Table I. Reaction in Diethyl Ether of 4 Molar Equiv of Nucleophilic Reagents with Complex 2

nucleophilic reagent	reactn conditns time, h	reactn conditns *t*, °C	product (yield %)
PhMgBr	0.25	20	Ph_4Ge (77)
EtMgBr	0.5	20	Et_4Ge (83)
n-BuMgBr	0.5	20	*n*-Bu_4Ge (87)
$CH_2{=}CHCH_2MgBr$	0.5	20	$(CH_2{=}CHCH_2)_4Ge$ (68)
$MeC{\equiv}CMgBr$	2	20	$(MeC{\equiv}C)_4Ge$ (64)
$Me_3SiC{\equiv}CMgBr$	0.5	20	$(Me_3SiC{\equiv}C)_4Ge$ (78)
$EtSLi/Et_2O$–THF	18	50	$(EtS)_4Ge$ (63)
1-NpMgBr	12	35	$(1\text{-}Np)_4Ge$ (45)

The reactivity of Grignard reagents having a hydrogen atom in the β-position and activated by Cp_2TiCl_2 (Cp = cyclopentadienyl) also was investigated. This system is known[8] to be a very efficient reducing agent. In this manner, organogermanes of type R_3GeH[9] have been prepared in one step directly from **2** (eq 4).

$$2 + 5\text{ equiv of RMgX} \xrightarrow[\text{Et}_2\text{O}\\ \text{4-h reflux}]{5\%\ \text{Cp}_2\text{TiCl}_2} \begin{array}{c} R_3GeH \\ R = Et\ (45\%) \\ R = n\text{-Bu}\ (75\%) \end{array} \qquad (4)$$

The reactivity of complex **3** toward Grignard reagents is lower than that of **2** since it was found that only three Ge–C bonds are formed with **3**, except in the case of PhMgX, which gives Ph_4Ge in good yield (75%). The "one-pot" preparation of R_3GeH from **3** is achieved by addition of 3 molar equiv of an alkyl Grignard reagent followed by reduction with $LiAlH_4$.

$$3 \xrightarrow[\text{2. LiAlH}_4\ \text{(2-h reflux)}]{\text{1. } 3n\text{-BuMgBr, Et}_2\text{O; 1 h at 0 °C; 0} \rightarrow \text{20 °C during 4 h}} \begin{array}{c} n\text{-Bu}_3GeH \\ 58\% \end{array} \qquad (5)$$

It is clear from the results described above that hexacoordinate, anionic germanium complexes, which are readily prepared from GeO_2, are useful starting materials in organogermanium synthesis.

Registry No. **2**, 112712-64-8; **3**, 112712-66-0; GeO_2, 1310-53-8; Ph_4Ge, 1048-05-1; Et_4Ge, 597-63-7; *n*-Bu_4Ge, 1067-42-1; $(CH_2{=}CHCH_2)_4Ge$, 1793-91-5; $(MeC{\equiv}C)_4Ge$, 20143-28-6; $(Me_3SiC{\equiv}C)_4Ge$, 13963-42-3; $(EtS)_4Ge$, 15800-73-4; $(1\text{-}Np)_4Ge$, 112712-65-9; PhMgBr, 100-58-3; EtMgBr, 925-90-6; *n*-BuMgBr, 693-03-8; $CH_2{=}CHCH_2MgBr$, 1730-25-2; $MeC{\equiv}CMgBr$, 16466-97-0; $Me_3SiC{\equiv}CMgBr$, 61210-52-4; EtSLi, 30383-01-8; 1-NpMgBr, 703-55-9; Cp_2TiCl_2, 1271-19-8; Et_3GeH, 1188-14-3; *n*-Bu_3GeH, 998-39-0; catechol, 120-80-9; 2,3-Butanediol, 513-85-9.

