Organometallics **1996,** *15,* 3859−3867

Unusual "Cation-like" Zirconocene Hydrosilyl Complex. Silylium Ligand or a Nonclassically Bonded Si−H?[1]

Vladimir K. Dioumaev and John F. Harrod*

Chemistry Department, McGill University, Montreal, QC, Canada H3A 2K6

Received April 2, 1996[⊗]

The novel zirconocene complexes $[Cp'_2Zr(\mu\text{-}H)(SiHR)]_2{}^{2+}[BR'_n(C_6F_5)_{4-n}]_2{}^{2-}$ ($Cp' = Cp$, MeCp, Me_5Cp; R = Ph or $PhCH_2$; R′ = Bu or H) were isolated from silane dehydropolymerization reaction mixtures catalyzed by $Cp'_2ZrCl_2/2BuLi/B(C_6F_5)_3$ or by $[Cp'_2Zr(\mu\text{-}H)H]_2/2B(C_6F_5)_3$ combination catalysts. A total structure analysis of these compounds, performed by multinuclear, multidimensional NMR spectroscopy, shows that each zirconocene fragment bears a positive charge, which is delocalized between the metal center and hydrosilane ligand.

Introduction

We recently reported a new type of cationic catalyst for the dehydrocoupling of primary silanes, which proved to have certain advantages over neutral analogues. Our preliminary results indicated significant positive charge on the silicon ligand.[1] In view of the controversy surrounding the existence of cationic silylium in the condensed phase,[2−12] it was of interest to investigate these metal bonded cation-like silylium compounds in more detail. We now report the total structure analysis of the reaction products in solution by multinuclear, multidimensional NMR spectroscopy.

Results and Discussion

I. Total Structure Determination Strategy. Compound **1a** was synthesized from a mixture of Cp_2ZrCl_2, BuLi, $B(C_6F_5)_3$, and $PhSiH_3$ at −20 °C (eq 1) and was

$$Cp'_2ZrCl_2 \xrightarrow[\substack{2.\ B(C_6F_5)_3 \\ 3.\ RSiH_3}]{1.\ 2BuLi} [Cp'_2Zr(\mu\text{-}H)(SiHR)]_2{}^{2+}\ [BBu_n(C_6F_5)_{4\text{-}n}]_2{}^{2-} \quad (1)$$

1a $Cp'_2 = (C_5H_5)_2$; R = Ph
1b $Cp'_2 = (C_5H_5)_2$; R = CH_2Ph
1c $Cp'_2 = (C_5H_5)(Me_5C_5)$; R = Ph
1d $Cp'_2 = (MeC_5H_4)_2$; R = Ph

precipitated from toluene−pentane. Attempts were made to obtain an X-ray quality crystal, but this compound always precipitated as an oil from all aromatic and chloroorganic solvents. The oil solidified to a microcrystalline powder upon washing it with pentane and drying under vacuum. The structure of **1a** has been determined by NMR, IR, and UV measurements as $[Cp_2Zr(\mu\text{-}H)(SiHPh)]_2{}^{2+}[BBu_n(C_6F_5)_{4-n}]_2{}^{2-}$.

The ^1H NMR spectrum of **1a** (Figure 1) contains five groups of signals, which can be readily assigned to the Ph, SiH, Cp, and μ-H−Zr groups in a 5:1:10:1 H ratio together with an alkyl fragment in the aliphatic region of the spectrum. The ^1H chemical shifts (Table 1) for most of these signals are quite characteristic and can also be cross-referenced with the ^{13}C chemical shifts of the directly bonded carbons, extracted from a $^1H-^{13}C$ HMQC experiment. Indeed, the ^{13}C resonances for the Ph and Cp groups (Table 2) appear in the expected regions, while the SiH and ZrH fragments do not show any H−C correlation, indicating a lack of direct bonding of those protons to any carbon atoms. On the other hand, the SiH proton resonance does show a cross-peak to silicon in the $^1H-^{29}Si$ HMQC spectrum ($^1J_{SiH} = 203.5$ Hz), while the ZrH signal shows only a long-range H−Si connectivity ($J_{SiH} = 32.2$ Hz) as expected.

The alkyl group, referred to above, gives rise to four multiplets in the ^1H NMR spectrum and four signals in the ^{13}C NMR spectrum. Their relative intensities indicate a linear $CH_3CH_2CH_2CH_2$ chain, while the chemical shifts and line shapes reveal bonding to quadrupolar boron nuclei.[13] The ^1H COSY spectrum confirms the presence of a linear butyl fragment, as shown by the one-by-one connectivity pattern of all four resonances, none of which has any COSY connectivities to the rest of the ^1H resonances outside the aliphatic region. Instead, the α-CH_2 of the butyl group exhibits a cross-peak due to the coupling to the boron nucleus in the $^1H-^{11}B$ HMQC spectrum and can be tentatively assigned to a $[BBu_n(C_6F_5)_{4-n}]^-$ borate anion structure. The ^{19}F NMR spectrum confirms a tetracoordinated borate structure (Table 3), which is very different from the spectrum of the starting tricoordinate borane. All ^{19}F signals can be separated into three distinct groups, either by a ^{19}F COSY experiment or by a simple intensity reasoning where possible. Each of these groups contains a full set of ortho, meta and para fluorines, representing different borates, $[BBu_n(C_6F_5)_{4-n}]^-$. They

---

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1996.

