## Isolation of a Triborylmethide Salt

Sir:

Anionic species derived from methanetetraboronic and methanetriboronic esters,[1] gem-diborylalkanes,[2] and deprotonation of trialkylboranes[3] have been found useful in a variety of synthetic processes, including condensation with aldehydes and ketones, alkylation by alkyl halides, and metalation by group IV triarylmetal halides. In all such reactions a boron-substituted carbanion has been postulated as an intermediate, but direct evidence for such a species has not been obtained.[4] We now have found that the lithium salt of the tris(trimethylenedioxyboryl)methide ion (2) can be precipitated free from major impurities by the addition of butyllithium to tetrakis(trimethylenedioxyboryl)-methane[1g] (1) in tetrahydrofuran at −70°.
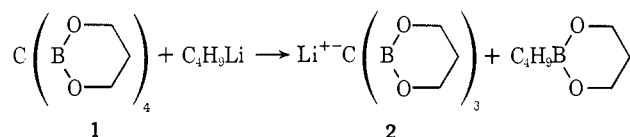
A solution of 2.0 g (5.6 mmol) of the methanetetraboronic ester 1 in 80 ml of anhydrous THF under argon in a Schlenk apparatus was cooled with Dry ice–acetone and stirred during the dropwise addition of 2.6 mmol of 1.6 M butyllithium in hexane from a syringe in 15 min. (A 1:1 molar ratio of reactants may be used for synthetic purposes but may lead to some gummy by-product formation.) The mixture was stirred 15 min at −78°, the bath was removed, and stirring was continued for 15 min (estimated maximum temperature −50°), and the precipitate was filtered while the apparatus was kept cold with a Dry Ice–acetone cooled towel (necessary to prevent gum formation). The collected triborylmethide salt 2 was washed with 10 ml of cold (0°) THF and dried under vacuum (0.1 mm) 2 hr; yields 75–100%. Since 2 chars in air and reacts very rapidly with water, all transfers were carried out under argon in a glove bag.

For characterization, a small portion of 2 was dissolved in D_2O and the proton nmr spectrum was found to have only the triplet (δ 3.67) and quintet (δ 1.77) characteristic of the –(CH₂)₃– group of 1,3-propanediol. Reaction of a 0.3-g portion of 2 suspended in 10 ml of THF with an equimolar amount of triphenyltin chloride yielded triphenylstannyltris(trimethylenedioxyboryl)methane[1g] (Ph₃SnC(BO₂C₃H₆)₃ (3)), 52–70% crude, up to 57% recrystallized, compared with an authentic sample by infrared and nmr spectra. The 32.1-MHz [11]B nmr spectrum of 2 in hexamethylphosphoramide (the only solvent found in which 2 is moderately soluble and does not react) showed the expected

single peak downfield 60–90 Hz from boron trifluoride etherate (external reference). Microanalysis of 2 (Schwarzkopf Laboratories) yielded reasonable results, considering the reactivity and the impossibility of further purification. *Anal.* Calcd for $C_{10}H_{18}B_3LiO_6$: C, 43.90; H, 6.63; B, 11.85; Li, 2.54. Found: C, 43.15; H, 7.53; B, 10.95; Li, 1.90.

The foregoing data support structure 2 and specifically exclude structures 4–7. From proton nmr spectra,
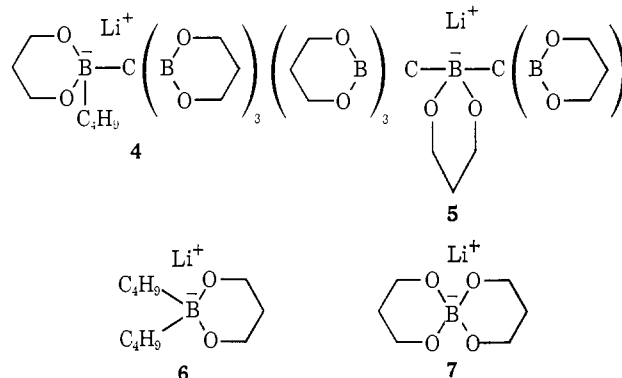
the maximum possible proportion of 4 is 2.5–7.5 mol %, and it is not clear whether the stray butyl peaks being integrated belong to 4, 6, or $C_4H_9BO_2C_3H_6$. Yields of triphenyltin derivative 3, elemental analysis, and the [11]B nmr spectrum are inconsistent with 5. Neither 6 nor 7 would give the triphenyltin derivative. The only reason for mentioning 7 is that its five-membered ring analog was obtained in earlier experiments with the ethylene glycol tetraboronic ester, C(BO₂-C₂H₄)₄. The solubility of the lithium salt 2 in dipolar aprotic solvents and insolubility in THF confirm its highly polar character and rule out its being a covalent organolithium reagent.

