Stable Biradicals

Synthesis of a 1,3-Diphosphacyclobutane-2,4-diyl from Mes*C≡P**

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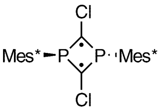
A biradical is defined as an even-electron molecular entity with two radical centers that act nearly independently of each other and they normally displays quite high reactivity.[1] Cyclobutane-1,3-diyl **1** is a biradical with a ring structure and is observed at very low temperature.[2] More recently several stable "singlet" biradicals with a four-membered-ring skeleton by incorporating main-group elements, such as phosphorus were reported.[3] In 1995 Niecke and co-workers reported 2,4-dichloro-1,3-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyl (**2**)[4] as the first stable congener of singlet **1** and afterwards they prepared several derivatives from **2**.[5] In addition to the carbon-based 1,3-biradicals, a 1,3-dibora-2,4-diphosphacyclobutane-1,3-diyl compound **3** was reported by Bertrand and co-workers.[6] These successes in obtaining biradical compounds that can be handled at room temperature stimulated further efforts to explore similar curious molecules and their role as functional materials, such as magnets.[1,3,7] Niecke and co-workers used **2** to prepare several four-membered biradical derivatives, in which two Mes*P moieties are incorporated (Mes* = 2,4,6-tri-*tert*-butylphenyl).[5] In contrast to the biradicals of Niecke, we succeeded in preparing a novel 1,3-diphosphacyclobutane-2,4-diyl derivative from phosphaalkyne **4**. Herein we report the method of preparation of the 1,3-diphosphacyclobutane-2,4-diyl derivative and its properties, especially its high stability.

1



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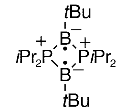


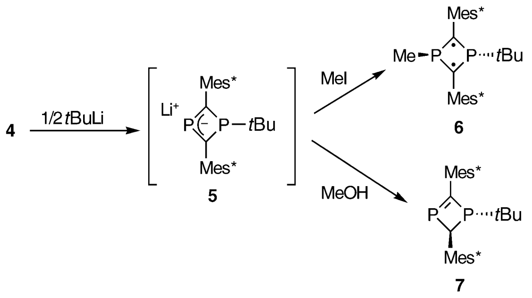
3

$\text{Mes*}-\text{C}\equiv\text{P}$

4

Mes* = 2,4,6-$t\text{Bu}_3\text{C}_6\text{H}_2$

Phosphaalkyne **4** was prepared from 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene by a nickel-catalyzed [1,2] rearrangement.[8,9,10a] Compound **4** was allowed to react with half an equivalent of *tert*-butyllithium, to generate the corresponding anion intermediate **5**, and was then quenched with iodomethane. 1,3-Diphosphacyclobutane-2,4-diyl **6** was isolated as a deep-blue/violet solid almost quantitatively from **4**. On the other hand, 1,3-diphosphacyclobutene **7** was obtained in the reaction of **4** with *tert*-butyllithium and methanol,[11] thus indicating the formal ambident nature of the PCP anion system (Scheme 1).[12] 1,3-diphosphacyclobutane-2,4-diyl **6** was stable at room temperature and even in air. Indeed, **6** did not decompose for several minutes when it was treated with water or silica gel, and in the solid state it could be washed with ethanol. This lack of reactivity of **6** is in sharp contrast with **2** or **3**, which are reported to immediately decompose on contact with air.



Scheme 1. Reaction of **4** with *t*BuLi followed by quenching with iodomethane or methanol.

