changes in translational entropy and we have termed it the macrocyclic effect. The stability of the complex is greatly increased despite the more restricted geometry which the macrocycle forces on the copper–nitrogen bonds. The macrocyclic effect, which adds stability beyond that of chelation, is about 10 times larger than the chelate effect observed for copper(II) and amine complexes. The configuration and solvation of the free macrocyclic ligand compared to the noncyclic ligand undoubtedly are very important to this effect.

The Cu(tet *a*)$^{2+}{}_{\text{blue}}$ complex is believed to have the macrocycle in a folded form. The blue complex reacts more rapidly with acid and is thermodynamically less stable than the square-planar Cu(tet *a*)$^{2+}{}_{\text{red}}$ complex.

The stability constants (concentration constants) for red and blue forms of Cu(tet *a*)$^{2+}$ were evaluated from the conditional stability constants measured in hydrochloric acid and from the protonation constants. Correction factors for the copper(II) chloride complexes were used.[4]

The most basic protonation constant was determined by a solvent extraction method and gave $\log K_1 = 12.6 \pm 0.1$. Values for K_2 and K_3 were determined by potentiometric titrations ($\log K_2 = 10.4 \pm 0.1$ and $\log K_3 = 0.8 \pm 0.2$). A value of K_4 was estimated using $\log K_3 - \log K_4 = 0.8$, as is the case for cyclam (1,4,8,11-tetraazacylotetradecane).[5]

The conditional stability constant ($K' = 10^{6.8}$) for the red complex in 0.1 *M* hydrochloric acid at 25° was obtained by extrapolation from a plot of $\log K'$ *vs.* the reciprocal of absolute temperature. The constant at each temperature was obtained by spectrophotometrically (for the red complex, ϵ 140 M^{-1} cm^{-1} at 520 mμ) determining the amount of complex remaining in solution after 47 days at 50 and 75°, and after 14 and 10 days, respectively, at 100 and 130°. The stability constant in Table I was calculated from this extrapolated value ($\log K = 28$ at 25°, $\mu = 0.1$). Other values obtained in a similar manner but with 0.2 to 0.6 *M* HCl were in agreement. Solutions with higher acid concentration (2–8 *M* HCl) were equilbrated for 133 days at 26° and the stability constant was significantly larger, $\log K = 30.8 \pm 0.4$, under these conditions.

The stability constant of the blue complex was determined spectrophotometrically (ϵ 193 M^{-1} cm^{-1} at 650 mμ) from a solution of copper(II) and tet *a* after 15 days at 25° (final pH 2.51). At this acidity the rate of formation of the red complex is negligible, and the fact that equilibrium was established between copper and the blue complex was ascertained from kinetic experiments followed potentiometrically and spectrophotometrically.

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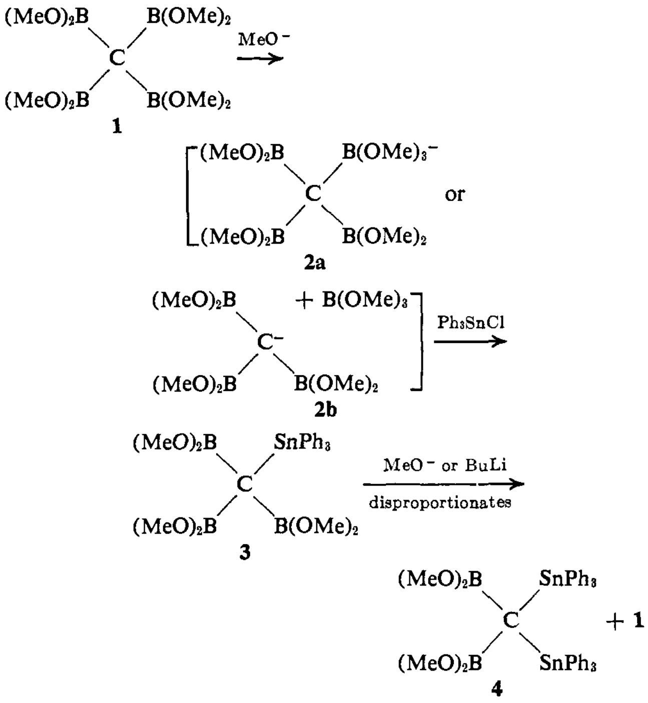
Boron–Tin and Boron–Lead Tetrametallomethanes

Sir:

Octamethyl methanetetraboronate (**1**) reacts with suitable bases to form an anionic intermediate, presumably the tris(dimethoxyboryl)methide ion (**2b**) or its methyl borate complex **2a**, which has been shown to undergo alkylation by alkyl halides[1] or condensation with aldehydes and ketones.[2] We have now extended this chemistry to prepare tetrametallomethanes having one or two tin and three or two boron atoms around the central carbon.



