

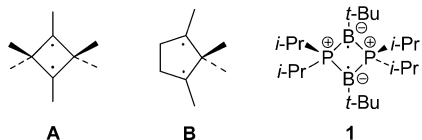
Radical-Type Reactivity of the 1,3-Dibora-2,4-Diphosphoniocyclobutane-1,3-diyl

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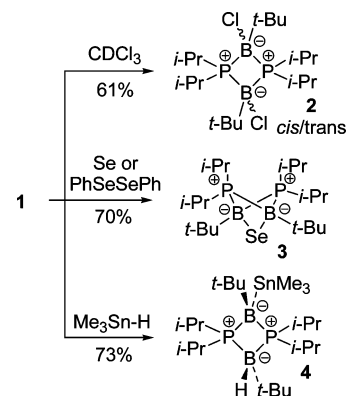
Over the last 10 years, considerable effort has been devoted to the understanding of the electronic structure of singlet diradicals¹ such as cyclobutane-1,3-diyls **A** or cyclopentane-1,3-diyls **B**. The major experimental difficulty resides in the fact that these species exist as either short-lived intermediates or even as transition states.² On optimizing the effects of substituents,³ a few singlet 1,3-diradicals have been observed.⁴ However, the half-life in solution at room temperature of the most persistent remains in the microsecond range,^{4b} and according to Abe, Adam, et al., they are reluctant to undergo intermolecular chemical reactions.^{4b,5} Taking advantage of the unique properties of hetero-elements, we have recently reported the synthesis and structural characterization of the 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl, **1**, that is indefinitely stable at room temperature.⁶ The presence of both through-space and through-bond B–B interactions has been revealed by theoretical investigations,^{6,7} and substituent effects on the extent of diradical character have been studied.^{7,8} Here we report the first results concerning the chemical behavior of **1**.



During NMR experiments, we observed that compound **1** slowly reacted with deuterated chloroform. The reaction was complete after 3 days at room temperature. The 2,4-dichloro adducts **2** were obtained in an approximate ratio of *cis*-**2**/*trans*-**2**: 3/1 (Scheme 1). The two isomers were separated by crystallization and characterized by multinuclear NMR spectroscopy and X-ray analyses.⁹ The relative positions of the two chlorine atoms were indicated by the presence in the ¹H and ¹³C NMR spectra of two and one CH isopropyl signals for *cis*-**2** and *trans*-**2**, respectively. Upon oxidation, the BPBP four-membered ring remains perfectly planar in *trans*-**2** and is only slightly folded in *cis*-**2**, probably for steric reasons. As expected, because of the cancellation of both through-space and through-bond B–B interactions, the PB bonds are elongated (**1**: 1.89 Å, *cis*-**2**: 2.05–2.07 Å, *trans*-**2**: 2.06–2.07 Å). Derivatives *cis*-**2** and *trans*-**2** do not interconvert in solution; however, the mechanism for the reaction of **1** with chloroform is not clear-cut.

Since **1** readily reacts with mild oxidizing agents such as chloroform, we subsequently studied its behavior toward elemental selenium. Complete conversion was observed after 8 h at room temperature in toluene solution. The [1.1.1]bicyclic structure (asterane) of the resulting derivative **3** (70% isolated yield) was

Scheme 1



unambiguously established by an X-ray diffraction analysis⁹ (Figure 1). The B–Se bond distances (2.13 Å) are at the upper limit for B–Se single bonds (2.00–2.10 Å),¹⁰ with the bridging selenium atom adopting a very narrow angle of 71.6° with the two boron centers.