(1) Part of this work was previously communicated. Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1994**, *13*, 1548−1550.

(2) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917−1918.

(3) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402−404.

(4) Olah, G. A.; Rasul, G.; Li, X.-y.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. S. *Science* **1994**, *263*, 983−984.

(5) Pauling, L. *Science* **1994**, *263*, 983−983.

(6) Lambert, J. B.; Zhang, S. *Science* **1994**, *263*, 984−985.

(7) Reed, C. A.; Xie, Z. *Science* **1994**, *263*, 985−986.

(8) Lickiss, P. D. *J. Chem. Soc., Dalton Trans.* **1992**, 1333−1338.

(9) Chojnowski, J.; Stanczyk, W. *Main Group Chem. News* **1994**, *2*, 6−15.

(10) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191−1201.

(11) Speranza, M. *Chem. Rev.* **1993**, *93*, 2933−2980.

(12) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1−28.

(13) Skrzypczak-Jankun, E.; Cheesman, B. V.; Zheng, B.; Lemert, R. M.; Asthana, S.; Srebnik, M. *J. Chem. Soc., Chem. Commun.* **1994**, 127−128.

S0276-7333(96)00254-3 CCC: $12.00

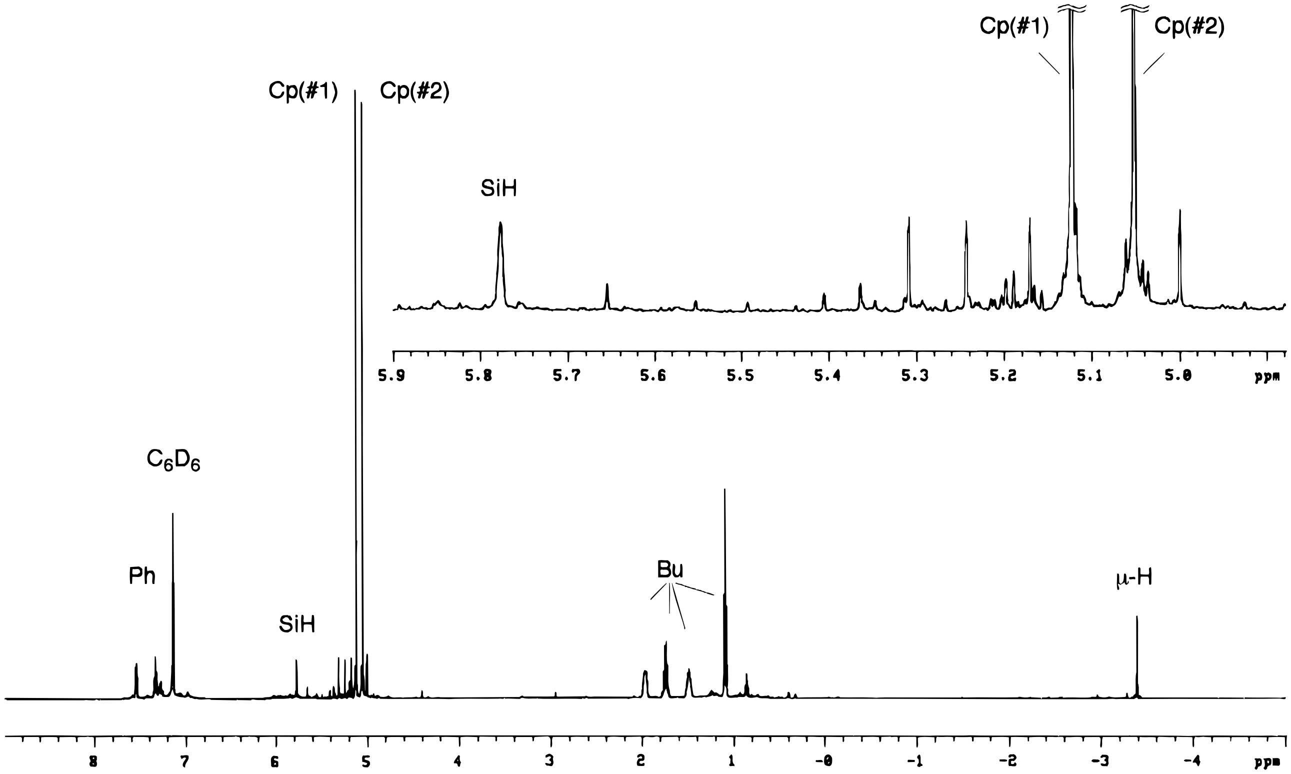


Figure 1. ^{1}H NMR spectrum of **1a** in C_6D_6.

