course of the oxidation of **3** to the alcohol **8** reveals (cf. Table 1) that depending on the nature of the oxidizing agent the one or the other mechanism may predominate. The molybdenum peroxide **9**,[15] the Davis oxaziridine **10**,[16] and the peroxyborate **11**[17] oxidize **3** to **8** under retention of configuration and essentially complete retention of the enantiomeric purity (>90%). On oxidation with bis(trimethylsilyl)peroxide **12**[18] racemization occurs to a noticeable extent. Extensive racemization was observed on oxidation of **3** with the peroxotitanium reagent **13**,[19] with lithium *tert*-butylhydroperoxide,[20] or with dioxygen.

We have described here a route to an enantiomerically enriched chiral secondary Grignard reagent **3** which may serve as a probe to give insights into the mechanisms of Grignard reactions, as demonstrated by the stereochemistry of its oxidation to the alcohol **8**.

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[10] The reaction of the sulfoxide **4** to give the Grignard reagent **3** requires at least three equivalents of ethylmagnesium chloride, since the sulfoxide coproduct **6** consumes a further equivalent of ethylmagnesium chloride leading to the formation of diethyl sulfoxide and *p*-chlorophenylmagnesium chloride. We applied more than three equivalents of ethylmagnesium chloride in order to increase the rate by which **5** is converted into **3**, thereby reducing the fraction of **5** which underwent competing racemization.

[11] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143893. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Unusually Stable Vinyl Cations[**]

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

Recent progress in silylium ion chemistry[1] has opened a novel route for the synthesis of stable carbocations in arene solvents at room temperature. The addition of an arene complex of triethylsilylium to the $C=C$ bond in 1,1-diphenyl ethene has been used to generate a room-temperature stable β-silyl-substituted carbenium ion.[2, 3] Similarly, we have used the intramolecular addition of a silylium ion to a $C=C$ bond to generate the 2-silanorbornyl cation.[4] Vinyl cations,[5] dicoordinated carbocations in which the positive charge is located at a sp-hybridized carbon of a double bond, have been established as reaction intermediates in numerous reactions, such as the solvolysis of activated haloalkenes[6] and alkenes bearing super leaving groups like triflate and nonaflate[7] and protonation reactions of alkynes and allenes.[8] Some persistent vinyl cations have been generated by protonation of alkynes[9] and allenes[10] in superacidic media at temperatures below −100 °C. These cations have been characterized by NMR spectroscopy supported by quantum-mechanical calculations. Herein we report the synthesis of unusually stable vinyl cations by intramolecular addition of transient silylium ions to $C\equiv C$ bonds.

Hydride transfer[11] between 1-alkyl- and 1-aryl-substituted 3,7-disila-3,3,7-dimethyl-octyne-1 (**1**) and trityl cation in benzene is expected to give silylium ion **2** as the first intermediate. The silylium ion **2** may react intermolecularly

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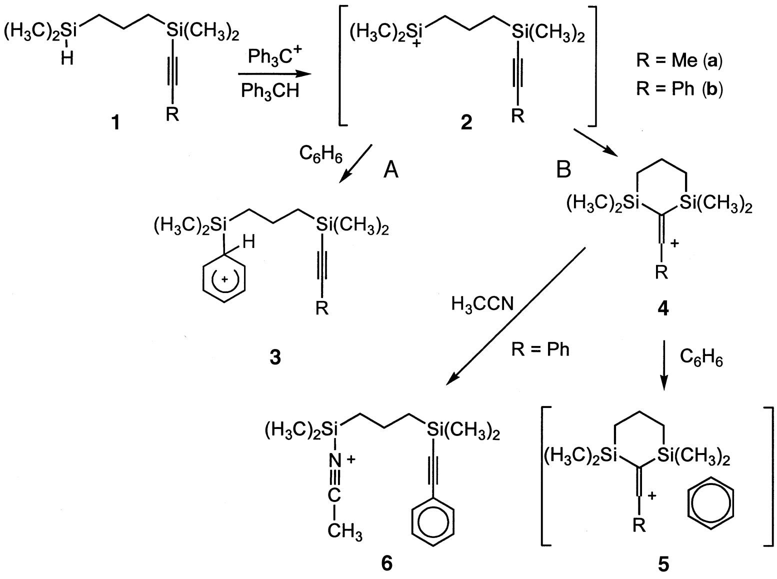
Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.



Scheme 1.

