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Isolation of a Highly Persistent Diphosphanyl Radical: The Phosphorus Analogue of a Hydrazyl**

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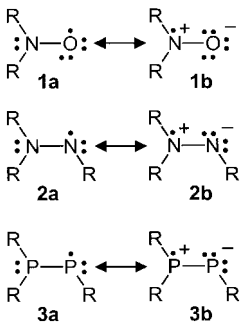
Despite the enormous importance of radicals in both chemical reactions and biological processes, very few organic free radicals have been isolated.[1, 2] Notable exceptions are nitroxides **1** and hydrazyls **2**, in which the unpaired electron is localized on a nitrogen center.[3] These stable radicals, which are described by the resonance structures **a** and **b** (Scheme 1), are applied as contrast agents, molecular markers, and reporters for molecular movements (spin labels).[4] Considerable effort has been invested in the synthesis of stable free radicals localized on phosphorus, the closest homologue to nitrogen.[5–9] Indeed, this element consists of only one isotope, ^{31}P, with a nuclear spin of ½ giving rise to a hyperfine coupling which is much larger than with the nitrogen isotope ^{14}N. This property is particularly interesting for spin-labeling experiments, since the anisotropy (orientation dependence) of the hyperfine coupling with ^{31}P would provide detail concerned



Scheme 1. Resonance structures **a** and **b** of nitroxide **1**, hydrazyl **2**, and diphosphanyl **3**.

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with much faster molecular movements than that available from nitroxides **1**. We report here a synthesis of a phosphorus analogue (**3**) of hydrazyls **2** and show that the anisotropy of the hyperfine coupling is very large, indeed.

Our synthetic route begins with the phosphonium salt [Mes*MeP=PMes*]$^+$(O_3SCF_3)$^-$ (**4**; Mes* = 2,4,6-*t*$Bu_3C_6H_2$), which contains a strong P–P double bond.[10] Its cyclic voltammogram (Figure 1) shows that **4** undergoes two successive chemically reversible single-electron reductions at potentials ($E^1_{1/2} = -0.37$ V, $E^2_{1/2} = -1.23$ V vs. Ag/AgCl) that are about 1 V lower than the ones of usual phosphonium salts.[11] The first step corresponds to the formation of the diphosphanyl radical [Mes*MeP–PMes*]$^\bullet$ (**7**) and the second to the formation of the phosphanyl phosphide anion [Mes*MeP–PMes*]$^-$ (**8**).

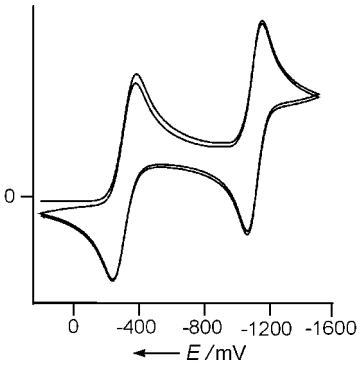
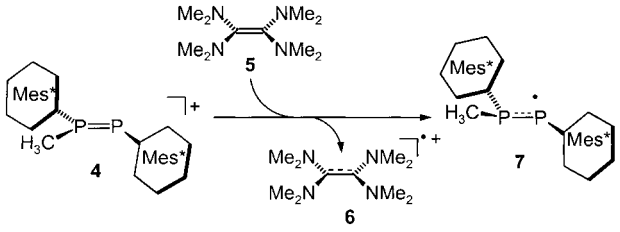
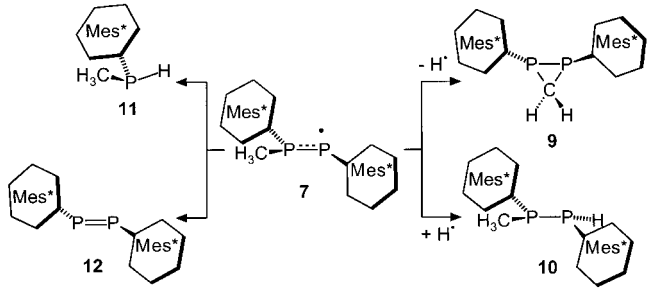


Figure 1. Cyclic voltammogram of a ca. 10^{-4} M solution of **4** in acetonitrile containing 0.1 mol L^{-1} nBu_4NPF_6 as electrolyte. Potentials versus Ag/AgCl, scan rate 100 mV s^{-1}.