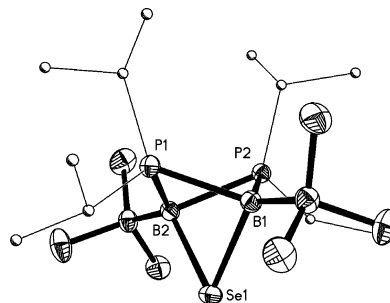


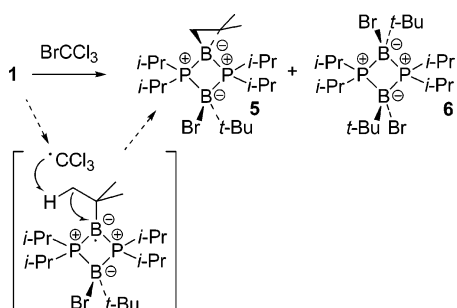
Figure 1. Thermal ellipsoid diagram (50% probability) of **3**. For clarity, the isopropyl groups have been simplified. Selected bond lengths (Å) and angles (deg): P1–B1 2.034(2), P1–B2 1.977(2), P2–B1 1.972(2), P2–B2 2.024(2), B1–Se1 2.129(2), B2–Se1 2.132(2), B1–Se1–B2 71.61(9), B1–P1–B2 76.82(10), P1–B2–P2 87.93(9), B2–P2–B1 77.17(10), P2–B1–P1 87.79(9).

Interestingly, compound **3** was also obtained in high yield by reacting **1** with diphenyl diselenide.¹¹ This prompted us to investigate the reactivity of **1** toward typical reagents for radical-type reactions. A spontaneous and clean reaction was observed with trimethyltin hydride at room temperature, the *trans* 1,3-adduct **4** being isolated as colorless crystals in 73% yield (Scheme 1). Two signals in the range typical for tetracoordinated anionic boron centers were observed in the ¹¹B NMR spectrum (δ –3.8 and –10.0 ppm), while the BH proton appeared as a broad triplet in the ¹H NMR spectrum (δ 2.66 ppm, $J_{\text{PH}} = 14.6$ Hz). The *trans* geometry of **4** was unambiguously deduced from the X-ray analysis,⁹ and is likely to result from a stepwise, rather than a concerted reaction.

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Scheme 2



The reaction with bromotrichloromethane afforded further evidence for the radical-type behavior of **1**. The reaction did not require any radical initiator and was complete in few minutes at room temperature in toluene solution. Compound **5** was obtained in 56% yield along with a small amount of the *trans* 1,3-dibromo adduct **6**.⁹ Crystallization from a saturated dichloromethane solution at -30 °C afforded single crystals of **5**. The X-ray diffraction study revealed a novel B-spiro structure (Figure 2). The BPBP four-membered ring is retained; one of the boron centers bears a bromine atom, while the other is engaged in a BCC three-membered ring.¹² The formation of **5** most probably results from a stepwise reaction: (i) **1** abstracts a bromine atom from the bromotrichloromethane, (ii) the resulting radical pair disproportionates to give **5** and chloroform.¹³ Although the exact structure of the radical intermediate (opened or bridged) could not be determined, to date, the postulated mechanism is supported by the formation of an increasing amount of the 1,3-dibromo adduct **6** when increasing amounts of bromotrichloromethane were used. These results as a whole demonstrate that although the heteroatom-containing 1,3-diradical **1** benefits from an increased thermal stability compared to its transient congeners, it does feature some radical-type behavior. Further investigations are currently in progress to define the possible uses of such stable 1,3-diradicals as initiators for radical reactions¹⁴ (such as atom-transfer reactions or olefin polymerizations) and/or as radical scavengers.

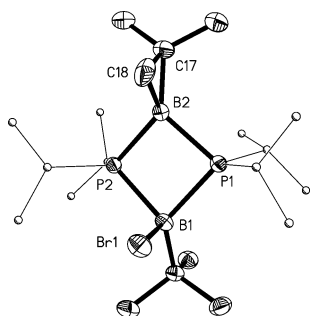


Figure 2. Thermal ellipsoid diagram (50% probability) of **5**. For clarity, the isopropyl groups have been simplified. Selected bond lengths (Å) and angles (deg): P1–B1 2.052(3), P1–B2 1.966(3), P2–B1 2.036(3), P2–B2 1.970(3), B1–Br1 2.084(3), B2–C17 1.602(4), B2–C18 1.600(4), C17–C18 1.612(5), C17–B2–C18 60.5(2), B1–P1–B2 89.07(12), P1–B2–P2 91.29(13), B2–P2–B1 89.43(12), P2–B1–P1 87.01(12).

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Supporting Information Available: Experimental details, spectroscopic data (PDF) and X-ray crystallographic data for **2–6** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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