our intent to determine if the dienylperoxyl rearrangement mechanism also involved a radical caged pair. Cage effect studies investigating ^{18}O incorporation as a function of solvent viscosity demonstrate ^{18}O incorporation approaching 100% in hexane and slightly decreased incorporation of atmospheric oxygen in octadecane. This implies a much smaller cage effect with pair escape dominating pair collapse and gives supportive evidence that, in contrast to the allyl radical, the pentadienyl radical reacts with molecular oxygen more slowly than the diffusion-controlled rate.[17,18]

Both theoretical investigations[9] and cage effect studies point to a dissociative mechanism for the allylperoxyl rearrangement. Solvent viscosity studies have previously been used to provide evidence for caged radical pair intermediates,[19,20] and a radical–dioxygen pair should have reactivity similar to that of a caged radical pair since the collapse of both pairs occurs at or near the diffusion-controlled rate. In contrast to pairs of radicals that couple with loss of stereochemistry in isotropic media,[21] collapse of the radical–dioxygen pair apparently occurs in solution with high stereoselectivity. These results demonstrate the importance of solvent viscosity on peroxyl radical rearrangements and suggest that viscosity effects might affect peroxyl radical rearrangements in biological systems of high microviscosity such as lipid bilayers.

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Formation of a Novel P–B–N–C Ring via an Intramolecular C–H Activation Process

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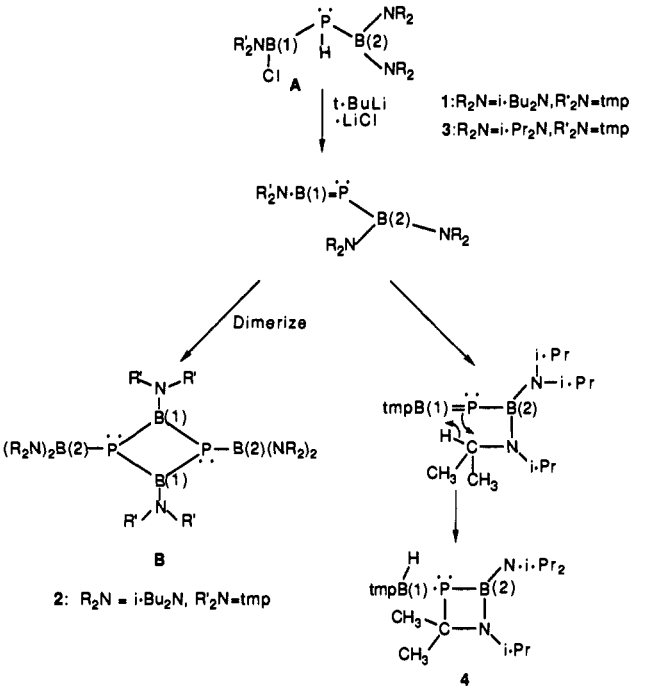
Recently, there has been new interest in the syntheses of phosphinoboranes, $R_2PBR'_2$,[1] but only limited chemistry of these species has been examined. We have previously found that tmpB(Cl)PH_2 (tmp = 2,2,6,6-tetramethylpiperidino), in combination with H_2PLi or *t*-BuLi, forms a diphosphadiboretane, $(tmpBPH)_2$,[2] and we assume dehydrohalogenation proceeds through a transient boraphosphene, tmpB=PH. Our interest here was to determine whether diborylphosphanes (A)[3] undergo dehydrohalogenation with formation of boraphosphenes $(R_2N)_2BP{=}B(NR'_2)$ and, via dimerization, synthetically useful diphosphadiboretanes (B).

