Phosphorus Heterocycles

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Preparation and Characterization of an Air-Tolerant 1,3-Diphosphacyclobuten-4-yl Radical**

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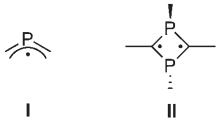
A radical is a species that contains an unpaired electron. These substances play an important role in organic, inorganic, physical, material, and biological chemistry from the point of view of reactivity, structure, and electronic properties. Radicals are generally highly reactive species with extremely short lifetimes; however, their stability can be improved thermodynamically by incorporation into a conjugated system. Kinetic enhancement of their stability can be accomplished through the use of steric encumbrance.[1,2]

The allyl radical is a fundamental organic radical and is an important research subject in both experimental and theoretical organic chemistry.[3] Streitwieser and co-workers reported the preparation and structure of stable pyridinium-substituted allyl radicals.[3c] Azuma et al. revealed the molecular and crystal structures of the 1,3-bis(diphenylene)-2-phenylallyl radical as complexes with benzene and acetone.[3d]

Parallels between the P=C and C=C double bonds have been formulated to develop phosphorus chemistry based on an organic chemistry model.[4] Allyl and 2-phosphaallyl radicals are examples of such "parallel" chemistry.[5] Schoeller et al. reported the generation of 2-phosphaallyl radical **I** by electrochemical reduction of 2-phosphaallyl cations and theoretical models of this radical provide insight into its structure.[6] We recently reported the synthesis



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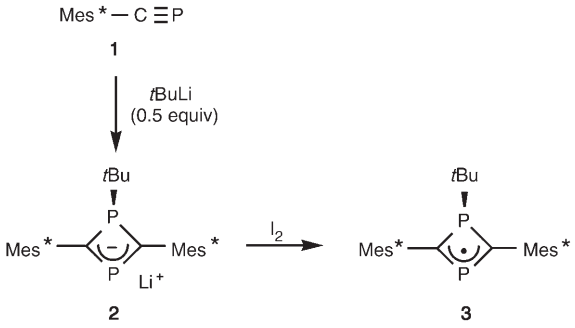
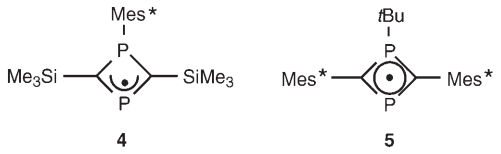
of 1,3-diphosphacyclobutane-2,4-diyl biradicals of type **II** from a phosphaalkyne via a 1,3-diphosphacyclobutenyl anion.[7] Anions of **II** could also afford 1,3-diphosphacyclobuten-4-yl radicals (structure **I**) by an oxidative route. We now report the preparation and characterization of an air- and room-temperature-stable 1,3-diphosphayclobutenyl radical. A cyclobutenyl radical that is a C-congener of a 1,3-diphosphacyclobutenyl radical can be generated by H abstraction of cyclobutene or bicyclo[1.1.0]butane under cryogenic conditions,[8] thus suggesting that thermodynamic stabilization with phosphorus atoms and kinetic stabilization with the 2,4,6-tBu$_3$C$_6$H$_2$ (Mes*) groups are advantageous for producing stable organic radicals.

Phosphaalkyne **1** was treated with 0.5 equivalents of *tert*-butyllithium in THF to generate 1,3-diphosphaallyl anion **2** as a deep blue solution (Scheme 1).[7] When **2** was mixed with



Scheme 1. Preparation of **3**.

iodine, the solution turned deep red. After removal of the volatile materials, **3** was obtained and crystallized from dichloromethane. A single crystal was employed for X-ray crystallography structure analysis. Figure 1 displays the structure of **3** with a *Cs* symmetric form. The C_2P_2 four-membered ring is almost planar (Θ(P1-C1-P2-C2) = 7.7(3)°), whereas the two aromatic rings of the Mes* groups have torsional angles of 57.7(3) and 58.4(3)° with the C_2P_2 plane (thereby alleviating steric congestion). The sums of the bond angles at the C1 and C2 atoms are 360.0 and 359.8°, respectively, thus indicating sp^2 hybridizations. On the other hand, the P2 atom is strongly pyramidalized with a sum of the bond angles of 302.5°. Although the quality of structure refinement was not sufficient to allow discussion of the metric parameters in detail (because of the presence of disorder), the P2–C lengths in the four-membered ring indicate a P–C single bond, whereas the P1–C lengths are the same as the mean value between the P–C single- and the P=C double-bond lengths (ca. 1.85 Å[9] and 1.68 Å,[4] respectively). Compared with the 1,3-diphosphacyclobutane-2,4-diyls from our previous report,[7a,c] the transannular P1···P2 distance of 2.65 Å is longer than that for the biradical, whereas the C1···C2 distance of 2.40 Å is shorter. Accordingly, the bond angles of C1-P1-C2 and C1-P2-C2 are more acute than the corresponding data for the 1,3-diphosphacyclobutane-2,4-diyls.[7a,c] In spite of steric bulkiness, the Mes* groups tilt toward the *t*-butyl group, as was observed in the structure of a 1-*tert*-butyl-3-methyl-1,3-diphosphacyclobutane-2,4-diyl.[7a] Such structural properties might reflect a CH–π interaction[10] or the influence of crystal packing. The intermolecular P1···P1 distance (5.35 Å) indicates no substantial covalent bond and that the radical does not form dimers in the crystalline state.[11] Recently, Niecke and co-workers observed that the radical **4**, prepared through