A single crystal of **6** was used for X-ray crystallography and Figure 1 shows the molecular structure. The P_2C_2 four-membered ring is almost planar, to within 0.069 Å, whereas a butterfly conformation is observed in the structure of **7**.[11] C1 and C2 are sp^2 hybridized with a planar environment, and the sum of the bond angles around C1 and C2 are 360(1) and 358(1)°, respectively. There is no covalent bond between the C1 and C2 (C1···C2, 2.50 Å). The P1−C1 and P1−C2 bond lengths are shorter than the corresponding bond lengths for P2. The geometry around P1 is less pyramidal (more planar) than that of P2, as shown by the sum of bond angles (341(1)°

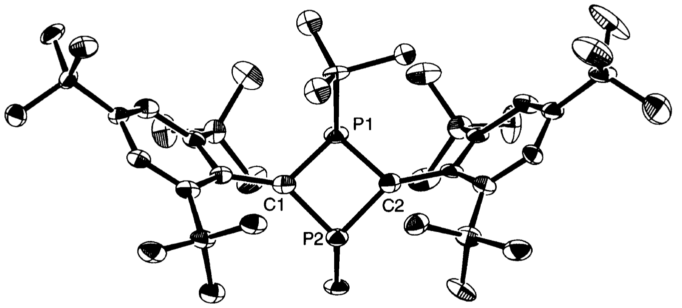


Figure 1. ORTEP drawing of **6** with 40% probability ellipsoids. Hydrogen atoms are omitted for clarity. The *tert*-butyl group on the P1 atom is disordered and the atoms with the predominant occupancy factor (0.53) are shown. Bond lengths (Å) and Angles (°): P1-C1 1.70(1), P1-C2 1.72(1), P1-C_{tBu} 1.877(10), P2-C1 1.77(1), P2-C2 1.79(1), P2-C_{Me} 1.85(1), C1-C_{Mes*} 1.50(1), C2-C_{Mes*} 1.49(1), C1-P1-C2 94.0(5), C1-P1-C_{tBu} 123.1(5), C2-P1-C_{tBu} 124.3(5), C1-P2-C2 89.1(5), C1-P2-C_{Me} 116.0(5), C2-P2-C_{Me} 113.9(5), P1-C1-P2 89.0(5), P1-C1-C_{Mes*} 127.5(7), P2-C1-C_{Mes*} 143.3(7), P1-C2-P2 87.6(5), P1-C2-C_{Mes*} 126.2(7), P2-C2-C_{Mes*} 144.4(7).

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for P1; 319(1)° for P2). This difference might indicate some influence of the dimethylenephosphorane structure on the P1 side,[5c] although the P1–C1/C2 bond lengths are indeed longer than the isolated dimethylenephosphoranes [1.65–1.67 Å].[13] The two Mes* rings make the mean angle to the P_2C_2 plane of 60(1)° (C1) and 59(1)° (C2), respectively. The lack of reactivity of **6** is due to the steric congestion around the radical centers formed by the bulky Mes* groups.

The NMR data was also used to characterize the singlet biradical structure of **6**. In the ^{13}C NMR spectrum, the (radical) sp^2 carbon was observed at $\delta_C = 111.3$, which is similar to that of **2** ($\delta_C = 98.8$)[4] and its derivatives.[5a,b] In the ^{31}P NMR spectrum of **6**, two kinds of phosphorus atoms were observed at $\delta_P = 55.9$ (*t*BuP) and -11.3 (MeP) with a large *J*(P,P) coupling constant (362.8 Hz). In ^{1}H NMR spectrum, a larger ^3J(P,H) value (13.6 Hz) was observed for the *t*BuP group rather than the ^2J(P,H) for the MeP part (5.8 Hz). In UV/Vis spectrum of **6** the absorption was observed at 612 nm, which is a large red shift compared with the absorptions of **2** (478 nm)[4] and **3** (446 nm).[6] This difference indicates that the energetic separation between the HOMO and LUMO in **6** is smaller than those of **2** and **3**. The ground state of 1,3-diphosphacyclobutane-2,4-diyl is theoretically assigned as a singlet due to the interaction between the symmetrical nonbonding molecular orbital (NBMO) and the lonepair of the phosphorus atoms.[4,5c] As discussed on cyclobutane-1,3-diyl, spin-multiplicity is controlled by substituents on the 2,4-positions,[14] and therefore the spin-multiplicity of 1,3-diphosphacyclobutane-2,4-diyl could operate to configure the triplet state. The red-shift absorption of **6** might indicate the small energetic gap between the singlet and triplet states.