A solution of 3.0 g (10 mmol) of methanetetraboronic ester (**1**) in 15 ml of tetrahydrofuran was stirred under nitrogen with 0.42 g (11 mmol) of dry lithium methoxide, beginning at room temperature and heating to reflux 10 min. The resulting orange solution was added from a dropping funnel in 10 min to a stirred refluxing solution of 5.8 g (15 mmol) of triphenyltin chloride in 20 ml of tetrahydrofuran, and refluxing was continued an additional 15 min. To ensure acidity, 0.2 ml of dimethoxyboron chloride was then added, as well as 3 ml of 2,2-dimethoxypropane to reverse any accidental boronic ester hydrolysis. The solution was decanted from the lithium chloride and concentrated under vacuum. The semisolid residue was recrystallized from 30 ml of methanol and 5 ml of acetone to yield 3.0 g (52%) of triphenylstannyltris(dimethoxyboryl)methane (**3**), mp 155–156°; nmr (CCl_4) τ 2.83 (m, 15, C_6H_5) and 6.66 (s, 18, CH_3O).[3] Triphenyltin bromide gave a somewhat better yield (65%) of **3**.

Base-catalyzed interchange of electrophiles in $Ph_3SnC[B(OMe)_2]_3$ (**3**) is unusually facile and results in disproportionation. One gram (1.7 mmol) of **3** in 10 ml of tetrahydrofuran was treated with 1.2 ml (1.9 mmol) of 1.6 *M* butyllithium at −75° and allowed to warm to room temperature, then treated with 0.2 ml (2 mmol) of dimethoxyboron chloride and 1 ml of 2,2-dimethoxypropane, concentrated, and crystallized from 40 ml of hot methanol to yield 0.69 g (93%) of bis(triphenylstannyl)bis(dimethoxyboryl)methane (**4**), mp 159–160°; nmr (CCl_4) τ 2.87 (m, 30, C_6H_5) and 6.66 (s, 12, CH_3O).[3]

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[1] R. B. Castle and D. S. Matteson, *J. Amer. Chem. Soc.*, **90**, 2194 (1968); *J. Organometal. Chem.*, in press.

[2] D. S. Matteson and P. B. Tripathy, submitted for publication.

[3] Elemental analyses were correct for C, H, B, and Sn or Pb.

This disproportionation is so rapid that $(Ph_3Sn)_2C[B(OMe)_2]_2$ (**4**) is the major product if $C[B(OMe)_2]_4$ (**1**) is treated with butyllithium or lithium methoxide and mixed all at once with an equimolar amount of triphenyltin chloride in tetrahydrofuran, then refluxed. However, the yield by this route is only 20% (based on **1**).

The extreme lability of the boron in $Ph_3SnC[B(OMe)_2]_3$ (**3**) is further demonstrated by the reaction with ethylene glycol, which replaces one boryl group by a proton while forming the usual cyclic ester with the other two. Treatment of 1.0 g of **3** with 0.4 ml of ethylene glycol in 5 ml of acetone at 25° for 3 hr yielded 0.80 g (90%) of $Ph_3SnCH(BO_2C_2H_4)_2$, mp 142–143°; nmr ($CDCl_3$) τ 2.50 (m, 15, C_6H_5), 6.18 (s, 8, OCH_2), and 8.80 (s, 1, $SnCHB_2$, satellites ^{117}Sn $J = 78$ and ^{119}Sn $J = 80$ Hz).[3] Both $C[B(OMe)_2]_4$ and $HC[B(OMe)_2]_3$ have been converted to their ethylene glycol esters without such protodeboronation,[4] though they are very labile to water.[1]

Protodeboronation of 0.78 g of $(Ph_3Sn)_2C[B(OMe)_2]_2$ (**4**) by refluxing 2 hr in 10 ml of methanol with 50 mg of sodium methoxide gave 0.4 g (57%) of $(Ph_3Sn)_2CHB(OMe)_2$, mp 104–105°; nmr (CCl_4) τ 2.81 (m, 30, C_6H_5), 6.66 (s, 6, CH_3O), and 9.97 (s, 1, Sn_2CHB, too dilute to observe satellites).[3]

Preliminary work with trimethyltin chloride has yielded $Me_3SnC[B(OMe)_2]_3$, bp 105–115° (0.1 mm), structure supported by nmr but analytical purity not yet attained.