Scheme I



The equimolar reaction of tmpB(Cl)P(H)B(N-*i*-Bu_2)$_2$ (**1**) and *t*-BuLi in hexane produces the anticipated diphosphadiboretane, $(i\text{-}Bu_2N)_2BPB(tmp)P[B(N\text{-}i\text{-}Bu_2)_2]B(tmp)$ (**2**).[4] On the other hand, combination of tmpB(Cl)P(H)B(N-*i*-Pr_2)$_2$ (**3**) and *t*-BuLi (1:1) leads to $[tmpB(H)]PB(N\text{-}i\text{-}Pr_2)N(i\text{-}Pr)C(CH_3)_2$ (**4**)[5] (Scheme I), which with $Fe_2(CO)_9$ (1:1) gives a yellow, crystalline complex, $Fe(CO)_4$·**4** (**5**).[6] Spectroscopic data[7] indicate that **4** is not a diphosphadiboretane and that its general structure is not affected by metal complexation. Therefore, the molecular structure of **5** was determined in order to elucidate the nature of **4**.[8] The structure (Figure 1) reveals a novel, planar, asymmetric, four-membered azacarbaphosphaboretane ring with $Fe(CO)_4$ and tmpBH fragments as exo substituents on the phosphorus atom.

The structure of **4** does not preclude formation of a boraphosphene during this reaction. However, if produced, it does not dimerize as does the transient boraphosphene formed from **1**. Instead, the P=B(1) bond apparently undergoes intramolecular

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(4) A hexane solution of **1** (18.1 mmol, 8.8 g) was cooled to −78 °C, and *t*-BuLi (10.7 mL, 1.7 M) was added dropwise. The mixture was stirred at −78 °C (2 h) and at 23 °C (16 h) and then filtered, and the solvent was vacuum evaporated. The residue deposited yellow crystalline solid (5.0 g, 61%) **2**, mp 167–169 °C.

(5) Addition of *t*-BuLi (1.2 mL, 1.7 M) to a cooled (−78 °C) hexane solution of **3** (0.9 g, 2.1 mmol), followed by stirring at −78 °C (2 h) and 23 °C (24 h), resulted in a cloudy, yellow solution that was filtered, and the solvent was removed by vacuum evaporation. The residue crystallized upon standing (23 °C). Two recrystallizations from cold hexane gave white solid **4** (0.50 g, 61%), mp 87–89 °C.

(6) A sample of **4** (0.60 g, 1.5 mmol) in 50 mL of hexane was combined with $Fe_2(CO)_9$ (0.56 g, 1.5 mmol) and stirred (3 days). Solvent and volatiles were removed by vacuum evaporation, and the residue was extracted with hexane (25 mL). The extract was filtered, concentrated, and cooled to −10 °C, and brown crystals of **5** (0.4 g, 47%) were collected; mp 154–156 °C.

(7) Characterization data for **2**, **4**, and **5** (microanalysis, MS, IR, and ^{31}P, ^{11}B, ^{13}C, and ^{1}H NMR) are provided in the supplementary material.

(8) Selected crystal data for **5**, $C_{25}H_{46}B_2N_3O_4PFe$: orthorhombic, *Pbca* with a = 18.373 (3) Å, b = 17.845 (4) Å, c = 19.172 (3) Å, Z = 8, R_F = 0.088 and R_{wf} = 0.063.

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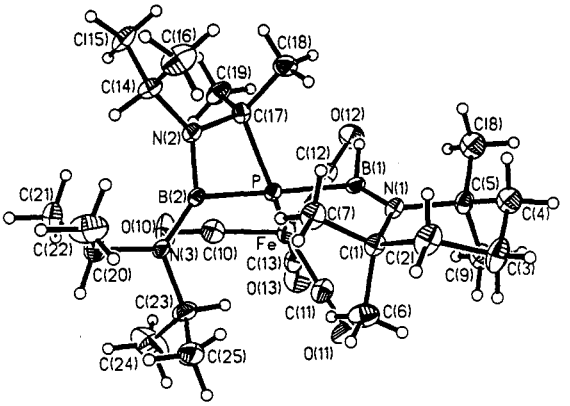

Figure 1. Molecular structure and atom labeling scheme for [tmpB(H)][$Fe(CO)_4$]PB(i-Pr_2N)N(i-Pr)C(Me_2) (**5**). Selected bond distances (Å): Fe–P = 2.297 (2); P–B(1) = 1.965 (8); P–B(2) = 1.964 (8); P–C(17) = 1.900 (7); B(1)–N(1) = 1.362 (10); B(2)–N(2) = 1.417 (10); B(2)–N(3) = 1.398 (10); N(2)–C(14) = 1.478 (9); N(2)–C(17) = 1.493 (9).