(path A, Scheme 1) with the aromatic solvent to give the silylated areniumion **3**,[12] or could add intramolecularly (path B, Scheme 1) to the C≡C bond yielding the β-disilacyclohexenylidene-substituted vinyl cation **4**. The results of density functional calculations[13] at the hybrid B3LYP/6-31G(d)[14] + ZPVE level of theory reveal that the reactions of the intermediate silylium ions **2a** and **2b** and benzene to form the arenium ions **3a** and **3b**, respectively, are exothermic (by 20.9 and 20.6 kcal mol^{-1}, respectively). The intramolecular cyclization reactions of **2a**,**b** to give the vinyl cations **4a**,**b**, however, are exothermic by 33.0 and 41.7 kcal mol^{-1}, respectively, and thus are more favorable. The association energies A_E between vinyl cations **4a**,**b** and benzene as calculated for the complexes **5a**,**b** are relatively small ($A_E = 3.8$ and 3.1 kcal mol^{-1}, respectively). Therefore, it is unlikely that these complexes are stable at ambient conditions in benzene and the vinyl cations **4a**, **b** are best described as free cations with no direct coordination to the solvent. In conclusion, the analysis of the computational data suggests that vinyl cations **4** should be assessable by the reaction sequence B (Scheme 1) and that they should be stable compounds at ambient conditions in the absence of strong nucleophiles.

Addition of **1b** to a vigorously stirred solution of trityl tetrakis(pentafluorophenyl)borate (TPFPB) in benzene at room temperature instantaneously gives a deeply colored solution which separates into two layers. ^1H and ^{13}C NMR spectra show that the slightly yellow upper layer contains only triphenylmethane. The ^1H, ^{13}C, ^{29}Si, and ^{19}F NMR spectra obtained from the red-brown lower layer of the solution are consistent with the formation of the vinyl cation **4b** (Table 1, Figure 1).[15] The ^{29}Si NMR spectrum shows only one signal at $\delta = 22.8$, indicating the formation of a symmetrical species. This is also supported by the number of signals in the ^{13}C NMR spectrum.[15] The ^{13}C chemical shifts of $\delta = 185.8$ (C^α) and 84.1 (C^β) are characteristic for the $C^\beta{=}C^{\alpha+}$ moiety of vinyl cations. The relatively high-field resonance of the aromatic *ipso*-carbon atom $C^{\beta'}$ ($\delta = 113.7$) is typical for the *ipso*-C(sp^2)-C^α(sp) linkage in aryl-substituted vinyl cations.[16] The strongly deshielded *ortho*- and *para*-carbon atoms of the phenyl substituent indicate considerable charge transfer into the phenyl ring. The NMR chemical shifts of **4b** do not change significantly when the cation is generated in toluene instead of benzene. However, noteworthy changes occur when dry acetonitrile is added to a solution of **4b** in benzene. Two new ^{29}Si NMR signals at $\delta = +35$ and -16 indicate the formation of the linear nitrilium ion **6**.[17] ^{13}C and ^1H NMR data give further support for the formation of **6** (see Table 1 and Supporting Information).

The α-methyl-substituted vinyl cation **4a** is formed analogously to **4b** in a clean reaction by addition of **1a** to a benzene solution of TPFPB. The structure of **4a** is fully supported by the measured ^1H, ^{19}F, ^{13}C, and ^{29}Si NMR data.[18]

Table 1. NMR Chemical shifts of cations **4** and **6**.

	^{13}C NMR						^{29}Si NMR
	$\delta(C^\alpha)$	$\delta(C^\beta)$	$\delta(C^{\beta'})$	$\delta(C^{ortho})$	$\delta(C^{meta})$	$\delta(C^{para})$	δ(Si)
4a[a]	184.8	77.7	9.3	–	–	–	24.1
4b[a]	185.8	84.1	113.7	141.6	130.9	143.0	22.8
4b[b]	185.3	84.1	113.7	141.7	130.9	143.0	22.8
6[c]	106.7	93.0	123.4	128.7	132.1	129.1	33.2, −16.4

[a] At 300 K, in [D$_6$] benzene. [b] At 300 K, in [D$_8$] toluene 300 K, in [D$_6$] benzene/CH_3CN.

