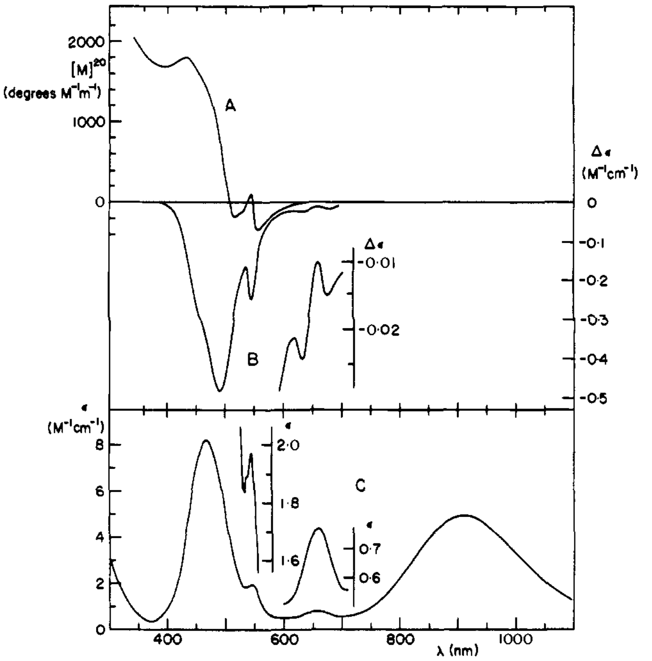

Figure 3. Rotatory dispersion (A), circular dichroism (B), and visible absorption spectra (C) of aqueous solutions of (*S*)-$[Co(sep)]^{2+}$ obtained by reducing (*S*)-$[Co(sep)]Cl_3{\cdot}H_2O$ in water with Zn (dust).

O_2 quantitatively to the Co(III) ion and H_2O_2 with retention of absolute configuration (>99%). The oxidation of $[Co^{II}(sep)]^{2+}$ by O_2 was followed spectrophotometrically over the range $0.1 \geqslant [H^+] \geqslant 10^{-3}$ at $\mu = 0.2$ M (NaCl, HCl) and 25 °C. For pseudo-first-order conditions with excess O_2 and Co(II) a rate law of the form, $-d[O_2]/dt = -\frac{1}{2}d[(Co(sep)^{2+}]/dt = k_{ox}[Co(sep)^{2+}][O_2]$ was obtained, where $k_{ox} = 44 \pm 5\ M^{-1}\ s^{-1}$. The addition of O_2 to the Co(II) ion appears improbable because of the ligand insulation but attempts to detect the superoxide ion by rapid flow and EPR techniques were unsuccessful.[4]

The visible spectra for both oxidation states are given in Figures 2 and 3 along with their circular dichroism and rotatory dispersion curves. The symmetry requires all the chiral N atoms to have the same configuration (*S*) for the structure derived from $\Lambda[Co(en)_3]^{3+}$. The CD curves for the Co(III) ions around 500 nm for these two entities are essentially catoptric despite the origin of the sexadentate. This result is predicted by calculations based on the optical activity models of Richardson for both the C_3 and D_3 conformers.[5]

Interesting aspects of these results are the spectroscopic properties, the retention of chirality in the Co(II) ions, the quantitative oxidation of $[Co^{II}sep]^{2+}$ to $[Co^{III}sep]^{3+}$ without the formation of a peroxy-bridged dimer and the (essentially) reversible redox phenomena. The retention of chirality implies no loss of Co^{2+} ion from the ligand and this was confirmed using $^{60}Co_{aq}{}^{2+}$ as a tracer. Less than 1% exchange was observed in 24 h.

The electron transfer rate was measured by mixing (*R*)-$(+)_{490}$-$Co(sep)^{3+}$ and (*S*)-$(+)_{490}$-$Co(sep)^{2+}$. For equal concentrations of the two ions electron transfer leads to racemization and the electron transfer rate was followed by the change in optical rotation (α) at 500 nm. The data yield a rate law of the form $-\ d\ \ln\ (\alpha - \alpha_\infty)/dt = k_{et}[Co]_{total} = k_{obsd}$ where $k_{et} = 5.1 \pm 0.3\ M^{-1}\ s^{-1}$ ($\mu = 0.2$ M (NaCl, HCl); H^+, 10^{-7} to 10^{-2} M; 25 °C). The rate constant is $\sim 10^5$-fold greater than that for $Co(en)_3{}^{2+/3+}$ (at 25 °C, $k = 7.7 \times 10^{-5}\ M^{-1}\ s^{-1}$ measured by the same method[6] or $k = 5.2 \times 10^{-5}\ M^{-1}\ s^{-1}$ $\mu = 1$ M by the isotopic exchange method[7]) which is a dramatic difference considering the Co^{II}sep salt has the normal paramagnetism for high spin Co(II) ($\mu_{eff} = 4.72\ \mu_B$) and has essentially the same ligand field spectrum as the tris(ethylenediamine) molecule.[8] The Co(III) ions show analogous properties. At present we have no clear understanding of this pronounced electron transfer difference.