The ease with which **4** can be reduced prompted the chemical synthesis of radical **7** by a simple electron transfer reaction using tetrakis(dimetylamino)ethylene (TDE) (**5**) as electron donor ($E_{1/2}$(TDE$^{\bullet+}$/TDE) ≈ -0.55 V vs. Ag/AgCl; Scheme 2).[12] At the interface of the yellow acetonitrile solution of **4** layered with a solution of **5**, the color turns immediately green. Simultaneously, the characteristic red color of the stable radical cation TDE$^{\bullet+}$ **6** appears. Furthermore, yellow-orange crystals form on the wall of the reaction flask. Optimization of the reaction conditions yields crystals of **7** by filtration after a reaction time of 3 min. Radical **7** is soluble in *n*-hexane giving rise to an intense green solution (UV/Vis: $\lambda_{max} = 668$ nm). The EPR spectrum of this solution shows a simple four-line pattern due to coupling of the unpaired electron with two inequivalent ^{31}P nuclei proving the identity of **7** as a diphosphanyl radical.[6, 7] Magnetic measurements of crystals of **7** indicated that the radical exists up to about 90% as monomer and that the crystals are contaminated by solvent (MeCN). In the solid state, radical **7** is stable at temperatures below $-30\,^\circ$C for several days, but decomposes at room temperature slowly both in the solid state and in *n*-hexane solution ($t_{1/2} \approx 90$ min at 3×10^{-2} mol L^{-1}) as can be monitored by the fading of the green color. The decomposition products are shown in Scheme 3. The diphosphirane **9**[10] (ca. 30%) and diphosphane **10**[13] (ca. 43%) are formally the products of a disproportionation reaction, while phosphane **11**[14] (ca. 17%) and diphosphene **12**[15] (ca. 10%) most likely stem from cleavage of the P–P bond and cleavage of the P–P bond followed by dimerization.



Scheme 2. Synthesis of radical **7**.



Scheme 3. Decomposition of radical **7**.

So far, we have not been able to obtain crystals of **7** suitable for an X-ray analysis. However, a combination of solid-state EPR experiments and theoretical methods unambiguously determined the structure of **7**. Diphosphanyl **7** can be incorporated into the lattice of single crystals of the diphosphane Mes*MeP–PMes*Me (**13**).[10] Crystals of pure **13** are yellow but become deep green when doped with **7**. Such crystals can be stored at room temperature without notable decomposition of **7** and can even be handled in air. The angular dependence of the EPR signals recorded with such a crystal shows that the paramagnetic species **7** is indeed trapped in the guest lattice ($g_{average} = 2.008$). Owing to the symmetry of the host lattice, two magnetically inequivalent orientations of **7** are detected, each of which gives rise to a four-line pattern (Figure 2).

The resulting anisotropic ^{31}P coupling constants are listed in Table 1. A comparison with atomic constants[16] indicates that the unpaired electron is essentially confined to phosphorus p orbitals, with a larger spin density on P1 than on P2. The isotropic couplings (A_{iso}(P1) = 250 MHz, A_{iso}(P2) = 390 MHz) show that the s character of the orbital containing the unpaired electron remains modest: ρ_s(P1) = 0.019, ρ_s(P2) = 0.029. Furthermore, the complete molecule **7** was optimized by using the Amsterdam Density Functional (ADF 2.3) suite of programs[17, 18] and these results are also given in Table 1. Figure 3 shows the calculated structure overlaid with a graphical representation of the spin density. The agreement between the experimental and calculated anisotropic coupling constants is excellent; in particular, the experimentally

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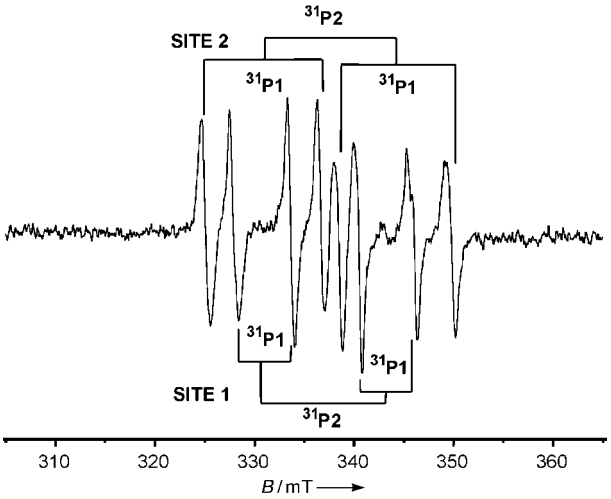

Figure 2. EPR spectrum of a single crystal of Mes*MeP–PMes*Me (**13**) doped with Mes*MeP–PMes* (**7**). Due to the crystal symmetry, the radical is trapped along two magnetically inequivalent orientations (site 1 and site 2).