cleavage of the P–C bond upon irradiation of a type **II** compound, undergoes a subsequent dimerization.[12a] This observation suggests that the radical moiety in **3** is successfully protected from dimerization as a result of the steric encumbrance.

In its crystalline state, radical **3** showed no apparent decomposition in air at room temperature for several months. The remarkable stability of **3** is likely derived from the electronic effect of the phosphorus atom in the allylic system and the adjacent phosphino moiety in addition to the steric encumbrance of the Mes* and the *tert*-butyl moieties. The UV/Vis spectrum of **3** in dichloromethane shows a relatively weak absorption at 759 nm and intense absorptions at 515 and 355 nm. Because of the broadening of the NMR spectrum of compound **3** as a result of the paramagnetic nature, no noticeable ^{31}P NMR signal was detected in the region between $\delta_P = 2000$ and -900 ppm ([D$_8$]toluene, 298 K).[13]

The electron paramagnetic resonance (EPR) spectrum of a solution of **3** in toluene ($T = 295$ K) exhibits a strong four-line signal with small outer peaks and the isotropic $g = 2.0025 \pm 0.0002$, which is characteristic of π–organic radicals[14] (see Figure 2a). The ^{31}P ($I = 1/2$) and ^{13}C ($I = 1/2$) isotropic hyperfine coupling (hfc) constants were determined by spectral simulation. The experimental spectrum was simulated by using the XSophe computer simulation software.[15] The best fit was obtained with the Lorentzian line width of 1.5 G, two different ^{31}P hfc constants $a_{P1} = 20.4$ G,

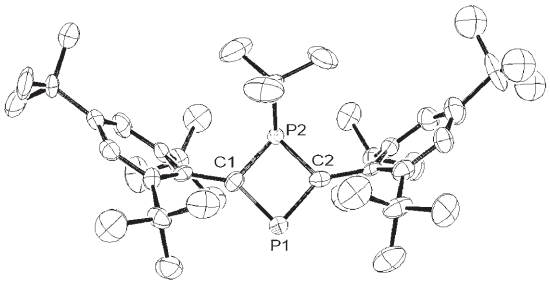


Figure 1. Molecular structure of **3** (ellipsoids set at 50% probability). Hydrogen atoms are omitted for clarity. The *p-tert*-butyl group in the Mes* group at C2 is disordered, and the atoms with the predominant occupancy factor (0.64) are displayed. Bond lengths [Å] and angles [°]: P1-C1 1.768(8), P1-C2 1.765(9), P2-C1 1.814(9), P2-C2 1.819(8), P2-C_{tBu} 1.881(8), C1-C_{Mes*} 1.48(1), C2-C_{Mes*} 1.49(1); C1-P1-C2 85.4(4), C1-P2-C2 82.5(4), P1-C1-P2 95.6(4), P1-C1-C_{Mes*} 142.3(7), P2-C1-C_{Mes*} 122.1(6), P1-C2-P2 95.5(4), P1-C2-C_{Mes*} 142.0(6), P2-C2-C_{Mes*} 122.3(6), C1-P2-C_{tBu} 109.8(4), C2-P2-C_{tBu} 110.2(3).