The apparent consequences of this work are that numerous metal ions, the complexes of which are normally labile, will become kinetically inert with stable chiral forms. All the chemistry will be mononuclear and therefore interesting in those areas where polymers are frequently observed, e.g., Mo and W. Stabilization of mononuclear Rh(II) and Pt(III) is a possibility and there will be a range of very stable oxidants and reductants for use in inorganic and organic chemistry, both for synthesis and as mechanistic probes, unfettered by the hydrolysis problems which frequently plague the use of aqua ions. Also there is a prospect for the use of the ligands as therapeutic agents. These aspects are currently being investigated with complexes derived from capping tris(ethylenediamine) and 1,1,1-tris(4-amino-2-azabutyl)ethane (sen) complexes with tris(methyleneamino) and substituted tris(methylenemethane) moieties.

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Supplementary Material Available: Five tables, listing final crystal parameters, distances and angles, thermal displacements, and intensity data (19 pages). Ordering information is given on any current masthead page.

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(9) On leave from the Chemistry Department, The Royal Veterinary and Agricultural University, DK-1871 Copenhagen V, Denmark.

I. I. Creaser, J. MacB. Harrowfield, A. J. Herlt
A. M. Sargeson,* J. Springborg[9]
Research School of Chemistry
Australian National University
Canberra 2600, A.C.T., Australia

R. J. Geue, M. R. Snow
Department of Physical and Inorganic Chemistry
University of Adelaide
Adelaide 5000, South Australia, Australia
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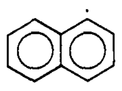
Naphthylboryne: a Monovalent Organoboron Carbene Analogue from Photolysis of Tri-1-naphthylboron

Sir:

With complete exclusion of oxygen and water, in carbon tetrachloride, cyclohexane, and cyclohexene solutions, tri-1-naphthylboron (**1**), when irradiated at wavelengths equal to or longer than its charge transfer maximum[1] at 350 nm, slowly undergoes two primary competing photochemical reactions (eq 1 and 2).

$$\underset{1}{(1\text{-}C_{10}H_7)_3B} \xrightarrow[>350\text{nm}]{h\nu} \underset{2}{1\text{-}C_{10}H_7B:} + \underset{3}{(1\text{-}C_{10}H_7)_2} \qquad (1)$$

$$\underset{4}{(1\text{-}C_{10}H_7)_3B \xrightarrow{h\nu} (1\text{-}C_{10}H_7)_2B\cdot} + \qquad (2)$$



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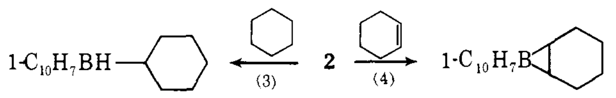
Photochemical pathway 2, simple boron-carbon bond cleavage, is known from the photochemistry of other arylboranes,[2] and in the photolysis of **1** in carbon tetrachloride, for example, produces the expected complexity of products in low yields: hexachlorethane (8%), chloronaphthalene (2%), trichloromethylnaphthalene (1%), naphthalene (8%), and large amounts of unidentified oils and tars, which do not, however, contain boron. Since the reaction products were worked up by standard procedures[3] of oxidation and hydrolysis in basic aqueous dilute hydrogen peroxide, the only boron-containing products isolated were naphthylboronic acid, $(1\text{-}C_{10}H_7)B(OH)_2$ (80%), and dinaphthylborinic acid, $(1\text{-}C_{10}H_7)_2BOH$ (10%).

The intervention of reaction 1 as a major photochemical pathway, however, is established by the isolation in good yields of cyclohexanol (80%) and *cis*-1,2-cyclohexandiol (40%) from the hydrolysis and oxidation of photolysis products of reactions carried out in cyclohexane and cyclohexene. The reactions of **2** with cyclohexane (3) and with cyclohexene (4) are therefore directly analogous to those of carbenes in terms of cis addition to double bonds and carbon-hydrogen bond insertion. These results represent the first evidence of a stable three-membered ring containing boron, **7**.

