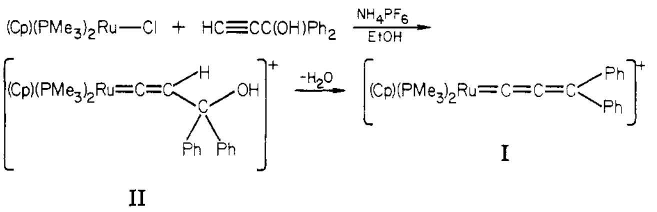
Scheme I



allenylidene ligand is a significantly less effective π-acid than the similar phenylvinylidene (η^1-C=CHPh) ligand (δ(Cp) 5.94)[10] but that it is similar in π-acid strength to a carbonyl ligand (δ(Cp) 5.47).[5a] The $^{13}C\{^1H\}$ NMR spectrum of complex I (50 MHz, $(CD_3)_2CO$; δ_C 295.8 (s, C1), 216.0 (s, C2), 153.8 (s, C3), 145.0 (s, C_{ipso}), 131.6 (s, C_{para}), 130.4 (s, C_{ortho}), 130.0 (s, C_{meta}), 92.0 (s, Cp), 22.9 (t, $^1J_{CP}$ = 17.9 Hz, PMe_3)) clearly reflects the presence of an unsaturated alkylidene ligand. Furthermore, the simplicity of the aromatic region of the ^{13}C spectrum suggests that both phenyl groups rotate freely and that rotation of the diphenylallenylidene moiety with respect to the $[Ru(PMe_3)_2(Cp)]$ symmetry plane is rapid on the ^{13}C NMR time scale at room temperature.

Because of the paucity of structural data on metallacumulene complexes, a single-crystal X-ray diffraction study of complex I was undertaken.[11] An ORTEP plot of the $[Ru(C_3Ph_2)(PMe_3)_2(Cp)]^+$ cation is shown in Figure 1, and selected bond distances and angles are presented in Table I. The diphenylallenylidene ligand is of primary interest. The ruthenium to carbon (C1) bond is considerably shorter than a typical Ru—C single bond length of ca. 2.1 Å[12] and slightly shorter than most ruthenium to carbonyl bonds (1.92–1.93 Å).[13] The C1—C2 bond length in I is nearly as short as a carbon–carbon triple bond (1.20–1.21 Å).[14] The C2—C3 bond length is typical of an allene C(sp)—C(sp^2) double bond (e.g., 1.31 Å in CH_2=C=CH_2[14b,c]). These structural parameters indicate a substantial contribution from two different mesomeric forms, Ia and Ib, $[CpL_2Ru{=}C{=}C{=}CPh_2]^+ \leftrightarrow [CpL_2Ru{-}C{\equiv}C{-}CPh_2]^+$ with the cationic charge stabilized by both the metal center and the diphenylcarbenium moiety. A similar conclusion was reached in the structural analysis of $[Cr(CO)_5\{\eta^1\text{-}C{=}C{=}C(NMe_2)Ph\}]$.[4a] The nearly linear metallacumulene moiety in I is oriented such that it lies approximately in the $[Ru(PMe_3)_2(Cp)]$ pseudomirror plane; i.e., the plane defined by C2, C3, C31, and C41 forms a dihedral angle of 10.6° with the plane defined by Ru, C1, and the centroid of the cyclopentadienyl ring. This allenylidene orientation is consistent with that predicted by Hoffmann and his co-workers to maximize π-orbital overlap in the model compound $[Fe(\eta^1\text{-}C{=}C{=}CH_2)(CO)_2(Cp)]^+$.[15]

A probable mechanism for the formation of I is indicated in Scheme I. Heterolytic dissociation of the highly polarized ruthenium–chlorine bond of $[RuCl(PMe_3)_2(Cp)]$[5,10] is followed by alkyne coordination and a 1,2-hydrogen shift to form the intermediate hydroxyvinylidene complex II.[2c,10] Although not observed in this case, such intermediates may be isolated from reactions of [FeCl(dppe)(Cp)] with alkynols.[17] Under the reaction conditions, complex II spontaneously dehydrates to form allenylidene complex I.[18]

Other reactions of $[MX(PR_3)_2(Cp)]$ (M = Fe, Ru; X = Cl, Br, I) with alkynols are under investigation. In particular, it appears that alkyl-substituted allenylidene complexes (e.g., $[Ru(C_3Me_2)(PPh_3)_2(Cp)]^+$) may be prepared similarly to I, but their chemistry is dominated by deprotonation of the alkyl groups.[17]

Acknowledgment. Thanks are due to Research Corp., Sigma Xi, and the Research Foundation and Graduate School of the University of Kentucky for financial support and to Engelhard Industries and Johnson Matthey, Inc., for generous loans of ruthenium trichloride.