Table 1. Experimental and calculated anisotropic hyperfine coupling constants $\tau_1-\tau_3$ [MHz], and spin densities ρ_p. The average of the g tensor = 2.008.

Atom	ρ_p [%]	τ_1	τ_2	τ_3
P1 in **7**	62[a]	– 243	– 214	457
P2 in **7**	15[a]	– 64	– 48	113
P1(calcd)	74	– 233	– 222	456
P2(calcd)	15	– 73	– 60	133

[a] Determined by comparison with atomic coupling constants.

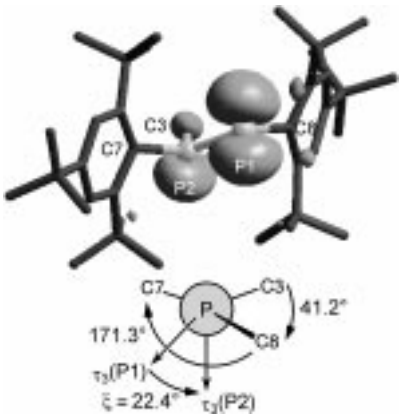

Figure 3. Geometry-optimized structure of **7** and graphical representation of the spin density distribution. Selected bond lengths [Å] and angles [°]: P1-P2 2.18, P1-C8 1.89, P2-C3 1.88, P2-C7 1.89; P2-P1-C8 96.1, C3-P2-P1 115.3, C7-P2-P1 105.9, C3-P2-C7 116.3.

determined angle ($\xi = 25°$) between the two "parallel" ^{31}P-eigenvectors is close to the calculated value ($\xi = 22.4°$).

It is interesting to compare the structure of **7** with that of 1,2-diphenylpicrylhydrazyl (DPPH). In this nitrogen radical the ξ angle is 13°, the N–N bond length lies between that of a single and of a double bond (bond order 1.5), and the three-coordinate nitrogen center lies in a planar coordination sphere. This is in contrast with **7** in which the P–P bond length (2.18 Å) approaches that of a P–P single bond (~2.22 Å), and the phosphorus center P2 resides in a pyramidal environment. Interestingly, the degree of pyramidalization in **7** (Σ(P2): 337.5°) is almost exactly halfway between the one in **4** (planar, Σ(P2): 360°) and the more pronounced one in **13** (Σ(P)°: 315.9), and agrees well with the one observed in the singlet diradicals (1,3-diphosphacylobutane-2,4-diyl) $[RPCR^1]_2$ (Σ(P): 337 – 341°) synthesized by Niecke et al.[19] Like in the latter, some degree of π donation from P2 to the electron-deficient center, here P1, may be assumed. The structural features of **7** are responsible for a large spin localization on P1, whereas in the nitrogen analogue the unpaired electron is almost equally delocalized over the two nitrogen centers. As expected, the anisotropy of the EPR spectrum is considerably more pronounced for the diphosphanyl radical **7** than for the nitrogen-centered hydrazyl species. For **7**, the low-field and high-field transitions are separated by 42 mT when the magnetic field H_o is oriented along the magnetic $3p_z$ orbital of P1 and by only 13 mT for H_o perpendicular to this direction. The corresponding anisotropy (820 MHz)—superior to that of DPPH (230 MHz) or nitroxides (150 MHz)—indicates that diphosphanyl radicals are well suited for the study of fast molecular movements.

The work described here demonstrates that diphosphanyl free radicals are much more stable than previously thought and can be isolated. Elucidation of the principal structural and physical properties in connection with the discovery of possible decomposition pathways will help to rationalize possible substitution patterns in $[RR^1P\text{-}PR^2]^{\bullet}$-type radicals to further enhance the stability of diphosphanyls.

