

The nature of this complex and the mode of its presumed association with the DNA substrate are under investigation.

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(15) A solution of 10 mM (-)-epicatechin and 1 mM Cu(ClO₄)₂ (50 mM sodium cacodylate, pH 7.0; -140 °C) gave an EPR signal indicative of Cu(II) complex formation, $g_{\perp} \approx 2.04$; $g_{\parallel} \approx 2.28$, as evidenced by splitting of the Cu(II) signal. No EPR signal was observed in the absence of Cu(II). The UV absorption maximum shifted from 280 nm to 295 nm upon addition of equimolar CuCl₂.

Novel 1,2-Migration Reactions of Organometals Containing Aluminum, Zinc, and Other Main Group Metals with α -Haloorganolithiums

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1,2-Migration or migratory insertion is, in principle, one of the most fundamental patterns for carbon-carbon and carbon-heteroatom bond formation. Indeed, the majority of carbon-carbon bond-forming reactions of organoboron compounds proceed via 1,2-migration.² Carbonylation and related reactions of organo transition metals are representative examples of the 1,2-migration reactions involving transition metals.³ At present, however, relatively little is known about 1,2-migration reactions involving main group metals other than boron. For example, although the reaction of organoalanes with diazomethane to give homologated organoalanes⁴ most likely involves 1,2-migration, virtually no other 1,2-migration reactions of organoalanes are known.⁵ We now wish to present experimental data which suggest that the 1,2-migration reactions of organo main group metals are much more widespread than the previously available data indicated.

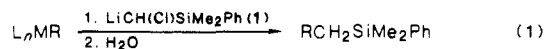
Typically, addition of *i*-Bu₃Al (0.505 mL, 2.0 mmol) to LiCH(Cl)SiMe₂Ph⁶ (**1**) at -78 °C, generated in situ by treating ClCH₂SiMe₂Ph (0.554 g, 3.0 mmol) and 0.452 mL (3.0 mmol) of tetramethylethylenediamine (TMEDA) in 9.2 mL of THF with 2.3 mL (1.3 M, 3.0 mmol) of *sec*-BuLi in cyclohexane at -78 °C, followed by warming the mixture to 23 °C, stirring at this temperature for 6 h, treatment with water at 0 °C, and the usual extractive workup and chromatography (silica gel, pentane) provided an 80% GLC yield (62% isolated) of *i*-BuCH₂SiMe₂Ph⁷ (**2**): ¹H NMR (CDCl₃, Me₄Si) δ 0.21 (s, 6 H), 0.5-0.8 (m, 2 H), 0.83 (d, $J = 6.5$ Hz, 6 H), 1.0-1.7 (m, 3 H), 7.3-7.7 (m, 5 H); ¹³C NMR (CDCl₃) δ -3.10, 13.07, 22.12, 30.92, 32.85, 127.69,

Table I. 1,2-Migration Reactions of Organometals Containing Aluminum and Other Main Group Metals with LiCH(Cl)SiMe₂Ph (**1**)^a

organometals	products	time, h	yield, ^b %
<i>i</i> -Bu ₃ Al	<i>i</i> -BuCH ₂ SiMe ₂ Ph	6	80 (62)
<i>i</i> -Bu ₂ AlCl	<i>i</i> -BuCH ₂ SiMe ₂ Ph	48	5
<i>n</i> -Pr ₃ Al	<i>n</i> -PrCH ₂ SiMe ₂ Ph	6	77 (53)
Me ₃ Al	MeCH ₂ SiMe ₂ Ph	6	83
(<i>E</i>)- <i>n</i> -HeptCH=CHAl(Bu- <i>i</i>) ₂ ^c	(<i>E</i>)- <i>n</i> -HeptCH=CHSiMe ₂ Ph and <i>i</i> -BuCH ₂ SiMe ₂ Ph	1	85 (65) 9
<i>i</i> -Bu ₂ AlPh ^d	PhCH ₂ SiMe ₂ Ph and <i>i</i> -BuCH ₂ SiMe ₂ Ph	6	48 31
<i>n</i> -Bu ₂ Mg ^e	<i>n</i> -BuCH ₂ SiMe ₂ Ph	0.5	72
<i>n</i> -Bu ₂ Zn ^e	<i>n</i> -BuCH ₂ SiMe ₂ Ph	0.5	61
<i>n</i> -Bu ₂ ZnCl ^f	<i>n</i> -BuCH ₂ SiMe ₂ Ph	24	10
<i>n</i> -Bu ₂ Cd ^f	<i>n</i> -BuCH ₂ SiMe ₂ Ph	1	55

^aUnless otherwise mentioned, all reactions were carried out under the standard conditions reported in the text. ^bBy GLC based on an organometal. The numbers in parentheses are isolated yield. ^cPrepared by the reaction of DIBAH with 1-octyne. ^dPrepared by the reaction of *i*-Bu₂AlCl with 1 equiv of PhLi. ^ePrepared by the reaction of the corresponding metal dichloride with *n*-BuLi.