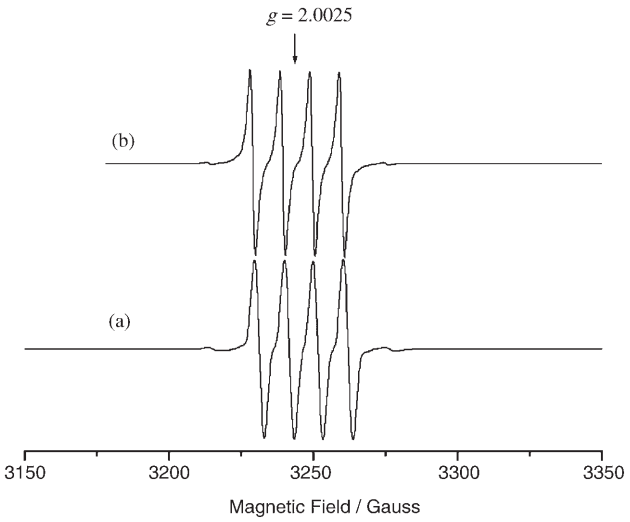
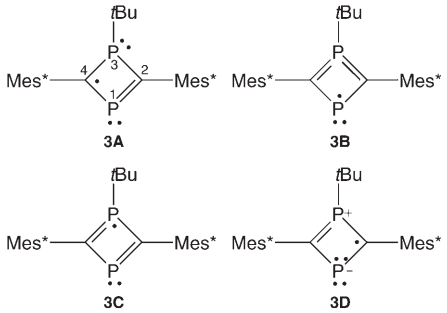


Figure 2. a) EPR spectrum of a solution of **3** in toluene at room temperature (experimental). EPR parameters: microwave frequency: 9.09823 GHz; modulation amplitude: 1 G; microwave power: 2 mW; gain 2×10^3. b) Simulated spectrum, see text.

$a_{P2} = 10.2$ G, and the ^{13}C isotropic hyperfine coupling of 30.2 G (Figure 2b). When hfc from naturally abundant ^{13}C was included in the simulation, small outer lines of the experimental spectrum were well reproduced. The large $^{31}P(a_{P1})$ hfc value corresponds to the phosphorus atom at P3 and the smaller $^{31}P(a_{P2})$ hfc value corresponds to that at P1 according to an ab initio calculation on $(P(CH)_2PCH_3)^{\bullet}$ as a model compound for **3**.[16] The Figure 3 shows that most of the electron spin density is concentrated on the C_2P_2 ring of the optimized structure, thus making the assignment of a_{P1} and a_{P2} possible. Contribution from the aromatic protons is probably negligible. The experimental spectrum was readily reproducible if the protons with a hfc value of < 1.0 G were used in the simulations. The ^{13}C hfc (30.2 G) determined from spectral simulations is consistent with the reported data for ^{13}C isotropic hfc.[17–20] This value is less than the ^{13}C isotropic coupling in the methyl radical $CH_3^{\bullet}$ (≈ 38 G)[17,18] and is more likely the observed ^{13}C isotropic coupling in the malonic radical $^{\bullet}CH(CO_2H)_2$ (≈ 33 G).[19,20] According to the EPR results and ab initio calculations, and based on the experimental ^{13}C couplings, 80–90% of the spin density in **3** will reside on the carbon atoms in the C_2P_2 ring and the remainder on the P atoms. This behavior explains small magnitudes of the ^{31}P hfc constants of **3**, which are considerably smaller than those of P-localized phosphinyl radicals $R_2P^{\bullet}$ (63–105 G)[1b,21] and diphosphanyl radicals $(R_2PPR)^{\bullet}$ (99–390 G).[1b,21c,22,23] On the other hand, the a_{P2} constant of **3** is similar to the ^{31}P hfc value of the 1,3-diphophaallyl radical $(R_2NP(CNR_2)PNR_2)^{\bullet}$ (R = *i*Pr, 9.4 G),[5a] thus featuring a spectroscopic property of organic radicals that contain conjugated P=C double bonds.

Both X-ray and EPR spectroscopic analysis support that the compound is well described as **3** (rather than fully delocalized **5**), as a resonance structure of **3A** and its symmetry equivalent, because the contribution of betaine structure **3D** (of **3A**) as well as **3B** and **3C** appears to be small based on the observed molecular geometry.