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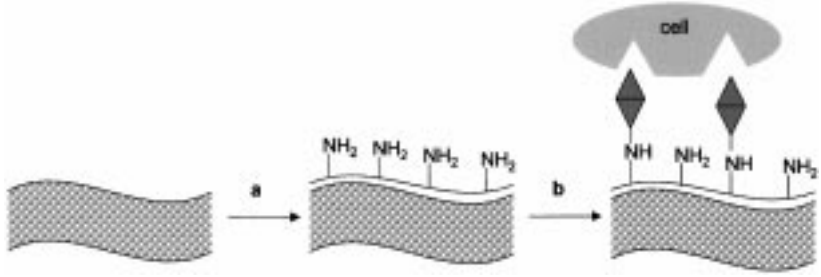
Synthesis of Amino[2.2]paracyclophanes—Beneficial Monomers for Bioactive Coating of Medical Implant Materials**

Jörg Lahann, Hartwig Höcker, and Robert Langer*

Substituted [2.2]paracyclophanes have received increasing interest over the past few years.[1] Beside their use as chiral auxiliaries for asymmetric synthesis[2] and as ligands in metal clusters,[3] they were reported to be suitable monomers for chemical vapor deposition (CVD) polymerization.[4] CVD-based polymer coatings were of interest as interfaces for biomedical applications due to their potential for the incorporation of functional groups (Scheme 1). These functional groups can be used to conjugate biomolecules such as proteins, antigens, or cell receptors to implant surfaces.[5] The resulting biomimetic coatings provide interfaces that may allow control of the interactions between biomaterials and organisms. There is an increasing demand for bioactive surfaces, particularly in rapidly growing fields such as tissue engineering.[6]



Scheme 1. Concept of bioactive coating for tissue engineering based on CVD polymerization of amino[2.2]paracyclophanes. a) CVD polymerization of amino[2.2]paracyclophane provides a reactive interface. b) Linkage of cytokines to the interface, for example cell receptors, growth factors, antigens, or cell adhesion mediators, controls interactions with cells.

Several substituted [2.2]paracyclophanes were reported to undergo CVD polymerization.[7] Although amino-substituted polymers are interesting polymers for biomedical applications, their synthesis by CVD is limited by the lack of facile and effective syntheses of amino-functionalized [2.2]paracyclophanes. 4-Amino[2.2]paracyclophane (**3a**) is commonly synthesized from **1** by a five-step synthesis[8] via [2.2]paracyclophanecarboxylic acid and Curtius rearrangement. This synthesis provides poor yields of **3a**, and diamino[2.2]paracyclophane (**3b**) has yet to be synthesized following this approach. Alternatively, **3a** was recently prepared from 4-bromo[2.2]paracyclophane by metalation with butyllithium and successive amination in 46% yield.[9] The direct synthesis of amino[2.2]paracyclophanes by nitration and subsequent reduction of the nitro[2.2]paracyclophanes suffers from the poor resistance of [2.2]paracyclophanes to oxidation and its tendency to polymerization. In early studies, Cram et al. reported the synthesis of nitro[2.2]paracyclophanes by treatment of [2.2]paracyclophane with mixtures of nitric acid and sulfuric acid that resulted in yields of 26% for the mononitro compound **2a** and of 8% for the dinitro product **2b**.[10] In addition to poor yields, purification of the products from polymeric by-products was difficult, which limited the broad application of this route. Herein we describe a new convenient high-yield synthesis route to **3a** and **3b**.

Treatment of anhydrous nitric acid with trifluoromethanesulfonic acid delivers free nitronium ions[11] which exhibit high nitration power even at low temperatures (Scheme 2). We found that **1** is completely nitrated at temperatures as low as $-78\,^{\circ}C$. Due to the low temperatures and short reaction times, side reactions like oxidation or polymerization of **1** are not favored and were not observed. As a result, yields of the nitro[2.2]paracyclophane **2b** were increased from 8% to 93%.

These nitration conditions could be adjusted to synthesize selectively either **2a** or **2b**. Using the superacidic ion-exchange resin Nafion/nitric acid, **2a** is obtained in 95% yield. Synthesis of dinitro[2.2]paracyclophane **2b** is best carried out with stirring for 30 min at $-78\,^{\circ}C$ and an additional 2 h at $-20\,^{\circ}C$. Only traces of **2a** were found under these conditions. The main product **2b** (93%) was determined to comprise mainly the pseudo-*para* isomer **2b′** (75%), with about 25% of the pseudo-*meta* isomer (**2b″**). Other isomers were less than 2%, as shown by gas chromatography. This ratio was not affected by the subsequent reduction and is responsible for the fact that **3b** contains 22.7% pseudo-*meta* diamino[2.2]paracyclophane (**3b″**) (Table 1).

Reduction of the nitro[2.2]paracyclophanes was previously carried out with hydrogen using platinum catalysts.[12] However, these reaction conditions are unfavorable and yields are low to moderate. Therefore, more efficient routes are necessary if amino-substituted [2.2]paracyclophanes are to be exploited as potential monomers for CVD. Several

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