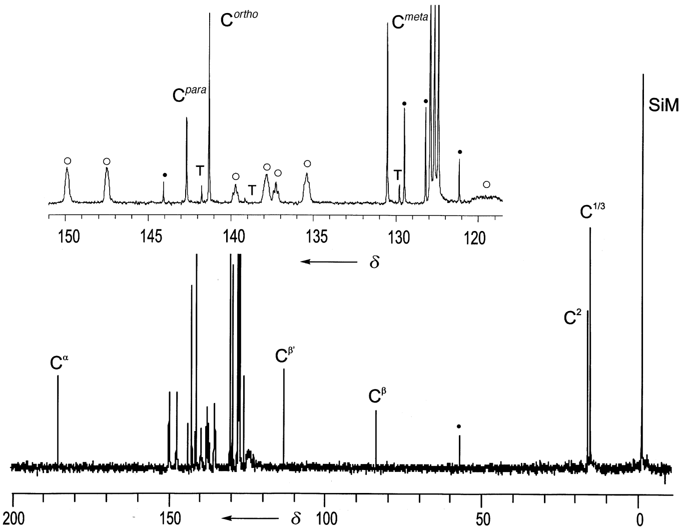


Figure 1. 100 MHz ^{13}C NMR spectra of **4b** in C_6D_6 at 300 K. (○: $[B(C_6F_5)_4]^-$, ●: Ph_3CH, T: Ph_3C^+)

The NMR spectra obtained from a solution of **4b** in benzene remained unchanged for weeks in the absence of nucleophiles; **4a**, however, decomposes during a period of several days into unidentified products. Both compounds, **4a** and **4b**, are strongly stabilized by the well-documented hyperconjugative effect of two β-silyl substituents.[3, 19] Cation **4b** is further stabilized by the electron-donating ability of the α-phenyl group. Both effects become apparent in the calculated geometry and in the natural bond orbital (NBO) charge distribution[20] of **4b** (Figure 2). The high thermostability of the β-disilyl-α-aryl vinyl cation **4b** is in contrast to previous results for β-monosilyl-substituted α-aryl vinyl cations, as for example the α-mesityl-substituted cation **7**, which could be observed in superacidic media only at temperatures below −130 °C.[9a, 16]

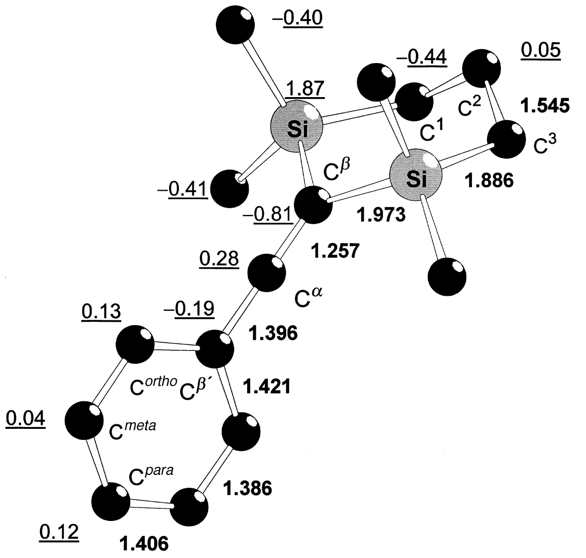
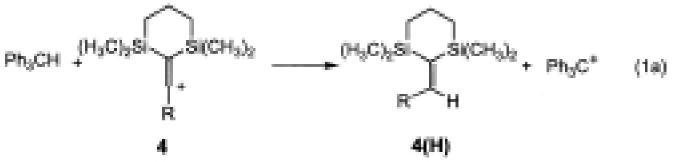
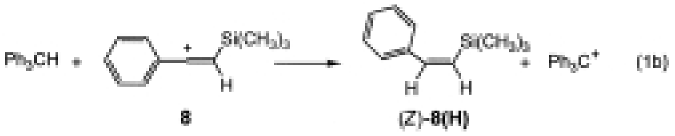
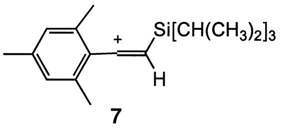


Figure 2. Calculated structure and NBO charge distribution of **4b** (at B3LYP/6-31G(d), H atoms are omitted for clarity). Bond lengths in Å (bold), NBO charges summed in heavy atoms in au (underlined).

