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Oxidation of 1,3-Diphosphacyclobutane-2,4-diyl with Ammoniumyl Antimonate and EPR Study of the Corresponding Cation Radical

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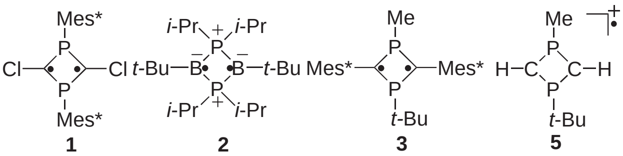
A sterically protected biradical species, 1-*tert*-butyl-3-methyl-2,4-bis(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyl was allowed to react with tris(4-bromophenyl)ammoniumyl hexachloroantimonate as an oxidant and the product was analyzed by EPR to show that the biradical was oxidized to give the corresponding radical cation species. The structure of the cation radical was also supported by ab initio calculations on a model compound.

By use of steric protection technique, we have been successful in isolation and characterization of various unusual phosphorus compounds.[1] An extremely bulky substituent such as 2,4,6-tri-*tert*-butylphenyl (here after abbreviated as Mes*) enables us to isolate compounds containing multiple bonds to phosphorus (cf. diphosphenes[2] and phosphaalkynes[3,4]).

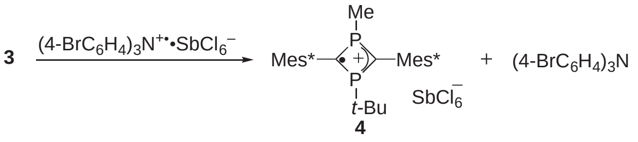
In a seminal report Niecke and co-workers described an isolable phosphorus-containing four-membered cyclic biradical, 2,4-dichloro-1,3-diphosphacyclobutane-2,4-diyl (**1**).[5] Compound **1** is sterically stabilized by Mes* at the phosphorus atoms and electronically stabilized by P atoms in the four-membered ring together with Cl at the radical carbon center. The chemical properties of **1** are those of a singlet ground state biradical. Bertrand et al. reported the synthesis of a four-membered B_2P_2 ring system **2**,[6] which is the first stable singlet biradical. We recently reported the formation of 1,3-diphosphacyclobutane-2,4-diyl (**3**) in the reaction of a bulky phosphaalkyne, 2-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethyne (Mes*C≡P) with *tert*-butyllithium and iodomethane.[4] This latter species is highly stabilized by Mes* groups at the carbon atoms, as can be recognized from the X-ray analysis (Scheme 1).

Indeed, compound **3** is extremely stable even at room temperature.[4,7] The parent peak in the mass spectrum (ESI-positive) for **3** was pronounced (Found: m/z 648.4949; Calcd for $C_{43}H_{70}P_2$: m/z 648.4947). We have also investigated the electrochemistry (CV) of **3**.[4] The biradical **3** is easily and reversibly oxidized; an observation that suggests a stable cation radical might also be formed by chemical oxidation. We report here chemical one-electron oxidation of **3** to produce a P-heterocyclic radical cation (Scheme 2). The EPR-spectroscopic properties are discussed in light of ab initio calculations on a model system.



Mes* = 2,4,6-*t*-$Bu_3C_6H_2$

Scheme 1.



Scheme 2.

Ledwith and co-workers have developed an efficient and clean one-electron oxidizing reagent, tris(4-bromophenyl)ammoniumyl hexachloroantimonate,[8] which prompted us to carry out an oxidation reaction of **3** with this ammoniumyl antimonate, since radical cation **4** is expected to be generated without formation of EPR-active by-product.

A blue solution of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (slightly less than one equivalent) in dichloromethane was added to a dark blue dichloromethane solution of compound **3** (ca. 1 µmol) in an EPR sample tube producing a green solution. The reaction mixture containing the putative cation radical **4** was sealed under nitrogen and analyzed by EPR spectroscopy.[9] A qualitative UV–vis spectrum (dichloromethane) of the adduct (cation radical) showed absorptions at 510, 625, 732, and 846 nm as well as an intensive absorption due to $(4\text{-BrC}_6H_4)_3N$ at 310 nm.[10,11]

Figure 1a shows the spectrum which is an overlap of the reaction product and the starting material.[12] Subtraction of this signal from the EPR spectrum (a) gives us a four-line signal with small outer peaks and the isotropic $g = 2.0025 \pm 0.0002$ which

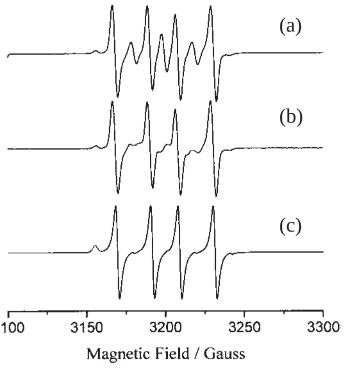


Figure 1. (a) EPR spectrum of the reaction mixture of **3** with (4-bromophenyl)ammoniumyl antimonate measured at room temperature in dichloromethane (experimental). Parameters: microwave frequency 9.09096 GHz; modulation amplitude 1 G; microwave power 2 mW; gain 4 × 10^3. (b) EPR spectrum of **4** obtained by subtraction of the starting material spectrum from spectrum (a). (c) Simulated (b) spectrum, see text.