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(9) The following preparation is given as an example. Complex **2** (7.11 g, 0.015 mol) was suspended in 100 mL of anhydrous diethyl ether with 5 mol % of Cp_2TiCl_2 (0.187 g) under nitrogen. Five molar equiv of *n*-BuMgBr was added dropwise at room temperature. The reaction mixture was heated under reflux for about 4 h, then hydrolyzed with an aqueous solution of 4 M HCl, and extracted three times with ether. The combined organic extracts were washed once with water, twice with a 2 M solution of NaOH, twice more with water, and then with brine and dried over $MgSO_4$. After evaporation of the solvent, the organogermane was purified by distillation to give 3 g of tri-*n*-butylgermane (83%), bp 123–125 °C (2.66 kPa) [Lit.[2] bp 123 °C (2.66 kPa)].

Preparation and Reaction with $(CH_3)_3SiF_2^-$ of an Iron [(Trimethylsilyl)vinyl]carbene Complex. An Unprecedented and Highly Stereoselective Si to C Methyl Migration

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Summary: Introduction of $[(CH_3)_2N]_3S^+SiF_2(CH_3)_3^-$ to $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)Fe{=}C(OCH_3)C{=}CHSi(CH_3)_3{}^+BF_4^-$ induces stereoselective methyl migration from Si to an adjacent carbon in the carbene ligand to give the (methoxyallyl)silane complex $(\eta^5\text{-}C_5H_5)(CO)(PPh_3)FeC(OCH_3){=}CHCH(CH_3)Si(CH_3)_2F$.

Organic synthetic applications focussed on stereospecific conversions of organic ligands complexed to chiral transition metals is of interest due to the metal center's steric and electronic flexibility.[1] Among recent reports, carbene complexes have been utilized as enolate equivalent synthons[1,2] and acyl complexes of iron and cobalt have been studied as carbonyl–enolate synthetic reagents.[3]

We have recently initiated studies concerning the preparation and reactions of (trimethylsilyl)vinyl-substituted carbene complexes. Such compounds are unique, having in theory a partial cationic charge resident on the carbon (C_α) adjacent to the silicon (i.e., Figure 1), and are potentially useful as synthetic reagents in organic synthesis.[4] Here we report our initial studies concerning the preparation, and stereoselective reaction with fluoride, of a [(trimethylsilyl)vinyl]carbene complex of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)^+$ to give a σ-complex containing an allylsilane

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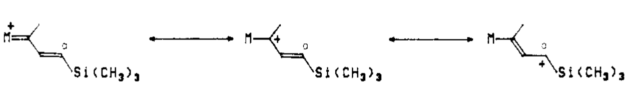
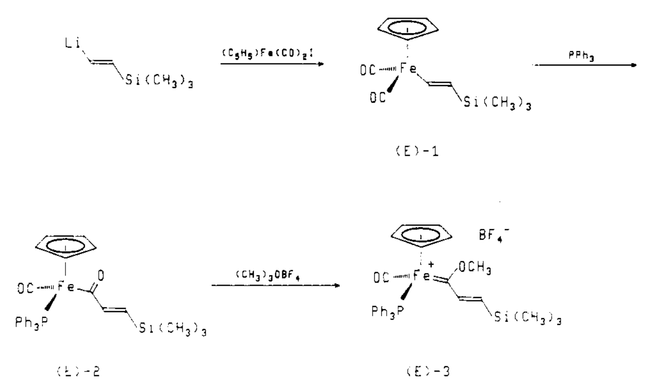


Figure 1. Resonance contributors of $CpFeL_2^+$ [(trimethylsilyl)vinyl]carbene complexes ($M^+ = CpFeL_2^+$).

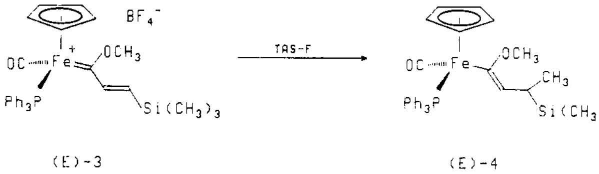
moiety. This is the first example of a diastereoselective fluoride induced Si to C_α methyl migration and represents a new method for preparing multifunctional chiral allylsilanes.