Registry No. I, 79152-77-5; $[RuCl(PMe_3)_2(Cp)]$, 74558-74-0; $Ph_2C(OH)(C{\equiv}CH)$, 3923-52-2.

Supplementary Material Available: Listings of positional and thermal atomic parameters (Table II) and experimental and calculated structure factors (Table III) (27 pages). Ordering information is given on any current masthead page.

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(11) Crystal data for complex I: space group $P2_1/n$, a = 10.815 (2) Å, b = 13.602 (3) Å, c = 20.268 (2) Å, α = 103.06 (1)°, V = 2904.38 Å, Z = 4, ρ_{calcd} = 1.495 g·cm^{-3}. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares procedures: R = 0.069 and R_w = 0.085 using 4318 reflections with $F^2 \geq 3\sigma(F^2)$. The relatively high R factors are probably due to unresolvable disorder in the $[PF_6]^-$ ion.

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(16) The stable hydroxyvinylidene complex $[Mn\{\eta^1\text{-}C{=}CHC(OH)(CMe_3)_2\}(CO)_2(Cp)]$ undergoes dehydration in the mass spectrometer.[2i]

(17) Selegue, J. P., unpublished results.

(18) A similar dehydration reaction occurs when *trans*-$[PtHCl(PPh_3)_2]$ reacts with α-hydroxyalkynes, e.g., $Me_2C(OH)(C{\equiv}CH)$ yields *trans*-$[PtCl(C{\equiv}CCMe{=}CH_2)(PPh_3)_2]$. Furlani, A.; Licoccia, S.; Russo, M. V.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1980**, 1958.

Synthesis of the Elusive 1,8-Bis(trimethylsilyl)naphthalene and Its Facile Rearrangement to the 1,7 Isomer

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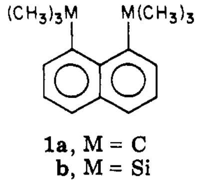
Peri-substituted naphthalenes are an important subset of the class of overcrowded molecules.[1] Most notable in this group are 1,8-di-*tert*-butylnaphthalenes (**1a**) in which



1a, M = C
b, M = Si
c, M = Ge
d, M = Sn

the steric interaction is so great that the naphthalene skeleton is severely distorted from planar geometry.[2] It

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(1) For a review of early work, see: Balasubramanian, V. *Chem. Rev.* **1966**, *66*, 567.

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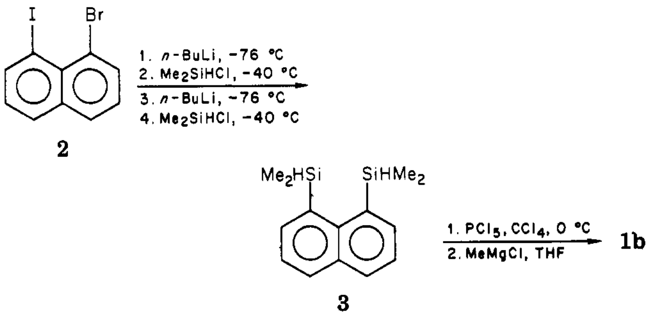
Scheme I



was logical then that interest should accrue to the silicon, germanium, and tin analogues of **1a**. Recently, the heavier congeners, **1c**[3] and **1d**,[4] have been prepared and fully characterized, including structural determinations by X-ray crystallography[5] and conformational analyses by NMR spectroscopy.[6] Both compounds show deviations from planarity but are significantly less distorted than **1a**, i.e., **1a** ≫ **1c** > **1d**.[5] The rotation barriers decrease in the same order,[6,7] a trend opposite to that predicted.[8] Most useful would be a study of **1b** for comparison purposes.

