complex, $[Cu_2(bpy)_4(OH)](ClO_4)_3$.[10] A disordered perchlorate group also bridges the resulting μ-hydroxo-dicopper(II) unit through axial bonds similar to those found previously in the structure of α-$[Cu(DMAEP)(OH)(ClO_4)]_2$, where DMAEP = 2-[2-(dimethylamino)ethyl]pyridine.[11] The hydrogen atom of the bridging hydroxide group could not be located on a final difference Fourier map. Geometric considerations suggest that it is disordered over two hydrogen bonded positions to the two ether oxygen atoms of the macrocycle (Table I). Charge balance considerations and the infrared spectral results[6] leave no doubt that this bridging ligand has been properly identified. Additional geometric information is summarized in Table I.

The magnetic properties of a solid sample of $[Cu_2(OH)(ClO_4)\subset A](ClO_4)_2 \cdot CHCl_3$ were investigated by the Faraday method over the temperature range $4.2\ K \leq T \leq 300\ K$. The effective magnetic moment of 0.29 μ_B at 280 K shows that the two copper atoms are strongly antiferromagnetically coupled. The 150-300-K susceptibility data were fit by least-squares methods to the Bleaney-Bowers equation resulting in $J \sim -500\ cm^{-1}$.[8,12] The powder electron spin resonance spectra are also indicative of a strongly coupled system. The room temperature spectrum exhibits appreciable zero-field splitting ($D \sim 0.1\ cm^{-1}$), and the only feature in the 150-K spectrum is readily assigned to a mononuclear copper(II) impurity. From the low temperature susceptibility results, we estimate the latter to be no more than 1.7% of the sample.

The antiferromagnetic coupling observed for the $[Cu_2(OH)(ClO_4)\subset A]^{2+}$ cation is larger than found for di-μ-hydroxo-dicopper(II) complexes with square-pyramidal structures and J values between +86 and $-255\ cm^{-1}$, depending upon the Cu-O-Cu bridge angles.[9] This difference may be due to the greater sp character of the bridging oxygen orbitals that arises when the Cu-O-Cu bond angle opens to a value as large as 143.7°. The present J value of $-500\ cm^{-1}$ also exceeds that found for other monohydroxo bridged dicopper(II) complexes $[Cu_2(OH)(bpy)_4](ClO_4)_3$ ($J = -161\ cm^{-1}$)[10] and $[Cu_2(OH)(tren)_2]X_3$ (X = PF_6^-, $J = -350\ cm^{-1}$; X = ClO_4^-, $J = -380\ cm^{-1}$).[13] This difference probably does not arise from an additional spin exchange pathway through the bridging perchlorate group, since it is only weakly coordinated to the copper atoms through orbitals that are nearly orthogonal to the copper $d_{x^2-y^2}$ orbitals containing the unpaired electrons.

The preservation of the 637 nm visible absorption band over the pH range 6-11 in aqueous solution suggests that the hydroxo bridged dicopper(II) center is exceptionally stable. Preliminary work with other $[Cu_2L_n\subset A]^{m+}$ cations, where L_n is one or more of a variety of bridging anions, shows them to be easily converted to the hydroxo bridged dicopper(II) unit in basic solution.[14] A μ-hydroxo bridged dicopper(II) complex of a related Schiff base macrocycle has also been mentioned in the recent literature;[15] while this paper was being reviewed, a μ-monohydroxo bridged complex having a Cu-OH-Cu angle of 132.2° and $J = -410\ cm^{-1}$ was reported.[16] The near agreement between the exchange coupling constants in $[Cu_2(OH)(ClO_4)\subset A]^{2+}$ and those estimated for laccase and oxyhemocyanin,[1] the presence of a 330 nm band in the optical spectrum of $[Cu_2(OH)(ClO_4)\subset A]^{2+}$, which is characteristic of binuclear copper centers in biology,[3] and the similarity between the Cu-Cu distance in $[Cu_2(OH)(ClO_4)\subset A]^{2+}$ and those reported for oxyhemocyanin (3.67[17] and 3.55 Å[18]) all support the viability of proposals that the biological chromophore incorporates the Cu-O(R)-Cu unit, where R = protein side chain.[19] In fact, the stability and ubiquity of the Cu_2OH^{3+} unit suggest that the "endogenous" protein bridging ligand might simply be the hydroxide ion.