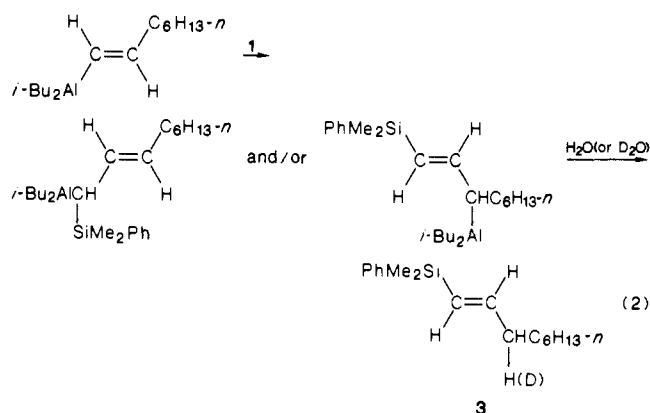
128.71, 133.55, 139.52; IR (neat) 1250 (s), 1110 (s), 840 (s) cm⁻¹; high resolution MS calcd for C₁₃H₂₂Si 206.1491, found 206.1478. Also obtained was Me₃SiPh (0.45 equiv out of 1.5 equiv of ClCH₂SiMe₂Ph). Little or no ClCH₂SiMe₂Ph was recovered. As shown in Table I not only some other organoalanes, such as *n*-Pr₃Al (77%, 6 h) and Me₃Al (83%, 6 h), but also organometals containing Mg, Zn, and Cd, such as *n*-Bu₂Mg (72%, 0.5 h), *n*-Bu₂Zn (61%, 0.5 h), and *n*-Bu₂Cd (55%, 1 h), have produced the corresponding RCH₂SiMe₂Ph in the yields indicated in parentheses within the indicated reaction times under otherwise the same conditions (eq 1). On the other hand, the reaction of Me₃SnCl with **1** merely gave Me₃SnCH(Cl)SiMe₂Ph in 75% yield.



R = Me, *n*-Pr, *n*-Bu, or *i*-Bu ML_n = Al-, Mg-, Zn, or Cd-containing group

The reaction of (*E*)-*n*-HexCH=CHAl(Bu-*i*)₂ with **1** under the above-mentioned conditions gave isomerically >98% pure (*E*)-*n*-HeptCH=CHSiMe₂Ph (**3**) in 85% yield along with a 9% yield of **2**. The same reaction run at 0 °C under otherwise the same conditions produced **2** and **3** in 4% and 75% yields, respectively. Thus, the reactivity of the (*E*)-1-octenyl group relative to the *i*-Bu group at 23 or 0 °C is 19 or 38, respectively. Workup with D₂O gave essentially pure (*E*)-3-deuterio-1-nonenylidimethylphenylsilane (**4**) in 80% yield, indicating that an Al atom was bonded to the C-1 or C-3 atom of the alkenyl group (eq 2). The reaction of *i*-Bu₂AlPh with **1** gave within 6 h at 23 °C PhCH₂SiMe₂Ph and **2** in 48% and 31% yields, respectively. Thus, the Ph/*i*-Bu reactivity ratio is 3.1.

The above described reactions can, in principle, proceed by various mechanisms. The three most likely paths deserving our attention are those involving (i) 1,2-migration (eq 3), (ii) direct displacement (eq 4), and (iii) carbene insertion (eq 5).



(7) All new isolated products have been adequately characterized by ¹H and ¹³C NMR, IR, and mass spectrometries. All new isomerically homogeneous compounds have been further characterized by elemental analyses.

(1) John Simon Guggenheim Memorial Foundation Fellow (1987).