Synthesis of the title iron carbene complex is outlined in Scheme I. Introduction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ to (*E*)-LiCH═CHSiMe$_3$[5] gave σ complex (*E*)-**1**.[6] Although sensitive to most workup conditions, this compound could be purified by chromatography on deactivated neutral alumina. Triphenylphosphine-induced carbonyl insertion (CH_3CN solution) followed by chromatography on alumina gave a red glass identified as acyl complex (*E*)-**2**.[6] Methylation with $(CH_3)_3OBF_4$ gave carbene complex (*E*)-**3**.[6]

Scheme I



Introduction of the [(trimethylsilyl)vinyl]carbene complex (*E*)-**3** to $[(CH_3)_2N]_3S^+SiF_2(CH_3)_3^-$ [TAS-F][7] gives the yellow solid (methoxyallyl)silane complex (*E*)-**4** (eq 1) in 81% yield.[6] To ensure the highest yield, selected reaction temperatures (−78 to +100 °C) and solvents (ethyl ether, THF, dioxane, and CH_2Cl_2) were tested. In all these experiments **4** was generated. Optimal reaction conditions, however, were obtained by addition of the solid fluoride reagent to a cold (−74 °C) THF solution of carbene (E)-**3**.



(1)

This reaction occurs with stereoselective formation of the asymmetric carbon center. The NMR spectral data are indicative of the diastereomeric purity of (*E*)-**4**. Most informative are the proton-decoupled ^{13}C NMR data where the most intense signal of (*E*)-**4** is the cyclopentadienyl resonance at 84.3 ppm. Also present is a smaller resonance at 85.4 ppm tentatively attributed to the diastereomer. Although the high sensitivity of these compounds to various chromatographic media has precluded us from separating the presumed minor isomer for further identification, assigning the 85.4 ppm resonance as the minor diastereomer cyclopentadienyl's absorption gives a (*E*)-**4** diastereomeric ratio of >92:8.[8]

The methyl migration reaction from (*E*)-**3** to form an allylsilane moiety is unprecedented although fluoride-induced migrations from Si to an adjacent carbon (C_α) have been observed in studies of reactions of alkyl- and arylsilanes when a chloride or iodide is present on C_α.[9] In our