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Supplementary Material Available: Tables S1 and S2 listing, respectively, positional and thermal parameters and the observed and calculated molar susceptibilities and effective magnetic moments for $[Cu_2(OH)(ClO_4)\subset A](ClO_4)_2 \cdot CHCl_3$ (3 pages). Ordering information is given on any current masthead page.

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α-Silyl- or -Stannyl-Substituted Crotyl-9-borabicyclo[3.3.1]nonane as a New Reagent for the Stereoregulated Synthesis of Acyclic Systems

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Macrolide, ansamycin, and polyether antibiotics belong to the rapidly expanding class of natural products. Their biological activities and considerable commercial importance, coupled with the intriguing structural problems, have stimulated intense efforts directed toward their total synthesis.[1] The procedures for the stereo-, regio-, and chemoselective synthesis of their key intermediates generally commence with the crossed aldol reactions,[2] the condensation of organometallic compounds with aldehydes,[3] the reactions via bicyclic compounds,[4] the epoxidation of allylic alcohols,[5] the hydroboration of olefinic compounds,[6] the reduction of carbonyl derivatives,[7] or the conjugate addition.[8] A need for

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(7) Nakata, T.; Oishi, T. *Tetrahedron Lett.* **1980**, 1641. Glass, R. S.; Deardorff, D. R.; Henegar, K. *Ibid.* **1980**, 2467. Narasaka, K.; Pai, H. C. *Chem. Lett.* **1980**, 1415.

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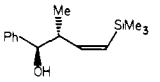
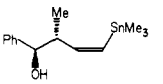
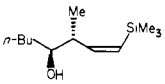
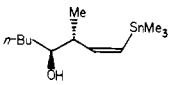
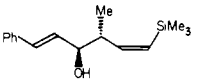
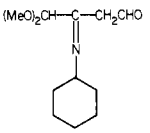
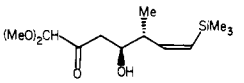
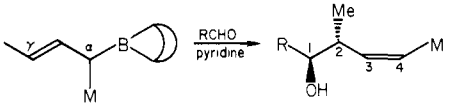
Table I. Stereoregulated Reaction of 1 with Aldehydes[a]

1	aldehyde	product	yield,[b] %	isomer ratio[c]
a	PhCHO	 3	75[d]	3 (threo, Z)-3 (erythro, Z)-3 (E)-others = 88:5:5:trace
a	PhCHO	3	90[e]	3 (threo, Z)-3 (erythro, Z)-3 (E)-others = 92:trace:1:6
a	PhCHO	3	50[f]	3 (threo, Z)-others = >98:<2
a	PhCHO	PhCH(OH)-*n*-Bu	45	
		3	56[g]	3 (threo, Z)-others = >98:<2
		PhCH(OH)-*sec*-Bu	40	
b	PhCHO	 4	90[e]	*h*
a	*n*-BuCHO	 5	70[d]	5 (threo, Z)-α isomer-others = 90:6:4
a	*n*-BuCHO	5	62[f]	5 (threo, Z)-others = >98:<2
b	*n*-BuCHO	 6	70[e]	*h*
a		 7	85[e]	*h*
a		 8	40[e]	*h*

[a] All reactions were carried out on 1-mmol scale as described in the text. The structures of products were determined mainly by ^{1}H NMR spectra and their chemical reactions, e.g., the demetalation followed by comparison with an authentic material obtained from ref 3a,b. See also ref 15. [b] Isolated yield through the column of silica gel. [c] The ratio was determined from ^{1}H NMR spectra of the reaction mixture. [d] 1 equiv of pyridine was used as a base. [e] 2 equiv of pyridine was used. [f] 1 equiv of *n*-BuLi was used. [g] 1 equiv of *sec*-BuLi was used. [h] Other isomers were not fully analyzed. [i] Prepared by the combination of the reported methods.[10] The aldehyde exists mainly as an enamine form rather than an imine form. Filtration of the reaction mixture through the column gave directly the corresponding ketone.

more efficient methods for construction of the partial structural units, e.g., RCH(OH)CH(Me)CH(OH)CH(Me)..., found in such antibiotics is clearly existent. Unfortunately, however, no methodology has yet been established to realize the stereoregulated synthesis of four consecutive carbon units by a simple operation.[9] We wish to report that the reaction of α-silyl or -stannyl substituted crotyl-9-borabicyclo[3.3.1]nonane (**1**) with aldehydes in the presence of certain bases provides a new approach to this problem (eq 1 and Table I.)