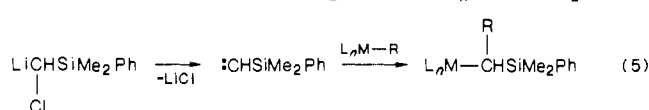
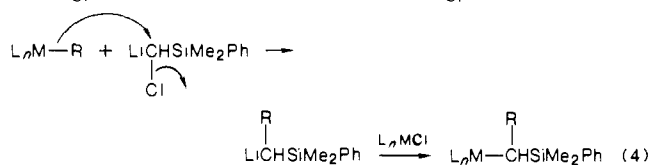
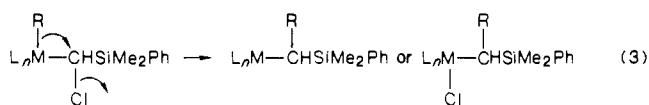
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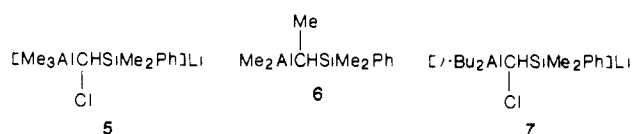
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The currently available data on the reaction of organoalanes with **1** clearly favor the 1,2-migration path over the other two. First, the reaction of either *i*-Bu₃Al or Me₃Al with **1** monitored at 23 ± 0.1 °C by GLC follows first-order kinetics ($k = 2.0 \times 10^{-2} \text{ min}^{-1}$, $r = 0.998$ or $k = 3.4 \times 10^{-3} \text{ min}^{-1}$, $r = 0.998$) in a 4:1 mixture of THF and cyclohexane, but it does not obey second-order kinetics, disfavoring the direct displacement path (eq 4). Mixing *i*-Bu₃Al with ClCH₂SiMe₂Ph does not induce any reaction under comparable conditions. Second, examination of the mixture of the reaction of Me₃Al with **1** by ¹H NMR indicates that, upon mixing the two reagents, the Me signal for Me₃Al at -1.03 ppm initially shifts to -1.24 ppm, although the signal at -1.03 ppm is quite insensitive to various solvents such as cyclohexane, THF, and even TMEDA, staying well within the -1.01 to -1.03 ppm range. The Me signal for LiAlMe₄ appears at -1.33 ppm. As the reaction proceeds, the signal at -1.24 ppm shifts back to -1.02 ppm over several hours. The signals at -1.24 and -1.02 ppm, we believe, are attributable to the formation of **5** and **6**. Although we have not monitored the reaction of *i*-Bu₃Al with **1** by ¹H NMR, quenching an aliquot of this reaction mixture shortly after raising the reaction temperature to 23 °C gave 0.79 equiv of ClCH₂SiMe₂Ph and 0.16 equiv of *i*-BuCH₂SiMe₂P along with 0.45 equiv of Me₃SiCH₂Ph out of 1.5 equiv of ClCH₂SiMe₂Ph. Under comparable conditions, quenching a solution which initially contained only **1** without *i*-Bu₃Al gave a considerable amount of an unidentified but apparently dimeric product but little or none of ClCH₂SiMe₂Ph. These results again indicate the formation of an aluminate complex **7** which slows down decomposition of the ClCHSiMe₂Ph anion and releases ClCH₂SiMe₂Ph upon quenching.



The reaction of organoalanes with LiCHCl₂⁸ leads to formation of two new carbon-carbon bonds within one molecule. Thus, the reaction of *i*-Bu₂AlPh, generated in situ from *i*-Bu₂AlCl and PhLi, with LiCHCl₂ (1.3 equiv) at -100 to 40 °C in a mixture of THF-ether-hexane-cyclohexane (5:3:3:1) produced, after hydrolysis, *i*-BuCH₂Ph in 53% yield. Under similar conditions the reaction of *i*-Bu₂AlCH=CHHex-*n*(*E*) with LiCHCl₂ produced a 75% combined yield of a nearly 1:1 mixture of *i*-BuCH₂CH=CHHex-*n* and *i*-BuCH=CHHept-*n*, each of which was an *E* and *Z* mixture. Although this reaction needs to be further developed, it appears to represent the first example of double-transfer reactions in which two carbon groups of an organoalane get transferred to one molecule, i.e., LiCHCl₂.

We believe that the results presented here have just opened up a major new area of 1,2-migration reactions of organo main group metals other than organoboranes. Unlike the latter, organometals containing Al, Mg, Zn, Cd are readily hydrolyzed to produce

organic products. This would make the synthetic significance of their 1,2-migration reactions quite distinct from those of organoboranes.

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Supplementary Material Available: IR, ¹H NMR, and ¹³C NMR data for **2-4** and other unnumbered compounds in this paper. (2 pages). Ordering information is given on any current masthead page.

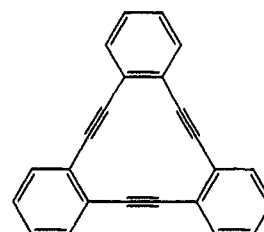
Synthesis and Characterization of a Silver(I) Triflate Sandwich Complex of 1,2:5,6:9,10-Tribenzocyclododeca-1,5,9-triene-3,7,11-tri-ene. The First Example of a 12-Membered Macrocycle Sandwich Complex

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The ligand 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triene¹ (TBC) has shown much versatility in its reaction chemistry with various transition-metal compounds via binding of the transition-metal center to the carbon-carbon triple bond.



TBC

Complexes of TBC already synthesized and structurally characterized include mononuclear nickel(0) and copper(I) complexes,^{2,3} a trinuclear copper(I) complex,⁴ and a tetranuclear cobalt(0) cluster.⁵ This communication reports the synthesis of a novel silver(I) sandwich complex **1** from the reaction of AgSO₃CF₃ with TBC. Numerous examples of 3-8-membered hydrocarbon ring transition-metal sandwich complexes⁶ have been previously reported, but complex **1** is the first example of a 12-membered macrocycle sandwich complex.

All manipulations were performed by using standard inert atmosphere techniques. In a typical reaction, AgSO₃CF₃⁷ (0.171 g, 0.666 mmol) and TBC⁸ (0.100 g, 0.333 mmol) were allowed

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