According to the isodesmic reactions (1 a) and (1 b), **4b** is only 1.7 kcal mol^{-1} less stable than the trityl cation, and 19.6 kcal mol^{-1} lower in energy than the α-phenyl-β-trimethylsilyl-substituted vinyl cation **8**,[21] a close model for the experimentally investigated cation **7** (at B3LYP/6-31G(d)).[9a]







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The facile generation and stability of **4b** in solution at ambient temperature as compared to β-monosilyl-substituted vinyl cations such as **7** can be attributed to the electronic and steric effects of the second β-silyl substituent which enhances the thermodynamic and kinetic stability. The α-methyl-substituted vinyl cation **4a** is thermodynamically significantly less stabilized than **4b** (i.e. it is 12.5 kcal mol^{-1} higher in energy than Ph_3C^+, [Eq. (1 a)]) due to the weaker electron-donating effect of the α-methyl group, however, it is still lower in energy than **8** by 8.8 kcal mol^{-1}.

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[15] Spectroscopic data of **4b** · $[B(C_6F_5)_4]$: ^1H NMR (400.14 MHz, [D$_6$]benzene, 300 K, $\delta(C_6D_5H) = 7.20$): $\delta = 7.2-7.5$ (m, 3H; H^{ortho}, H^{para}), 6.9 (m, 2H; H^{meta}), 1.42 (m, 2H; H^2), 0.4–0.3 (m, 4H; H$^{1/3}$), −0.05 (s, 12H; CH$_3$); $^{19}F\{^1H\}$ NMR (254.17 MHz, [D$_6$]benzene, 300 K,

$\delta(CF_2Cl_2) = 0$, external): $\delta = -136.9$ (d, 2F, J(F,F) = 8.4 Hz; F^{meta}), -167.7 (tr, 1F, J(F,F) = 20.7 Hz; F^{para}), -171.5 (tr, 2F, J(F,F) = 16.8 Hz; F^{ortho}); $^{13}C\{^1H\}$ NMR (100.63 MHz, [D$_6$]benzene, 300 K, $\delta(C_6D_6) = 128.0$): $\delta = 185.8$ (s; C^{α}), 149.1 (d, ^1J(C,F) = 241.5 Hz; C^{meta} [$B(C_6F_5)_4$]), 143.0 (s; C^{para}), 141.6 (s; C^{ortho}), 139.2 (d, ^1J(C,F) = 251.6H; C^{para} [$B(C_6F_5)_4$]), 137.0 (d, ^1J(C,F) = 251.6H; C^{ortho} [$B(C_6F_5)_4$]), 130.9 (s; C^{meta}), 125.2 (br; C^{ipso} [$B(C_6F_5)_4$]), 113.7 (s; $C^{\beta'}$), 84.1 (s; C^{β}), 16.3 (s; C^2), 15.0 (s; $C^{1/3}$), -0.7 (s; CH_3); $^{29}Si\{^1H\}$ NMR (79.50 MHz, [D$_6$]benzene, 300 K, $\delta((H_3C)_2SiHCl) = 11.7$, external): $\delta = 22.8$.

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[18] Spectroscopic data of **4a**·[$B(C_6F_5)_4$] (For spectroscopic data of the anion, see **4b**). ^1H NMR (400.14 MHz, [D$_6$]benzene, 300 K, $\delta(C_6D_5H) = 7.20$): $\delta = 1.42$ (s, 3H; C^{α}-CH_3), 1.26 (m, 2H; H^2), 0.4–0.3 (m, 4H; $H^{1/3}$), -0.06 (s, 12H; CH_3); ^{13}C NMR (100.63 MHz, [D$_6$]benzene, 300 K, $\delta(C_6D_6) = 128.0$): $\delta = 184.8$ (q, ^2J(C,H) = 9 Hz; C^{α}), 77.7 (s; C^{β}); 15.9 (t, ^1J(C,H) = 131 Hz; C^2), 15.0 (t, ^1J(C,H) = 126 Hz; $C^{1/3}$), 9.3 (q, ^1J(C,H) = 136 Hz; $C^{\beta'}$), -0.8 (q, ^1J(C,H) = 121 Hz; $Si(CH_3)_2$); $^{29}Si\{^1H\}$ NMR (79.50 MHz, [D$_6$]benzene, 300 K, $\delta((H_3C)_2SiHCl) = 11.7$, external): $\delta = 9$.

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[21] For calculating Equation (1 b), the energy of the less stable isomer *Z*-**8(H)** was used. The conformation of the phenyl group relative to the C=C bond is in *Z*-**8(H)** (dihedral angle C^{ortho}-C^{ipso}-C-C $\Theta = 33.7°$) very similar to that in **4b(H)** ($\Theta = 31.0°$), while in *E*-**8(H)** phenyl ring and C=C bond are coplanar ($\Theta = 0.0°$). Using the energy of *E*-**8(H)** in Equation (1 b) would include the more favorable conjugation between the C=C bond and the phenyl substituent. Thus, the comparison between **4b** and **8** would be not balanced.