(1)

1a, M = $SiMe_3$
b, M = $SnMe_3$

2a, b

Clearly, the most remarkable feature of the reaction via **1** is the high regulation of the stereochemistries over four consecutive acyclic carbon atoms, the threo relation between C-1 and C-2 and the cis configuration at C-3 and C-4. It is essential to use an additive such as pyridine, *n*-butyllithium, or *sec*-butyllithium to realize the high stereoregulation.[11] Probably, the formation of "ate" complexes between **1** and such bases may influence the reactivity and selectivity of the crotyl-9-borabicyclo[3.3.1]nonane derivatives.[12] Use of *n*-butyl- or *sec*-butyllithium sometimes caused the migration of the butyl groups. The inspection through CPK model clearly indicates that Me_3Si or Me_3Sn group occupies the axial position of the six-membered cyclic transition state owing to the steric repulsion by the protons of 9-borabicyclo[3.3.1]nonane (9-BBN) ring (Figure 1). This leads to the selective formation of **2** among 8 possible combinations.[13]

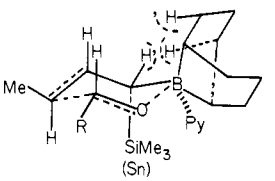
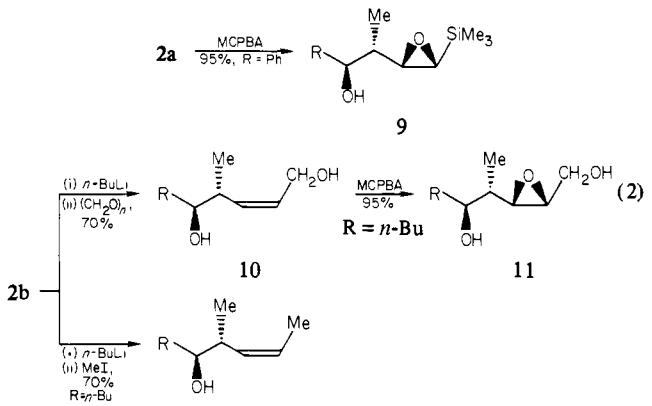


Figure 1.

(8) Isobe, M.; Kitamura, M.; Goto, T. *Tetrahedron Lett.* **1980**, 4727.
(9) The stereo- and regioselective synthesis of three consecutive carbon units is achieved via several steps; Johnson, M. R.; Nakata, T.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4343.
(10) Meyers, A. I.; Shaw, C. C. *Tetrahedron Lett.* **1974**, 717. *Org. Synth.* **1970**, *50*, 66.
(11) Without an additive, a complex mixture of products coupled both at the α and at the γ positions of **1** along with erythro and trans isomers was obtained. See also ref 3c.
(12) For the control of the reactivity and selectivity of such organometallic derivatives via the formation of "ate" complexes, see ref 3b. Also see: Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.*, in press.

The following procedure for the synthesis of **3** is representative. In a 50-mL flask, equipped with a magnetic stirrer and maintained under a static pressure of N_2, was placed dry ether (2 mL) and **1a** (1 mmol, 0.27 mL) which was prepared by the method previously described.[14] The solution was cooled to −78 °C and dry pyridine (2 mmol, 0.16 mL) was added. After stirring for a while, benzaldehyde (1 mmol, 0.11 mL) was added at this temperature. After 30 min, the reaction was quenched at −70 °C with MeOH (0.5 mL)–ethanolamine (2 mmol, 0.12 mL), and the mixture was allowed to warm to room temperature. The solvents were removed under vacuum, and the residual material was washed several times with hexane. The combined hexane extracts were condensed, and filtration through a column of silica gel by using petroleum ether–ether (10:1) as an eluant gave the desired isomer: 0.21 g, 90%.[15]

The *threo,cis*-alkenylsilanes or -stannanes (**2**) thus obtained are highly useful for the further elaboration of complex molecules. Several examples of eq 2 illustrate the flexability inherent in these species.[16] We are now extending this method to the stereoregulated synthesis of five consecutive carbon units and also the synthesis of some antibiotics.