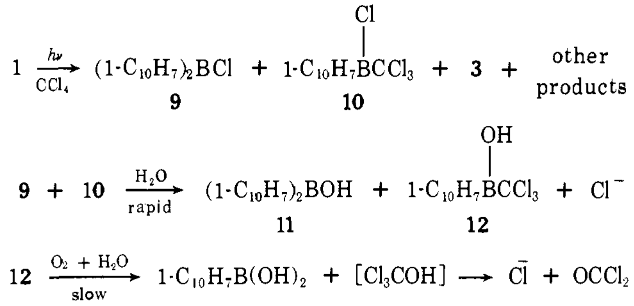


6 7

In all solvents, 5-10% yields of 1,1′-binaphthyl **3** are obtained prior to oxidation or hydrolysis as determined by gas phase chromatography. In the absence of reaction 2, we would expect the yields of 1,1′-binaphthyl and cyclohexanol or *cis*-1,2-cyclohexanediol to be equal. As shown by the thermal decomposition of naphthoyl peroxide in the presence of binaphthyl, most of the binaphthyl is, however, consumed in subsequent reactions with **5** and with solvent radicals, and thus far less than half of the naphthyl groups are accounted for. No detectable amounts of binaphthyl are obtained when **5** is generated in the presence of tri-1-naphthylboron by the thermal composition of naphthoyl peroxide, demonstrating that **3** is not formed in secondary reactions between **5** and **1**.

Carbon-chlorine insertion of **2** is indicated when photolysis reactions are carried out in carbon tetrachloride. The photolyzed solution fumes strongly when exposed to moist air, and, when treated with oxygen-free water, there is an immediate hydrolysis reaction producing 90 mole % of chloride ion, determined gravimetrically as silver chloride. On admission of air, however, after the initial hydrolysis, there follows a very slow reaction which proceeds over several days to produce an additional 50 mole % of chloride ions plus phosgene which was trapped with aniline to form *N,N*′-diphenylurea. We believe these results are most consistent with the reaction scheme (Scheme I) below since reactions 1 and 2 should, taken together, form 100 mole % of B-Cl bonds, and borinic acids such as **12** oxidize only slowly in aqueous solutions.[4]

Scheme I

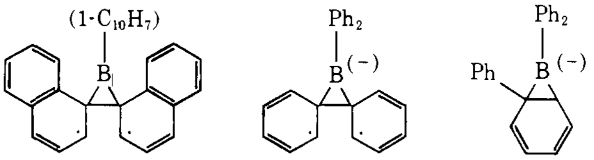


$$1 \xrightarrow[CCl_4]{h\nu} \underset{9}{(1\text{-}C_{10}H_7)_2BCl} + \underset{10}{1\text{-}C_{10}H_7\overset{Cl}{B}CCl_3} + 3 + \text{other products}$$

$$9 + 10 \xrightarrow[\text{rapid}]{H_2O} \underset{11}{(1\text{-}C_{10}H_7)_2BOH} + \underset{12}{1\text{-}C_{10}H_7\overset{OH}{B}CCl_3} + Cl^-$$

$$12 \xrightarrow[\text{slow}]{O_2 + H_2O} 1\text{-}C_{10}H_7B(OH)_2 + [Cl_3COH] \longrightarrow \bar{\text{Cl}} + OCCl_2$$

Tetravalent arylborane anions, such as tetraphenylborate, undergo[5] what is apparently an analogous photochemical reaction to form in the case of tetraphenylborate large yields of biphenyl and other products consistent with the formation of the diphenylborene anion, $Ph_2B:^{(-)}$. We suggest that these reactions proceed through intermediates **13** and **14** which are analogous to those proposed for the di-π-methane rearrangement.[6] A di-π-methane mechanism would also lead directly to intermediates, such as **15**, already implicated[5c,7] in the photolysis of tetraarylborate anions. Intermediate **13** prefers elimination of boryne rather than following the normal course of rearrangement to an analogous product of **15**.



13 14 15

As a matter of nomenclature, we suggest the generic name *boryne* for neutral monovalent boron species. 1-Naphthylboryne would then be the name of **2**. The name *borene* might then be reserved for the species $R_2B:^{(-)}$ proposed by Eisch and coworkers as the intermediate resulting from tetraarylborate anion photolysis.[7]

After submission of this communication, a paper appeared[8] postulating methylboryne (methyl borylene) as an intermediate in the formation of an unusual *B*-methylboranorcarane dimer from the reaction of methyldibromoborane with C_8/K alloys in the presence of cyclohexene. If the proposed product structure is correct, the reaction may equally well have proceeded by a free radical mechanism involving $\text{Me}\dot{\text{B}}\text{Br}$ addition to cyclohexene followed by ring closure on boron with $\dot{\text{B}}\text{r}$ elimination to form the boranorcarane which dimerizes.

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Brian G. Ramsey,* Dennis M. Anjo
Department of Chemistry, San Francisco State University
San Francisco, California 94132

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