The salt 2 is a very strong base and abstracts protons from dimethyl sulfoxide, in which it is readily soluble. It was found possible to dissolve 2 in perdeuteriodimethyl sulfoxide and react it with triphenyltin chloride to obtain a 50% yield of the triphenyltin derivative 3, but a satisfactory [11]B nmr spectrum of 2 could not be obtained in this solvent. When 2 was dissolved in nondeuterated anhydrous dimethyl sulfoxide, the proton nmr spectrum showed a peak at δ −0.15, characteristic of the methanetriboronic ester (HC(BO₂C₃-H₆)₃), within a few minutes, and the yield of the triphenyltin derivative 3 was only about 10%.

Use of the isolated lithium salt 2 may permit syntheses which fail if crude preparations are used. Thus, reaction of 1.06 g of 2 under 10 ml of methylene chloride with an equivalent amount of bromine in methylene chloride at −78° followed by warming to room temperature, evaporating the solvent, precipitating the product with ether, and recrystallizing from chloroform–ether yielded 0.52 g (42%) of bromotris(trimethylenedioxyboryl)methane (BrC(BO₂C₃H₆)₃), mp 124–138°, characterized by nmr and mass spectra and elemental analysis.[5] Attempts to carry out this synthesis without filtering the salt 2 from the THF in which it was prepared yielded 0–10% of the brominated product.

(1) (a) R. B. Castle and D. S. Matteson, *J. Amer. Chem. Soc.*, 90, 2194 (1968); (b) R. B. Castle and D. S. Matteson, *J. Organometal. Chem.*, 20, 19 (1969); (c) D. S. Matteson and G. L. Larson, *J. Amer. Chem. Soc.*, 91, 6541 (1969); (d) D. S. Matteson and P. B. Tripathy, *J. Organometal. Chem.*, 21, P6 (1970); (e) D. S. Matteson and J. R. Thomas, *ibid.*, 24, 263 (1970); (f) D. S. Matteson and G. L. Larson, *ibid.*, in press; (g) D. S. Matteson and R. J. Wilcsek, *ibid.*, in press.

(2) (a) G. Cainelli, G. Dal Bello, and G. Zubiani, *Tetrahedron Lett.*, 4329 (1965); 4315 (1966); (b) G. Zweifel and H. Arzoumanian, *ibid.*, 2535 (1966); *J. Amer. Chem. Soc.*, 89, 291 (1967).

(3) M. W. Rathke and R. Kow, *J. Amer. Chem. Soc.*, 94, 6854 (1972); R. Kow and M. W. Rathke, *ibid.*, 95, 2715 (1973).

(4) The B-phenylborabenzene anion (A. J. Ashe, III, and P. Shu, *J. Amer. Chem. Soc.*, 93, 1804 (1971)) is stabilized by aromaticity and therefore not directly relevant to the present question.

(5) In previous work with R. A. Davis, we have prepared the analogous pinacol boronic ester, BrC(BO₂C₂Me₄)₃; manuscript to be published.

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Structural Evidence for Franck–Condon Barrier to Electron Transfer between Low-Spin Cobalt(II) and Cobalt(III)[1]

Sir:

Although electron transfer reactions between coordination complexes have been extensively investigated[2] and although sophisticated theoretical treatments of these reactions have been developed,[3,4] some rather glaring fundamental problems remain. Among these must be counted the approximately 10^{15}-fold difference in the rate of the self-exchange reactions for the $Co(NH_3)_6{}^{3+}-Co(NH_3)_6{}^{2+}$ [5,6] and the $Ru(NH_3)_6{}^{3+}-Ru(NH_3)_6{}^{2+}$ [7,8] couples. The extraordinarily slow rate for the cobalt(III)–cobalt(II) couple has been variously attributed to a spin multiplicity restriction[9] (the cobalt(II) complex is high spin in this case) and to the large ligand reorganizational barriers which must accompany the transfer of electron density between metal centered antibonding orbitals.[9,10] The early discussions of the magnitude of the reorganizational barrier were based on a 0.3 Å difference in the cobalt–nitrogen distance reported for $Co(NH_3)_6{}^{3+}$ and $Co(NH_3)_6{}^{2+}$.[11] More recently Ibers and coworkers[12] have determined structural parameters in $Co(NH_3)_6Cl_2$ and $Co(NH_3)_6I_3$ and have inferred a reorganizational barrier of about 7 kcal/mol, too small to account for the slow self-exchange rate, but consistent with a kinetically significant spin multiplicity restriction.

On the other hand, very recent work has indicated that intramolecular changes in spin multiplicity (*i.e.*, intersystem crossing rate constants) in transition metal complexes are probably too fast to be rate determining in most intermolecular electron transfer processes.[13]

(1) Partial support of this research by the Public Health Service (Grant AM 14341) and the National Science Foundation (Grant GP-15070) is gratefully acknowledged.

(2) For recent reviews see (a) R. G. Linck, "MTP International Review of Science, Inorganic Chemistry," Vol. 9, Ser. 1, M. L. Tobe, Ed., University Park Press, Baltimore, Md., 1971, p 303. (b) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967); (c) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970.