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[6] **Preparation of (*E*)-1.** A stirred solution of 6.59 g (16.9 mmol) of (*E*)-1-(tri-*n*-butylstannyl)-2-(trimethylsilyl)ethene[5] in 75 mL of cold THF (−85 °C) was treated with 11.0 mL (17.6 mmol, 1.6 M solution in hexane) of *n*-butyllithium. The faint gold solution was stirred for $^1/_2$ h, warmed to −30 °C, and stirred for $^1/_2$ h. After being recooled to −85 °C, a solution of 5.92 g (19.5 mmol) of dicarbonylcyclopentadienyliron iodide (mp 116–117 °C) in 75 mL of THF was added dropwise via cannula over 20 min. The solution was stirred for $1^1/_2$ h with slow warming to −40 °C. After the solution was warmed to room temperature, chromatography (2.5 × 45 cm, alumina, 7.5% H_2O, pentane) afforded 1.482 g (2.9 mmol, 32%) of gold oil: IR (CCl_4) 2010, 1975 cm^{-1} (CO); ^1H NMR (C_6D_6) δ 7.72 (d, *J* = 17 Hz, 1 H, FeCH), 6.54 (d, *J* = 17 Hz, 1 H, ═CHSi), 4.02 (s, 5 H, Cp), 0.18 (s, 9 H, $SiCH_3$); ^{13}C NMR (C_6D_6) δ 216.36 (CO), 152.82 (FeC═), 152.44 (═CSi), 85.64 (Cp), −0.38 (SiC); mass spectrum calcd *m/z* 276.027, found *m/z* 276.028; fast atom bombardment MS (thioglycerin), *m/z* 277 ($[M + H)^+$). Anal. Calcd for $C_{12}H_{16}FeO_2Si$: C, 52.19; H, 5.84. Found: C, 51.91; H, 5.85. **Preparation of (*E*)-2.** A mixture of 1.35 g (4.9 mmol) of (*E*)-**1** and 1.50 g (5.7 mmol) of triphenylphosphine in 50 mL of acetonitrile was refluxed for 24 h. The solution was then cooled to room temperature, and the solvent was removed in vacuo. Chromatography (0.8 × 15 cm, alumina, 7.5% H_2O, elution series from pentane to 20% ether/pentane) afforded 1.072 g (2.0 mmol, 41%) of red solid: mp 135.6–136.2 °C; IR (CH_2Cl_2) 1940, 1595 cm^{-1} (CO); ^1H NMR (C_6D_6) δ 6.6–7.6 (m, 16 H, Ph and COCH═), 5.58 (d, *J* = 18 Hz, 1 H, ═CHSi), 4.2 (s, 5 H, Cp), 0.05 (s, 9 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 273.02 (d, J_{CP} = 24.4 Hz, acyl CO), 220.42 (d, J_{CP} = 31.7 Hz, CO), 155.47 (d, J_{CP} = 4.88 Hz, C═), 136.34 (d, J_{CP} = 41.5 Hz, Ph), 133.37 (d, J_{CP} = 9.9 Hz, Ph), 129.68 (Ph), 127.95 (d, J_{CP} = 9.8 Hz, Ph), 124.48 (═CSi), 85.48 (Cp), −1.30 (SiC); mass spectrum calcd *m/z* 538.118, found *m/z* 538.118; fast atom bombardment MS (thioglycerin), *m/z* 539 ($[M + H]^+$). Anal. Calcd for $C_{30}H_{31}FeO_2PSi$: C, 66.92; H, 5.80. Found: C, 67.14; H, 5.90. **Preparation of (*E*)-3.** A mixture of 1.072 g (2.0 mmol) of (*E*)-**2** and 0.311 g (2.1 mmol) of solid trimethyloxonium tetrafluoroborate in 30 mL of dichloromethane was stirred for 30 h at room temperature. The solvent was reduced in half by volume, and 20 mL of diethyl ether was added dropwise until a tan precipitate was formed. The solvent was removed by decanting and then by vacuum. This afforded 0.924 g (1.4 mmol, 70% tan glass) of crude product. Recrystallization by dissolving the crude product in CH_2Cl_2, filtering, and then adding ether until precipitation occurred afforded 0.600 g (0.9 mmol, 47%) of red powder: mp 131–132 °C; IR (CH_2Cl_2) 1985 cm^{-1} (CO); ^1H NMR δ 7.3–7.7 (m, 15 H, Ph), 6.67 (d, *J* = 19.3 Hz, 1 H, CH═), 6.26 (d, *J* = 19.3 Hz, 1 H, ═CHSi), 5.17 (d, J_{HP} = 1.5 Hz, 5 H, Cp), 4.25 (s, 3 H, OCH_3), 0.13 (s, 9 H, $SiCH_3$); ^{13}C NMR (acetone-d_6) δ 333.58 (d, J_{CP} = 24.4 Hz, Fe═C), 217.45 (d, J_{CP} = 24 Hz, CO), 151.79 (C═), 150.05 (═CSi), 133.91 (d, J_{CP} = 48.8 Hz, Ph), 133.91 (d, J_{CP} = 9.8 Hz, Ph), 132.28 (Ph), 130.01 (d, J_{CP} = 9.8 Hz, Ph), 88.62 (Cp), 67.60 (OCH_3), −1.84 (SiC); fast atom bombardment MS, calcd *m/z* 553 (carbene cation), found *m/z* 553. Anal. Calcd for $C_{31}H_{34}O_2BF_4FePSi\cdot 0.5CH_2Cl_2$: C, 55.41; H, 5.17. Found: C, 55.51; H, 5.03. **Reaction of (*E*)-3 with TAS-F. Preparation of (*E*)-4.** To a cold (−74 °C) solution of 0.263 g (0.41 mmol) of (*E*)-**3** in 15 mL of THF was added 0.117 g (0.42 mmol) of solid tris(dimethylamino)sulfonium difluorotrimethylsilicate. After the solution was stirred for 3 h, the reaction mixture was warmed to room temperature. The solvent was removed in vacuo, and the crude reaction mixture was extracted thrice with 10 mL of pentane. Removal of solvent in vacuo and recrystallization with pentane afforded 0.187 g (0.33 mmol, 81%) of a pale yellow solid: mp 109.8–110.5 °C; IR (CH_2Cl_2) 1930 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 7.6–7.2 (m, 15 H, Ph), 4.46 (d of d, J_{HH} = 6, J_{HP} = 2 Hz, 1 H, ═CH), 4.24 (d, J_{HP} = 1.2 Hz, 5 H, Cp), 2.76 (s, 3 H, OCH_3), 1.10 (d, *J* = 6 Hz, 3 H, CH_3), 0.21 (d, J_{HF} = 7.5 Hz, 3 H, $SiCH_3$), 0.19 (d, J_{HF} = 7.5, 3 H, $SiCH_3$) (C_α–H was not observed); ^{13}C NMR ($CDCl_3$) δ 222.02 (d, J_{CP} = 35 Hz, CO), 178.00 (d, J_{CP} = 24 Hz, FeC═), 136.95 (d, J_{CP} = 42 Hz, Ph), 133.29 (d, J_{CP} = 9 Hz, Ph), 129.20 (Ph), 127.64 (d, J_{CP} = 9 Hz, Ph), 110.48 (═C), 84.34 (Cp), 54.99 (OCH_3), 24.18 (d, J_{CF} = 13 Hz, CHSi), 15.99 (CH_3), −2.97 (d, J_{CF} = 15.4 Hz, $SiCH_3$); mass spectrum calcd *m/z* 544.145 $[M - CO)^+$, found *m/z* 544.145; fast atom bombardment MS (thioglycerin), *m/z* 573 ($[M + H]^+$), found *m/z* 573.