1,2-addition with a C–H bond from an amino isopropyl group on B(2).[9] It is interesting that a related C–H bond addition to a transient phosphinoborane [$Br_2P{=}BMes_2$] occurs in an opposite sense with a mesityl methyl H atom migrating to the P atom. The resulting CH_2 group bonds to the boron atom, forming a five-membered P–B–CH_2–C–C ring.[10]

Several structural features in **5** are of interest. The exo P–B(1) and endo P–B(2) distances are identical, and they are comparable with the P–B(N-i-Pr_2)$_2$ distance in **3**, 1.979 (5) Å.[3] The exo B(2)–N(3) distance is identical to the endo B(2)–N(2) distance, and these are similar to the average i-Pr_2N–B distance in **3**, 1.426 Å. The B(1)–N(1) distance involving the tmp group is shorter than the B–N(tmp) distance, 1.397 (5) Å, in **3**, and this is consistent with greater B–N π overlap in the tmpB(H)P fragment of **5**. The P–C(17) bond length is comparable with the average endo P–C distance, 1.92 Å, in [Me_2CC(H)(Me)C(Me_2)P(Me)(Ph)$^+$](I^-).[11] The P–Fe bond distance is relatively long compared to the P–Fe distance in $(CO)_4$Fe·PPh_3,[12] 2.244 (1) Å. These distances and carbonyl stretching frequencies suggest that **4** is a slightly better σ donor than PPh_3.

The results of this study suggest that an interesting distinction in the reactivity of transient boraphosphene fragments may be induced by substituent group variations on a progenitor diborylphosphane. Efforts to isolate or trap boraphosphenes and additional studies of factors that influence the formation and reactivity of $X_2BP{=}BY$ species are in progress.

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Supplementary Material Available: Tables of X-ray data, collection parameters, atom coordinates, bond distances and angles, hydrogen atom coordinates, and thermal parameters for **5** and spectroscopic data (16 pages); listing of observed and calculated structure factors for **5** (15 pages). Ordering information is given on any current masthead page.

(9) The difference in behavior between **1** and **2** is consistent with the expected stability of alkyl carbocations. In an alternative mechanism, steric crowding may reduce the operational acidity of the P–H bond in **3**, and the first step could involve deprotonation of one i-Pr on B(2). Subsequent cyclization could occur by carbanion attack on the phosphane center accompanied by hydride transfer from the P atom to the B atom with elimination of LiCl.

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Photosensitized Formation of 7,8-Dihydro-8-oxo-2′-deoxyguanosine (8-Hydroxy-2′-deoxyguanosine) in DNA by Riboflavin: A Non Singlet Oxygen Mediated Reaction

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Increasing attention is devoted to the elucidation of the biological role of 7,8-dihydro-8-oxo-2′-deoxyguanosine[2] (8-oxodG, 8-hydroxy-2′-deoxyguanosine), an important oxidation product of the guanine moiety within DNA.[3] Hydroxyl radicals have been shown to induce the formation of 8-oxodG within both isolated and cellular DNA exposed to ionizing radiation.[4] In addition, several oxidizing agents, including hydrogen peroxide, Fenton type reagents, and radiomimetic agents, induced the formation of 8-oxodG in naked and cellular DNA.[3,5] Another interesting possibility to generate 8-oxodG within DNA is provided by the use of photodynamic agents such as methylene blue,[6] thiazines,[7] and phthalocyanines.[8] The type II mechanism for photooxidation, which involves the formation of singlet oxygen as the reactive intermediate,[9] appears to be the likely process for the photooxidized formation of 8-oxodG.[10]

We report that riboflavin, an endogeneous cellular photosensitizer,[11] efficiently photoinduces the formation of 8-oxodG according to a new mechanism which does not involve the participation of any reactive oxygen species. Exposure of calf thymus DNA (260 μg/mL) in phosphate buffer containing riboflavin to visible light was found to generate 8-oxodG,[12] whose formation was quantified by using a modification[13] of the high-performance liquid chromatographic–electrochemical detection assay,[14] subsequent to enzymatic digestion of the irradiated biopolymer. The

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