(3) For reviews see (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964); (b) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966.

(4) P. P. Schmidt, *Aust. J. Chem.*, **22**, 673 (1969); *J. Phys. Chem.*, **77**, 488 (1973); *J. Chem. Phys.*, **56**, 2775 (1972); **57**, 3749 (1972).

(5) k_{exch} estimated[6] as 10^{-2} M^{-1} sec^{-1} at 25° using the data of N. S. Biradar and D. R. Stranks, *Trans. Faraday. Soc.*, **58**, 2421 (1963).

(6) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

(7) k_{exch} estimated as about 10^3 M^{-1} sec^{-1} at 25°,[8]

(8) (a) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968); (b) G. Navon and D. Meyerstein, *J. Phys. Chem.*, **74**, 4067 (1970).

(9) L. E. Orgel, Reports of the 10th Solvay Conference on Chemistry, Brussels, 1956, p 329.

(10) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 21 (1960); *J. Phys. Chem.*, **67**, 853 (1963).

(11) D. R. Stranks, *Discuss. Faraday Soc.*, **29**, 73 (1960).

(12) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).

Furthermore, the self-exchange rate for the $Co([14]-dieneN_4)(OH_2)_2{}^{3+}-Co([14]dieneN_4)(OH_2)_2{}^{2+}$ [14,15] couple has been shown to be comparable in magnitude to that for the $Co(NH_3)_6{}^{3+}-Co(NH_3)_6{}^{2+}$ couple, despite the fact that $Co([14]dieneN_4)(OH_2)_2{}^{2+}$ is low spin.[15,16]
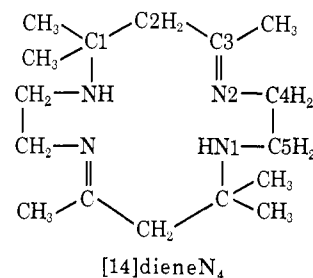
[14]dieneN₄

We are now able to report structural results for [Co([14]dieneN₄)(OH₂)₂](BF₄)₂ and for [Co([14]dieneN₄)(NH₃)₂](ClO₄)₃ and an estimated reorganizational barrier based on these results. Although one would prefer the identical axial ligands of both members of the redox couple, we could only obtain crystals suitable for X-ray analysis for the compounds indicated. Both compounds possess crystallographic inversion centers $(C_i\text{-}\bar{1})$ such that the cobalt ions and four nitrogen atoms are necessarily coplanar. Comparison of the macrocyclic ligands revealed no significant differences between them and the expected distance and angle patterns.[17] Bond distances and angles for the ligands and the coordination spheres about the metal centers are given in Table I.

Table I. Selected Bond Distances (Å) and Angles (deg)

	Co(II)	Co(III)
N1′–C1	1.506 (8)	1.517 (10)
N1–C5	1.469 (8)	1.474 (10)
N2=C3	1.285 (8)	1.277 (10)
N2–C4	1.485 (8)	1.478 (10)
C1–C2	1.545 (9)	1.516 (11)
C2–C3	1.495 (10)	1.500 (12)
Co–N1	1.968 (6)	1.986 (6)
Co–N2	1.936 (5)	1.916 (7)
Co–NH₃		1.954 (6)
Co–OH₂	2.482 (5)	
C5′–N1′–C1	114.0 (5)	115.5 (6)
N1′–C1–C2	105.6 (5)	106.3 (7)
C1–C2–C3	118.1 (5)	118.6 (8)
C2–C3=N2	120.7 (6)	121.4 (8)
C3=N2–C4	119.2 (6)	119.4 (7)
N2–C4–C5	105.6 (5)	107.5 (6)
C4–C5–N1	106.4 (5)	105.3 (7)
N1′–Co–N2	94.6 (2)	94.2 (3)
N2–Co–N1	85.4 (2)	85.8 (3)
N1–Co–NH₃		87.0 (3)
N1–Co–OH₂	83.1 (2)	
N2–Co–NH₃		91.6 (3)
N₂–Co–OH₂	92.5 (2)	

(13) (a) J. T. Yardley and J. K. Beattie, *J. Amer. Chem. Soc.*, **94**, 8925 (1972); (b) J. K. Beattie, N. Sutin, D. H. Turner, and G. W. Flynn, *ibid.*, **95**, 2052 (1973).

(14) Abbreviations: [14]dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

(15) (a) D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire, *J. Chem. Soc., Chem. Commun.*, 495 (1972); (b) manuscript in preparation.

(16) In aqueous solution at 25°, μ_{eff} = 1.85 BM.[15b]

(17) See also (a) R. R. Ryand, B. T. Kolbourne, and J. Dunitz, *J. Chem. Soc. A*, 2407 (1969); (b) M. F. Bailey and I. E. Maxwell, *Chem. Commun.*, 883 (1966); (c) D. R. Ireland and W. T. Robinson, *J. Chem. Soc. A*, 663 (1970).