[7] Middleton, W. J. In *Organic Syntheses*; Kende, A. S., Ed.; Wiley: New York, 1900; Vol. 64, p 221.

[8] Our efforts to obtain suitable X-ray quality crystals of **4** have thus far been unsuccessful. Assuming the thermodynamically more stable conformation of (*E*)-**3** reacts with fluoride from the face anti to the PPh_3 ligand (cf.: Davies, S. G.; Seeman, J. I. *Tetrahedron Lett.* **1984**, *25*, 1845) with concomitant methyl migration to give inversion of configuration at Si (cf.: Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. *Top. Stereochem.* **1984**, *15*, 43), then the major enantiomeric pair of (*E*)-**4** would be configured as (*E*)-(*R*,*R*)-**4** and (*E*)-(*S*,*S*)-**4** (configuration around the metal are based on the priority sequence Cp > PPh_3 > CO > C; cf.: Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598. Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1.

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case, the cationic character of C_α in (*E*)-**3** certainly ameliorates this rearrangement; however, with the (trimethylsilyl)tropylium cation, the only previous example where a partial formal cationic change is present on C_α in a stable compound, introduction of fluoride is reported to give desilation.[10]

The synthetic utility of chiral vinyl trimethylsilanes[4] and chiral allyldimethylfluorosilanes[11] has recently been of interest. Work on the preparation and synthetic applications of chiral transition-metal [(trimethylsilyl)vinyl]carbene complexes as well as achiral and chiral (methoxyallyl)silane complexes[12] is currently being pursued.

Acknowledgment. We wish to thank the National Science Foundation (CHE-8313644) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. (*E*)-1, 112655-64-8; (*E*)-2, 112655-65-9; (*E*)-3, 112655-67-1; (*E*)-4 (isomer 1), 112655-68-2; (*E*)-4 (isomer 2), 112710-88-0; TAS-F, 59218-87-0; (η^5-C_5H_5)Fe(CO)$_2$I, 12078-28-3; (*E*)-1-(tri-*n*-butylstannyl)-2-(trimethylsilyl)ethene, 58207-97-9.

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[10] Hoffmann, R. W.; Reiffen, M. *Tetrahedron Lett.* **1978**, 1107.