(2)

(13) The crotyl derivative (**1**) consists of a mixture of cis and trans isomers due to the rapid allylic rearrangement.[14] The formation of ate complexes prevents the rearrangement, and the geometry of crotyl unit is presumably fixed to trans.

(14) Yatagai, H.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548.

(15) ^{1}H NMR data of the product and its isomers in Table I are as follows. Chemical shifts, not important in the structure determination, are omitted. **3** (threo, *Z*), (CCl_4) δ 0.08 (s, 9 H), 0.76 (d, *J* = 6 Hz, 3 H, Me), 4.20 (d, *J* = 8 Hz, 1 H, CHO), 5.56 (d, *J* = 14 Hz, 1 H, CHSi), 6.10 (d-d, *J* = 14 and 10 Hz, 1 H, =CH). **3** (erythro, *Z*) δ −0.02 (s, 9 H), 0.90 (d, *J*. = 6 Hz, 3 H, Me), 4.42 (d, *J*. = 6 Hz, 1 H, CHO), 5.32 (d, *J* = 14 Hz, 1 H, CHSi), 6.10 (d-d, *J* = 14 and 10 Hz, 1 H, =CH). **3** (*E*, erythro or threo is not obvious) δ −0.06 (s, 9 H), 0.90 (d, *J* = 6 Hz, 3 H, Me), 4.42 (br d, 1 H, CHO), 5.50 (d, *J* = 20 Hz, 1 H, CHSi), 5.90 (d-d, *J* = 20 and 6 Hz, 1 H, =CH). These isomers were isolated from the reaction of **1a** with PcCHO in the absence of base, where considerable amounts of the byproducts were produced. **4** (threo, *Z*) δ 0.11 (s, 9 H), 0.75 (d, *J* = 6 Hz, 3 H, Me), 4.18 (d, *J* = 8 Hz, 1 H, CHO), 5.90 (d, *J* = 12 Hz, 1 H, CHSn), 6.26 (d-d, *J* = 12 and 10 Hz, 1 H, =CH). **5** (threo, *Z*) δ 0.06 (s, 9 H), 0.86 (d, *J* = 6 Hz, 3 H, Me), 3.08–3.32 (brm, 1 H, CHO), 5.51 (d, *J* = 14 Hz, 1 H, CHSi), 6.04 (d-d, *J* = 14 and 10 Hz, 1 H, =CH). **5** (*E*, threo or erythro is not obvious) δ 0.01 (s, 9 H), 0.99 (d, *J*. = 6 Hz, 3 H, Me), 3.24–3.44 (br m 1 H, CHO), 5.54 (d, *J* = 20 Hz, 1 H, CHSi), 5.90 (d-d, *J* = 20 and 6 Hz, 1 H, =CH). **5** (α isomer, *n*-BuCH(OH)CH)$SiMe_3$)CH=CHMe) δ −0.05 (s), 1.51 (d, *J* = 6 Hz, Me), 5.44 (br s, CH=CH). **6** (threo, *Z*) δ 0.08 (s, 9 H), 0.91 (d, *J* = 6 Hz, Me), 3.10–3.30 (m, 1 H, CHO), 5.88 (d, *J* = 12 Hz, 1 H, CHSn), 6.26 (d-d, *J* = 12 and 10 Hz, 1 H, =CH). **7** (threo, *Z*) δ 0.12 (s, 9 H), 1.01 (d, *J* = 6 Hz, 3 H, Me), 3.92 (br t, 1 H, CHO), 5.59 (d, *J* = 14 Hz, 1 H, CHSi), 6.10 (d-d, *J* = 16 and 7 Hz, 1 H, PhC=CH), 6.16 (d-d, *J* = 14 and 10 Hz, 1 H, CH=CSi), 6.52 (d, *J* = 16 Hz, 1 H, PhCH). **8** (threo, *Z*) δ 0.12 (s, 3 H), 1.00 (d, *J* = 6 Hz, 3 H, Me), 2.54 (d, *J* = 6 Hz, 2 H, CH_2CO), 3.84 (quartet, *J* = 6 Hz, 1 H, CHO), 5.49 (d, *J* = 14 Hz, 1 H, CHSi), 6.17 (d-d, *J* = 14 and 10 Hz, 1 H, =CH).