Disproportionation in the lead series appears to be even more facile than with the tin compounds, and we have been unable to prepare $Ph_3PbC[B(OMe)_2]_3$. Use of triphenyllead chloride in place of triphenyltin chloride in the procedure described for preparation of $Ph_3SnC[B(OMe)_2]_3$ yielded 25% (based on **1**) of $(Ph_3Pb)_2C[B(OMe)_2]_2$, mp 174–175°; nmr (CCl_4) τ 2.85 (m, 30, C_6H_5) and 6.66 (s, 12, CH_3O).[3]

We expect these boron–tin and boron–lead tetrametallomethanes to prove useful in the synthesis of other new types of organometallic compounds. The qualitative evidence obtained so far also suggests possible anchimeric accelerations of electrophilic displacements in these compounds, an interesting mechanistic question which has previously remained unexplored because of lack of suitable substrates.

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(4) Unpublished work with R. J. Wilcsek and J. R. Thomas.

(5) (a) Alfred P. Sloan Foundation Fellow, 1966–1968; (b) this work was supported in part by Public Health Service Grant CA-05513 from the National Cancer Institute; (c) National Institutes of Health Postdoctoral Fellow, 1968–1969.

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Reaction of Copper(I) Hydride with Organocopper(I) Compounds[1]

Sir:

A number of important transition metal catalyzed organic syntheses are carried out in solutions containing mixtures of intermediate transition metal hydrides and σ-alkyls.[2] The reactivity of transition metal hydrides toward metal alkyls has not been defined. However, the facility with which nontransition metal hydrides react with many σ-organometallic compounds[3,4] suggests that analogous reactions of transition metal hydrides might be important in the catalytic transition metal systems.

As part of a study of the mechanism(s) of thermal decomposition of copper(I) alkyls, we have prepared copper(I) hydride and examined its reactivity toward organocopper(I) compounds. The reactivity of copper hydride toward copper alkyls is of particular interest as a model for the reactivity of other transition metal hydrides and alkyls: since copper hydride does not catalyze olefin isomerization or deuterium exchange under the conditions used in this study, the structures of hydrocarbon products formed in the presence of copper hydride can be determined without ambiguity. Here we wish to report that hydridic and σ-organometallic derivatives of copper(I) react readily with one another, and that the mechanism of this reaction does *not* involve intermediate organic free radicals.

Copper(I) hydride was prepared by treating 1 equiv of copper(I) bromide dissolved in 100 equiv of pyridine with 1.1 equiv of diisobutylaluminum hydride (20% in heptane) at −50°. Vigorous mixing produced a homogenous, dark brown solution, from which copper(I) hydride could be precipitated by dilution with $\sim$300 equiv of ether. Centrifugation, separation of the supernatant liquid, and repeated washing of the precipitate with ether, all at −78°, permitted isolation of copper(I) hydride as a brown solid in greater than 90% yield.[5] The ratio of hydride to copper in this material is 0.96 ± 0.04; it contains less than 0.5% aluminum or bromine but retains $\sim$25% pyridine, based on copper.

Pure, anhydrous copper(I) hydride decomposes to hydrogen and metallic copper above −20°; it is indefinitely stable at −78°. Suspensions of copper(I) hydride in ether are relatively air insensitive; the dry solid is pyrophoric. Tri-*n*-butylphosphine and copper(I) hydride form a 1:1 complex, the high solubility of which has prevented its isolation. Attempts to detect a metal–hydrogen stretching vibration in the solution ir spectrum of copper hydride, or a hydride resonance in its nmr spectrum, have so far been unsuccessful.[8]

Hydrido(tri-*n*-butylphosphine)copper(I) reduces primary, secondary, and tertiary alkyl-, vinyl-, and aryl-copper(I) compounds to the corresponding hydrocar-

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(1) Supported by the National Science Foundation, Grant 7266, and by the International Copper Research Association, Inc.

(2) For reviews of representative reactions, see R. Heck, *Advan. Organometal. Chem.*, **4**, 243 (1966); L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience Publishers, New York, N. Y., 1966, Chapter IV; R. Cramer, *Accounts Chem. Res.*, **1**, 186 (1968).

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(5) This procedure is based on that developed by Wiberg and Henle,[6] but yields CuH of higher purity than that obtained using $LiAlH_4$ as a reducing agent.[7] The results of our examination of the material produced by the Wiberg–Henle procedure are in general agreement with those reported by Shriver;[7] in particular, we concur that this material *is* CuH, howbeit extensively contaminated.

(6) E. Wiberg and W. Henle, *Z. Naturforsch.*, **7b**, 250 (1952).

(7) J. A. Dilts and D. F. Shriver, *J. Amer. Chem. Soc.*, **90**, 5769 (1968); **91**, 4088 (1969).

(8) See also ref 7.