We performed cyclic voltammetry (CV) on **6**. A reversible oxidation peak ($^1E^{ox}_{1/2}$) is observed at $+0.35$ V (versus Ag/AgCl, Figure 2) and an irreversible oxidation peak ($^2E^{ox}_p$) appears at $+1.56$ V. The first oxidation probably occurs at the radical centers, which corresponds to the HOMO, and the other irreversible oxidation peak might indicate the oxidation at the phosphorus atoms. Thus a stable cationic species is generated by the oxidation. In the case of **7**, an irreversible oxidation peak was observed at $+1.36$ V. As for the reduction, the irreversible peak E^{red}_p is observed at -0.70 V for **6**, which is similar to the corresponding value of **7** (-0.68 V).

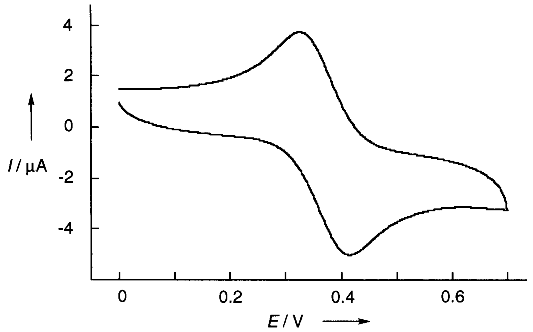

Figure 2. Cyclic volammogram of **6**: 1 mM in dichloromethane; supporting electrolyte: 0.1 M tetrabutylammonium perchlorate (TBAP); working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgCl ($E_{1/2}$ (ferrocene/ferricinium) = +0.60 V) at 20 °C; scan rate: 50 mV s^{-1}; *E* = potential, *I* = current.

We were interested in the reactivity of **6** on thermolysis. The biradical **6** was heated to reflux in toluene to produce **4**, which was isolated in a moderate yield. This result, that is, the breaking of the P–C(alkyl) bond together with the breakup of the four-membered ring, are in sharp contrast to the reactivity of **2**.[4] Any other products, such as the eliminated *tert*-butyl or methyl group that would prove the reaction mechanism, have not been identified. We did not observe any isomerization of **6** upon irradiation (medium pressure 100 W Hg lamp at 0 °C for 15 h) but only recovered **6**.

In conclusion, we demonstrated an alternative method to prepare 1,3-diphosphacyclobutane-2,4-diyl from phosphaalkyne **4**, and the novel compound **6** showed quite high stability. The structural elucidation of **6** revealed the effective steric protection given by the Mes* groups around the radical centers. The small HOMO–LUMO gap found in **6**, indicated by the absorption spectrum, suggests a triplet state, as demonstrated by its carbon congener (cyclobutane-1,3-diyl). The present synthetic method should be a promising approach in the development of novel stable biradical species.