(16) The epoxidation of **2a** or **10** with MCPBA proceeded with reasonable stereoselectivity, presumably owing to both the cis configuration and the presence of OH group. The isomer ratio was determined from the ^{1}H NMR spectra of the reaction mixture; **9**/its isomer = 85/15, being obtained from the area ratio of δ 4.53 (d, *J* = 7 Hz)/δ 4.29 (d, *J* = 8 Hz); **11**/its isomer = 88/12, from δ 4.62 (d, *J* = 7 Hz)/δ 4.36 (d, *J* = 9 Hz). See also: Johnson, M. R.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4347.

Absolute Rate Constants for Some Reactions Involving Triethylsilyl Radicals in Solution[1]

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There is growing interest in the chemistry and reactivity of trialkylsilyl radicals in solution,[2,3] but the absolute rate constants for very few of their reactions have been measured.[4] Among the more interesting and important reactions of these radicals are halogen abstractions from organic halides[2,3a,c,e,12-15] and additions to various types of multiple bond,[2,3d,f,9,14,16,17] but there are no reliable rate constants for such processes. In this communication we report a kinetic study of the formation of triethylsilyl by reaction of *tert*-butoxyl radicals with triethylsilane and decay of triethylsilyl by its reaction with some organic halides and benzil. The experiments were carried out using laser flash photolysis techniques[18,19] supplemented by kinetic EPR spectroscopy.

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO\cdot \quad (1)$$

$$Me_3CO\cdot + Et_3SiH \rightarrow Me_3COH + Et_3Si\cdot \quad (2)$$

Reaction 1 can be regarded as a virtually instantaneous process.[18] The transient absorption due to *tert*-butoxyl[21] are too weak to be convenient for kinetic studies. The same tends to be true of triethylsilyl which shows weak absorbtions below 340 nm. However, in isooctane and triethylsilane as solvents the $Et_3Si\cdot$ were shown to decay with second-order kinetics with $2k_1/\epsilon_{308} = 1.1 \times$

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‡ N.R.C.C. Research Associate, 1978–1979.

(1) Issued as N.R.C.C. No. 19377.

(2) For a concise review, see: Sakurai, H. *Free Radicals* **1973**, *2*, 741–808.

(3) For some interesting recent work, see, e.g.,: (a) Jung, I. N.; Weber, W. P. *J. Org. Chem.* **1976**, *41*, 946. (b) Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2369. (c) Aloni, R.; Rajbenbach, L. A.; Horowitz, A. *Int. J. Chem. Kinet.* **1979**, *11*, 899. (d) Chen, K. S.; Foster, T.; Wan. J. K. S. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1288. (e) Billingham, N. C.; Jackson, R. A.; Malek, F. *J. Chem. Soc. Perkin Trans. 1* **1979**, 1137. (f) Alberti, A.; Hudson, A.; Pedulli, G. F.; Zanirato, P. *J. Organomet. Chem.* **1980**, *198*, 145.

(4) Those known to us include only the following reactions, none of which are really suitable for competitive studies which would yield additional rate constant: $2Me_3Si\cdot \rightarrow$ products;[5-8] $Me_3Si\cdot + C_2H_4 \rightarrow Me_3SiCH_2CH_2\cdot$;[9,10] $Me_3Si\cdot + (Me_3Si)_2Hg \rightarrow Me_3SiSiMe_3 + Me_3Si\cdot + Hg$;[11] $Me_3Si\cdot + (Me_3Si)_2Hg \rightarrow (Me_3Si)_2Hg + Me_3Si\cdot$.[11]

(5) Frangopol, P. T.; Ingold, K. U. *J. Am. Chem. Soc.* **1970**, *25*, C9.

(6) Watts, G. B.; Ingold, K. U. *J. Am. Chem. Soc.* **1972**, *94*, 492.

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