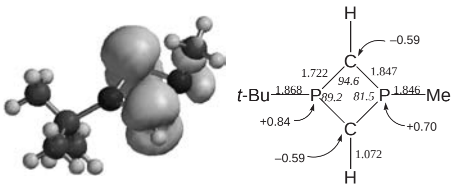


Figure 2. A visual map of electron spin density in the optimized structure of **5** at the UHF/6-31G* level. The geometry at the optimized structure is shown on the right: bond distances in Å and bond angles (italics) in degrees (°). The sums of the angles: Σ(C): 360.0°, Σ(P): 292.8° (P_{Me}), 350.0° ($P_{t\text{-Bu}}$). Mulliken atomic charges on the ring are also given.

is characteristic of π-organic radicals (Figure 1b) and could be attributed to the radical cation **4**. The radical cation spectrum (b) was simulated by using the XSophe computer simulation software.[13] The best fit was obtained with the Lorentzian line width of 2.2 G, two different $^{31}P(I = 1/2)$ hyperfine coupling constants (hfc) constants $a_{P1} = 39.5$ G, $a_{P2} = 22.3$ G and the ^{13}C ($I = 1/2$) hfc of 30 G (Figure 1c).[14] The large $^{31}P(a_{P1})$ hfc corresponds to the phosphorus atom with Me and the smaller $^{31}P(a_{P2})$ corresponds to that with *t*-Bu, according to an ab initio calculation using $[t\text{-BuP(CH)}_2\text{PMe}]^{+\bullet}$ (**5**) as a model for **4**.[15]

Figure 2 shows the optimized structure of **5** with the total energy of −954.3680984 au at the UHF/6-31G* level. The two carbon atoms assume sp^2 configurations while the two phosphorus centers are pyramidalized. The computation depicts that most of the electron spin density is concentrated equally on the two carbon atoms of the C_2P_2 ring, and there is much smaller electron spin density observed on the phosphorus atom attached to methyl (P_{Me}), while the spin density does not seem to reside on the other phosphorus attached to *t*-Bu ($P_{t\text{-Bu}}$). Accordingly, the unambiguous assignment of a_{P1} and a_{P2} was possible based on the model calculation. The experimental spectrum (Figure 1b) was well-reproducible if the protons with hfc < 1.0 G were used in the simulations. Most of the positive charges in **5** locate on the phosphorus atoms (with the larger charge at $P_{t\text{-Bu}}$), which supports the partially delocalized structure formula **4**.

Our results described herein constitute a chemical transformation of **3** to a novel heterocyclic radical ion through single-electron transfer procedure. This chemical process mirrors notable feature of the redox properties of 1,3-diphosphacyclobutane-2,4-diyls. Recently, Niecke and co-workers reported chemical reduction and protonation of 1,3-diphosphacyclobutane-2,4-diyls affording the intriguing heterocyclic anion and cation, respectively, through removal or addition of the substituents on the ring.[16,17] Therefore, such reactivity of the biradicals, 1,3-diphosphacyclobutane-2,4-diyls, promises to develop heterocyclic phosphorus chemistry by furnishing novel molecular functionalities.

In conclusion, we were successful in generating a cation radical chemically by the reaction of 1,3-diphosphacyclobutane-2,4-diyl with tris(4-bromophenyl)ammoniumyl hexachloroantimonate and characterized it by EPR measurement and ab initio calculation.

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10 UV–vis spectrum for $(4\text{-BrC}_6\text{H}_4)_3\text{N}^{+\bullet}\cdot\text{SbCl}_6^-$ was reported ($\lambda_{max} = 700$ nm) and the spectrum of the reaction mixture did not seem to contain the ammoniumyl antimonite: W. Schmidt, E. Steckhan, *Chem. Ber.* **1980**, *113*, 577.

11 An EI-MS (70 eV) spectrum of the adducts showed obvious ion peaks corresponding to **3**$^+$ (m/z 648) and $(4\text{-BrC}_6\text{H}_4)_3\text{N}^+$ (m/z 479).

12 The three-line spectrum of the starting reagent was also observed (not shown in Figure 1). It could be due to a trace of mono-radical admixture in **3**, the assignment of which is in progress. See: H. D. Brauer, J. Stieger, J. S. Hyde, L. D. Kispert, G. R. Luckhust, *Molecular Physics* **1969**, *17*, 457. The four-line signals due to **4** are reproducible and stayed alive at room temperature even after 2 months.

13 *XSophe Computer Simulation Software Suite (Version 1.1.4)*, **1993–2004**, developed in the Centre for Magnetic Resonance and Department of Mathematics, The University of Queensland, Brisbane, Queensland, Australia and Bruker Biospin, GmbH, Rheinstetten, Germany.

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