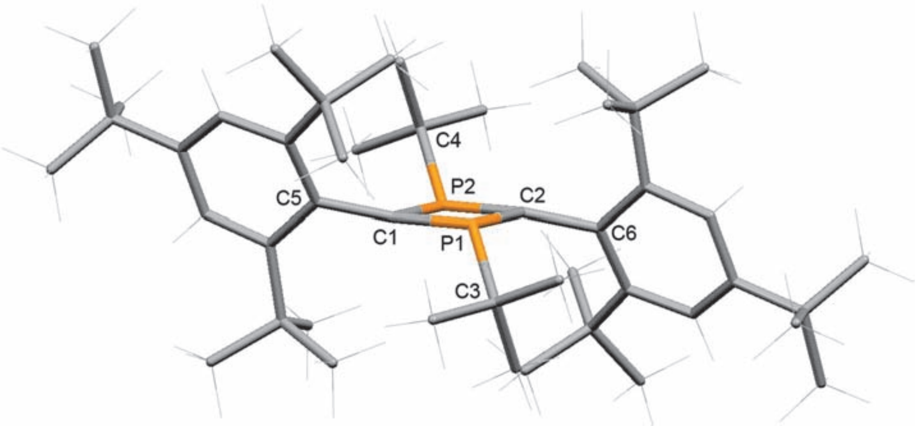

Fig. 2. *Optimum structure of* **2e** *by calculation [M06-2X] on the basis of 6-31G(d)*

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.

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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 × 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}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}P{^{1}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}P-NMR, removal of the solvent *in vacuo*, and then NMR recordings, CH$_2$Cl$_2$ (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$_2$Cl$_2$ (8 ml) at 4° to give blue-purple crystals of **2e**. M.p. 157 – 158° (dec.). UV (CH$_2$Cl$_2$): 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: ${}^2E^{ox}_{1/2} = 0.50$ V (looks like irreversible), ${}^1E^{ox}_{1/2} = 0.15$ V (reversible), ${}^1E^{ox}_p = -1.0$ 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{^{1}H}-NMR (THF, 121 MHz): 267.5 (*d*, *J* = 87); 86.8 (*d*, *J* = 87).

Data of **2e**. ^{31}P{^{1}H}-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 mml) 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. ^{1}H-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{^{1}H}-NMR ($CDCl_3$, 121 MHz): 38.7 (*s*).

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