[11] Hayashi, T.; Matsumoto, Y.; Ito, Y. *Organometallics* **1987**, *6*, 884 and references cited therein.

[12] Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 107.

Synthesis of Bis(3,4-dimethylcyclopentadienyl)acetylene and Bridged Metallocenes (η^5-C_5Me_5)M[(η^5-$C_5H_2Me_2$)C≡C(η^5-$C_5H_2Me_2$)]M(η^5-C_5Me_5) (M = Fe, Ni) Derived Therefrom

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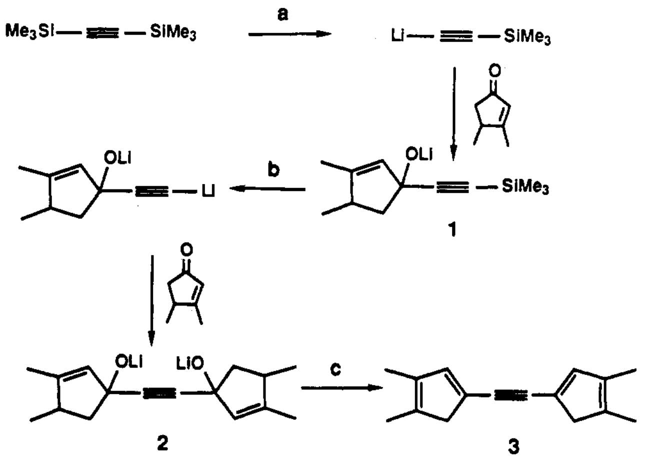
Summary: The synthesis of the binuclear cyclopentadienyl ligand $C_5H_3Me_2C{\equiv}CC_5H_3Me_2$ (**3**) is reported. Reaction of the dilithio salt of **3** with (η^5-C_5Me_5)M(acac) (M = Fe, Ni; acac = acetylacetonate) gives (η^5-C_5Me_5)M[($C_5H_2Me_2$)C≡C($C_5H_2Me_2$)]M(η^5-C_5Me_5) (**4a,b**). Cyclic voltammetry reveals two reversible waves with $\Delta E_{1/2}$ = 160 mV for M = Fe and 265 mV for M = Ni. Compound **4b** has been characterized by X-ray crystallography.

Bridged biferrocenes play a central role in the chemistry of mixed-valence compounds.[1] Since the metallocenes of the first-row transition elements exhibit high stabilities and interesting electronic structures, the bimetallocenes of these metals may be expected to provide additional insights into the nature of metal–metal interactions in coupled binuclear compounds. Owing to the special stability of ferrocene, a number of bridged ferrocenes have been prepared by direct functionalization of the cyclopentadienyl groups. Compounds such as biferrocene,[2] bis(fulvalene)diiron,[3] and bis(ferrocenyl)acetylene[4] were prepared and their properties have been extensively studied over the past years. Unfortunately, this same chemistry cannot be applied to the synthesis of the analogous bridged metallocenes of other metals. As a result, the series of such isostructural compounds is restricted to the bis(fulvalene)dimetal compounds of V,[5] Cr,[6] Fe,[7] Co,[8] Ni,[9] bis(pentalenyl)dinickel,[10] and bis(pentalenyl)dicobalt.[10]

Scheme I



a: MeLi, b: MeLi, c: 1. H_2O 2. p-TosOH

We wish to report a different synthetic strategy to binuclear systems, in which the bridging ligand is prepared by using standard organic procedures for the synthesis of methyl-substituted cyclopentadienes. Reaction of the dilithio salt of the ligand with 2 equiv of (η^5-C_5Me_5)M(acac) (acac = acetylacetonate)[11] provides a clean entry into bridged bimetallocenes. The general utility of this synthetic strategy for preparing bridged derivatives depends upon the availability of the (cyclopentadienyl)–X–(cyclopentadienyl) linking group. Thus, we have undertaken the syntheses of a number of such linked cyclopentadienyl ligands in which the unsaturated organic group X is varied systematically. In the present communication we describe the synthesis of bis(3,4-dimethylcyclopentadienyl)acetylene

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