[(Cp*RuCl)$_2$(μ-Cl)$_2$]: Bond-Stretch or Spin-State Isomerism?**

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The phenomenon of bond-stretch isomerism,[1] the ability of a single molecule to exist in two distinct forms differing only in the length of one or more bonds, has been the source of intense debate ever since the first example, *cis-mer*-[Mo(O)Cl$_2$(PMe$_2$Ph)$_3$], was reported by Chatt and co-workers.[2] Related examples such as [W(O)Cl$_2$(Me$_3$tacn)]$^+$[3] (Me$_3$tacn = *N*,*N'*,*N''*-trimethyl-1,4,7-triazocyclononane) and [Nb(O)Cl$_3$(PMe$_3$)]$^{[4]}$ subsequently emerged, and appeared to establish bond-stretch isomerism as a general feature of the chemistry of metal–ligand multiple bonds. This new form of isomerism naturally aroused much interest among theoretical chemists, notably Hoffmann and co-workers, who used extended Hückel theory to study strained cyclic hydrocarbon species,[1] and, much later, the metal–oxo species noted above.[5] As a result of these calculations, they postulated that a redistribution of electrons within the π framework of the molecule, involving either a crossing of occupied and unoccupied orbitals or a second-order Jahn–Teller effect, could account for the isomerism in [W(O)Cl$_2$(Me$_3$tacn)]$^+$ and *cis-mer*-[Mo(O)Cl$_2$(PMe$_2$Ph)$_3$], respectively. In 1991, however, Hall and Song used more sophisticated ab initio methods to reinvestigate these claims, and reported that they were unable to locate a double minimum on the potential energy surface in either case.[6] At around the same time, a reexamination of the structure of *cis-mer*-[Mo(O)Cl$_2$(PMe$_2$Ph)$_3$] showed that the apparently different Mo=O bond lengths were in fact an artifact of compositional disorder, caused by traces of *mer*-[MoCl$_3$(PMe$_2$Ph)$_3$].[7] This report, in conjunction with the available theoretical data, prompted Parkin to observe in his 1993 review that there was "presently no definitive evidence of bond-stretch isomerism".[8]

Three years previously, Kölle and co-workers[9] had reported that two isomers were present in the unit cell of [(Cp*RuCl)$_2$(μ-Cl)$_2$] (**1**)(Cp* = C$_5$Me$_5$; Figure 1) with very different Ru–Ru separations, 2.930(1) Å (**1a**) and 3.752(1) Å (**1b**). This system has not, however, been widely accepted as an example of bond-stretch isomerism because the nature of the coupling between the metal ions differs in the two isomers: antiferromagnetic in **1a**, ferromagnetic in **1b**. Hoffmann and Parkin have gone to some lengths[10] to distinguish "bond-stretch" isomerism, where both isomers lie on the same potential energy surface, from "spin-state" isomerism, where a change in multiplicity occurs.[11] Within the limits of Hoffmann's definition, the Kölle complex is therefore properly classified as an example of "spin-state" isomerism. Herein broken-symmetry density functional theory is used to establish the fundamental electronic reasons for the co-existence of two isomers in **1**. The validity of the distinction between "bond-stretch" and "spin-state" isomerism is then reexamined in the context of dimetallic clusters.

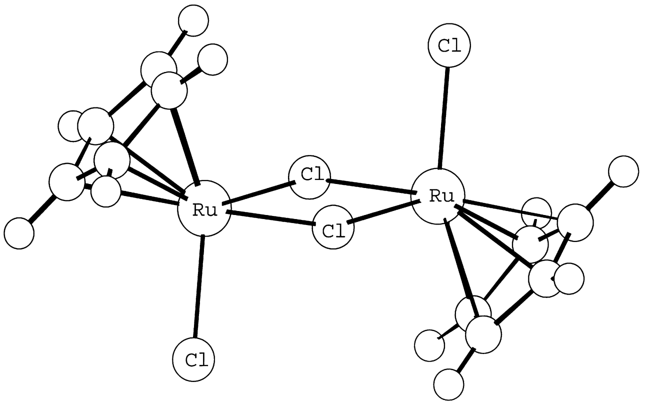

Figure 1. Molecular structure of [(Cp*RuCl)$_2$(μ-Cl)$_2$] (**1**).

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