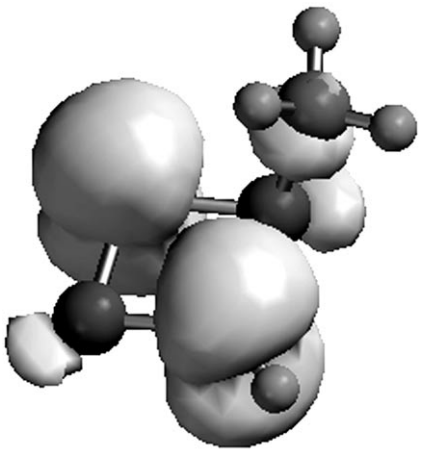


Figure 3. A visual map of electron spin density in the optimized structure of $[P(CH)_2PCH_3]^{\bullet}$ at the UHF/6-31G** level. Some important distances [Å] and angles [°] in the optimized structure: P-C(sp^2) 1.760, P(Me)-C(sp^2) 1.833, P-CH_3 1.856, C(sp^2)-P-C(sp^2) 83.31; P-C(sp^2)-P(Me) 98.33, 98.34, C(sp^2)-P(Me)-C(sp^2) 79.31, ΣP(Me) 287.59, ΣC-(sp^2) 359.70, P···P 2.721, C(sp^2)···C(sp^2) 2.340, Θ(P-C-P-C) 5.71. Total energy: −797.894357012 a.u.

A straightforward procedure for the preparation of the air-tolerant, thermally stable 1,3-diphosphacyclobutenyl radical **3** with a 2-phosphaallyl system has been developed. The radical structure was characterized by X-ray crystallographic and EPR spectroscopic analysis; furthermore, computational studies also support the proposed structure. Electronic perturbation of the phosphorus atoms and the spherical bulkiness of the Mes* groups provide the enormous stability of **3** in air by decreasing the reactivity of the radical. The unique properties of this class of compound will be further explored because stable radicals are expected to play an important role as starting compounds for intelligent materials, such as those employed in spintronics, molecular magnets, and spin-trapping.[24–26]

Experimental Section

Preparation of **3**: *tert*-Butyllithium (0.26 mmol, 1.4 M in hexanes) was added to a solution of **1** (150 mg, 0.52 mmol) in THF (3 mL) at −78 °C and stirred for 15 min. The reaction mixture was allowed to warm to room temperature, and subsequently mixed with iodine (0.26 mmol). The volatile materials were removed in vacuo, and the residue was extracted with hexane. The hexane extract was concentrated in vacuo,

and practically pure **3** was obtained as a dark red solid (154 mg, 93%). Compound **3** was recrystallized as dark red needles from dichloromethane at 0°C. M.p. 130–132°C (decomp); UV/Vis (CH_2Cl_2): λ_{max} ($\varepsilon \times 10^{-3}$) 298 (12.3), 355 (16.1), 423 (3.6), 515 (11.7), 759 (1.3) nm; ESI-MS calcd for $C_{42}H_{67}P_2$: 633.4718; found: 633.4713; elemental analysis (%) calcd for $C_{42}H_{67}P_2$: C 79.57, H 10.65; found: C 79.05, H 10.66.

X-ray crystallography for **3**: $C_{42}H_{67}P_2$, $M_r = 633.94$, dark red needle (dichloromethane), $0.15 \times 0.15 \times 0.10\ mm^3$, triclinic, space group (no. 2), $a = 13.620(1)$, $b = 14.955(1)$, $c = 10.9292(7)$ Å, $\alpha = 98.130(7)$, $\beta = 98.918(8)$, $\gamma = 67.887(2)°$, $V = 2029.0(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.038\ g\,cm^{-3}$, $F(000) = 698$, $\mu = 0.133\ mm^{-1}$, $T = 203$ K; a Rigaku RAXIS-IV imaging plate detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) was used; of 15420 reflections measured ($2\theta_{max} = 55.0°$), 8353 were observed ($R_{int} = 0.062$). The structure was solved by direct methods (SIR92),[27] expanded using Fourier techniques (DIRDIF94),[28] and then refined by full-matrix least squares on F^2 for 404 variable parameters. The non-hydrogen atoms without the disordered atoms in the *p*-*tert*-butyl group were refined anisotropically. Hydrogen atoms (calculated) were refined isotropically. $R1 = 0.116$ for $I > 2.0\sigma(I)$, and $R_w = 0.242$ for all data. Goodness of fit $S = 1.60$ for observed reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.60 and $-0.48\ e\,Å^{-3}$, respectively. The data were corrected for Lorentz polarization effect. Structure solution, refinement, and graphical representation were carried out using the teXsan package.[29] CCDC-295065 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

EPR measurement for **3**: EPR measurements at X-band (9.5 GHz) were carried out for **3** with a Varian E-12 EPR spectrometer, equipped with a rectangular cavity. The magnetic field was measured with a Bruker EPR 035M gaussmeter, and the microwave frequency was measured with a model HP 5245L frequency counter for *g* value determination.

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