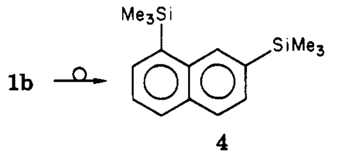
In this communication we report the successful synthesis of the elusive member of this series, 1,8-bis(trimethylsilyl)naphthalene (**1b**), and its facile rearrangement to the 1,7-isomer **4**. Earlier work[4] describing the preparation of **1b** from 1,8-dilithionaphthalene was reinvestigated,[9] and it was found that the product of that reaction was actually 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane.

Our approach to the synthesis of **1b** was a stepwise lithiation–silation procedure similar to one we recently described for the preparation of disilaacenaphthenes.[10] In this case we used the smaller dimethylchlorosilane as the silating agent to generate **3**. The structure of **3** was deduced from elemental analysis and mass spectral and ^{1}H NMR data. Chlorination of both Si–H functions with PCl_5[11] followed by methylation led to **1b** (Scheme I). This compound was obtained in ~25% yield (isolated, >98% pure) based on **2**.

The structure of **1b** is deduced mainly from spectroscopic data: ^{1}H NMR (90 MHz, CCl_4, acetone) δ 0.32 (s, 18 H, $SiCH_3$), 7.30–7.90 (m, 6 H, aromatic); ^{13}C NMR (90 MHz, $CDCl_3$) δ 3.18 (CH_3), 123.51, 130.34, and 136.26 (proton bearing aromatic carbons), 133.26, 139.70, and 141.26 (quaternary carbons). The off-resonance decoupled spectrum showed a quartet at δ 3.18 and doublets at δ 123.51, 130.34, and 136.26 supporting these assignments. The spectrum of **1b** was compared to that of the germanium analogue **1c** and found to be very similar.

Compositional data on **1b** were also obtained. Anal. Calcd for $C_{16}H_{24}Si_2$: C, 70.51; H, 8.88; Si, 20.61. Found: C, 70.49; H, 8.87; Si, 20.65. Mass spectral analysis (70 eV) showed an intense peak at 272, assignable to the molecular ion, M^+, and the base peak at 257, $M - CH_3^+$.

1,8-Bis(trimethylsilyl)naphthalene is a white crystalline solid (mp 64–66 °C) which can be purified by crystallization from methanol or by preparative gas chromatography. It was in using the latter technique that we accidentally discovered that **1b** rearranges to the 1,7 isomer **4** at temperatures above 150 °C. When the column (6 ft × 0.25 in., 5% SE-30 on Chromosorb W) is kept above 200 °C, the isomerization is quantitative. Complete conversion to **4** can also be effected by heating a solution of **1b** in carbon tetrachloride at 150 °C for 1 h. The structural assignment is based on mass spectral data and the comparison of its NMR spectrum with that of an authentic sample. This appears to be a simple thermal reaction although we have not yet ruled out the presence of traces of acid that could catalyze the isomerization. Relevant to this is the known acid-catalyzed rearrangement of 2-(1-naphthyl)-2,4,4-trimethyl-2,4-disilapentane to 2-(2-naphthyl)-2,4,4-trimethyl-2,4-disilapentane,[12] a reaction originally believed[4] to be the **1b** → **4** transformation we report here.



Determination of the molecular structure of **1b** by diffraction methods, conformational analysis by NMR, and further study of the 1,8 → 1,7 rearrangement are now in progress.

Acknowledgment. We are most grateful to Kurt Mislow for the discussions that led to our undertaking this project and for generously supplying samples and spectra of 1,8-bis(trimethylgermyl)naphthalene and 1,7-bis(trimethylsilyl)naphthalene. We also thank Vern Feil for the ^{13}C NMR spectra. Acknowledgment is also made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. 1b, 65197-00-4; 2, 4044-58-0; 3, 78685-92-4; 4, 65197-02-6.

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Carbon-to-Carbon Migration of the Dimetallic Group in Dinuclear Cobalt Alkylidene Complexes

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Summary: A series of terminal and internal (μ-alkylidene)cobalt complexes (**3a–g**) has been prepared. These complexes have the empirical formula $(\mu\text{-}CR_1R_2)(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2$. Isomers having doubly bridging, cis terminal, and trans terminal carbonyl groups have been detected spectroscopically, the relative amounts of each isomer depending in a sensitive way upon the alkylidene substituents. Complexes **3** in which both R and R′ are alkyl groups lose one molecule of CO, forming the corresponding unsaturated dinuclear complexes **4**. Upon