Experimental Section

Preparation of **6**: A solution of *tert*-butyllithium in pentane (0.56 mmol, 1.4 M) was added to a solution of **4** (300 mg, 1.0 mmol) in THF (8 mL) at −78 °C and stirred for 15 min. The solution was then warmed to room temperature, and stirred for 1 h, during which the solution turned blue. Iodomethane (0.64 mmol) was added to the reaction mixture and the solvent was removed in vacuo. The residue was extracted with hexane and the solvent was removed by evaporation to afford almost pure **6** (yield: 640 mg, 98 %). Compound **6** was crystallized in dichloromethane at 0 °C: deep-blue/violet prisms, mp 158–160 °C; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): $\delta = 55.9$ (d, ^2J(P,P) = 362.8 Hz, *t*BuP), −11.3 ppm (d, ^2J(P,P) = 362.8 Hz, MeP); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.45$ (s, 2 H, *m*-Mes*), 7.26 (s, 2 H, *m*-Mes*), 1.86, (d, ^2J(P,H) = 5.8 Hz, 3 H, MeP), 1.68 (s, 18 H, *o*-*t*Bu), 1.66 (s, 18 H, *o*-*t*Bu), 1.36 (s, 18 H, *p*-*t*Bu), 0.69 ppm (d, ^3J(P,H) = 13.6 Hz, 9 H, *t*BuP); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): $\delta = 150.2$ (pt, (^2J(P,C) + ^2J(P,C))/2 = 9.3 Hz, *ipso*-Mes*), 148.0 (d, ^3J(P,C) = 9.3 Hz, *o*-Mes*), 144.7 (s, *p*-Mes*), 133.8 (d, ^3J(P,C) = 2.8 Hz, *o*-Mes*), 123.0 (s, *m*-Mes*), 120.0 (s, *m*-Mes*), 111.3 (dd, ^1J(P,C) = 10.7 Hz, ^1J(P,C) = 3.3 Hz, CP_2), 46.7 (dd, ^1J(P,C) = 52.9 Hz, ^3J(P,C) = 15.8 Hz, P*C*Me$_3$), 38.9 (s, *o*-*C*Me$_3$), 37.7 (s, *o*-*C*Me$_3$), 35.4 (s, *p*-*C*Me$_3$), 33.8 (s, *o*-C*Me*$_3$), 33.7 (s, *o*-C*Me*$_3$), 31.9 (s, *p*-C*Me*$_3$), 29.4 (dd, ^2J(P,C) = 5.6 Hz, ^4J(P,C) = 3.7 Hz, PC*Me*$_3$), 13.6 ppm (dd, ^1J(P,C) = 58.5 Hz, ^3J(P,C) = 24.1 Hz, PMe); UV-Vis (hexanes) λ_{max} (ε) = 326 (16700), 382 (17500), 612 (1500) nm.

Thermolysis of **6**: A solution of **6** (0.092 mmol) in toluene (8 mL) was heated to reflux for 3 h and the solution changed from blue/purple to yellow. The mixture was cooled to room temperature and analyzed by ^{31}P NMR spectroscopy, which indicated that **4** was the major product, although the spectrum also had unidentified trace resonance signals. The solvent was removed in vacuo and the residual product was purified by silica gel column chromatography (hexane) to afford **4** (14 mg, 0.049 mmol).

X-Ray data for **6**: $C_{43}H_{70}P_2$: $M_r = 648.97$, deep-blue/violet prism crystallized from dichloromethane at 0 °C. Crystal dimensions $0.30 \times 0.25 \times 0.10$ mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.553(2)$, $b = 14.480(3)$, $c = 8.878(3)$ Å, $\alpha = 96.64(1)$, $\beta = 104.94(2)$, $\gamma = 106.812(7)$°, $V = 2044.2(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.054$ g cm^{-3}, $F(000) = 716.00$, $\mu = 0.133$ mm^{-1}, $T = 120$ K. A Rigaku RAXIS-IV imaging plate detector with graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) was used. Of 8092 reflections measured ($2\theta_{max} = 55.0°$), 6027 were observed ($R_{int} = 0.062$). The structure was solved by direct methods (SIR92),[15] expanded by using Fourier techniques (DIRDIF94),[16] and then refined by full-matrix least squares on F for 404 variable parameters. The non-hydrogen atoms without the disordered atoms in the P*t*Bu group were refined anisotropically. Hydrogen atoms (calculated) were refined isotropically. $R1 = 0.099$ for $I > 3.0\sigma(I)$, and $R_w = 0.136$ for all data. Goodness of fit $S = 1.80$ for observed reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.97 and $-0.34\,e\,Å^{-3}$, respectively. The data were corrected for Lorentz polarization effect. Structure solution, refinement, and graphical representation were carried out using the teXsan package.[17] CCDC-208433 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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