Table 1. ^{1}H NMR Data for 1a−e[a]

	for given compound (solvent)						
	1a (C_6D_6)	**1a** ($C_2D_2Cl_4$)	**1b** (C_7D_8)	**1c** (C_6D_6)	**1c** (C_7D_8)	**1d** (C_6D_6)	**1e**[b] (C_6D_6)
α-Bu	1.96, br m	1.11, br m	1.87, br m	1.99, br s	1.83, br s	1.98, br m	na
β-Bu	1.46, br m	0.76, br m	1.42, m	1.50, m	1.39, m	1.50, br m	na
γ-Bu	1.73, m	1.19, q	1.70, m	1.74, m	1.68, m	1.73, m	na
δ-Bu	1.08, t (7.25)	0.72, t (7.3)	1.08, t (7.3)	1.10, t (7.4)	1.07, t (7.8)	1.08, t (7.3)	na
μ-H	−3.39, s	−2.93, s	−3.90, s	−1.82, −2.85, AX q (15.0, 1.7)	−1.77, −2.81, AX q (15.0, 1.9)	−3.12, s	−3.13
Cp	5.12, s	5.71, s	5.12, s	5.16, s	5.15, s	*c*	*c*
Cp	5.06, s	5.79, s	5.03, s	5.10, s	5.21, s	*c*	*c*
Cp*	na	na	na	1.48, s	1.55, s	na	na
Cp*	na	na	na	1.47, s	1.58, s	na	na
CH_2Si	na	na	2.44, d (5.5)	na	na	na	na
Si−H	5.78, br s	6.17, br s	5.34, m	5.53, br s	5.54, br s	5.83, br s	5.83, br s
o-Ph	7.6−7.4, m	7.8−7.6, m	7.3−6.6, m	7.7−7.5, m	7.72, d (7.5)	7.66, d (7.5)	7.54, d (7.5)
m-Ph	7.0−6.8, m	7.6−7.2, m	7.3−6.6, m	7.3−6.8, m	7.39, t (7.8)	7.32, t (7.7)	7.31, t (7.8)
p-Ph	7.4−7.2, m	7.6−7.2, m	7.3−6.6, m	7.5−7.3, m	7.32, t (7.8)	7.27, t (7.8)	7.28, t (7.8)

[a] The chemical shifts are in parts per million, and the figures in parentheses are coupling constants in hertz. The coupling constants for most of the resonances are not reported as the signals are either second order multiplets or are too broad for an accurate value to be determined. Abbreviations: s, singlet; t, triplet; m, multiplet; br s, broad singlet; br m, broad multiplet; AX q, second order AX quartet; nd, not determined; na, not applicable. All spectra were recorded at +25 °C (except for **1a** in $C_2D_2Cl_4$, which was recorded at −40 °C).
[b] The borate counterion is $[HB(C_6F_5)_3]^-$. The B−H signal has a chemical shift of 2.58 ppm ($^1J_{BH} = 77.3$ Hz, equal intensity quadruplet).
[c] The ^{1}H (this table) and ^{13}C (Table 2) resonances for the directly bonded H and C nuclei in the MeCp ligand are reported in the same order. The Me*Cp* ^{1}H signals are all second order multiplets, *Me*Cp resonances are singlets. ^{1}H chemical shifts (ppm): for **1d**, 5.22, 5.22, 5.07, 5.04, 4.86, 4.86, 4.85, 4.68, 1.71, 1.66; for **1e**, 4.68, 4.83, 4.84, 4.85, 5.03, 5.06, 5.20, 5.20, 1.66, 1.71.

can be tentatively assigned by fitting various integer *n* values from 0 to 4 for each set of ^{19}F resonances so that an average number of Bu groups per borate, calculated this way, is equal to the value obtained from the ratio of ^{1}H NMR Cp and Bu integrals, assuming that there is one borate per zirconocene as the stoichiometry of the reaction requires. The ^{13}C chemical shifts can be extracted from ^{19}F−^{13}C HMQC and HMBC experiments (Table 4). Reactions leading to redistribution of substituents at the boron center and further proof of the ^{19}F resonances assignment will be reported elsewhere.

The zirconocene core of the molecule is established from a ^{1}H COSY experiment. The Cp signals give cross-peaks with the ZrH, which in turn shows connectivities to the SiH and Ph. The proposed structure then is $[Cp_2Zr(\mu\text{-}H)(SiHPhY)]_x$, where *x* is the degree of association and Y is a generic substituent which has yet to be identified. It cannot be another zirconocene group as the bonding electrons of zirconium are already exhausted. Elemental analysis of **1a** rules out Cl as a possible candidate for Y. On the other hand, the fact that the SiH signal is a simple singlet eliminates all elements with abundant magnetic isotopes (Li, B, and F) from being either directly attached to Si or in the α position of group Y. The only exception could be Y = H, where both protons (SiH and SiY) are chemically and

Table 2. ^{13}C and ^{29}Si NMR Data for 1a−e[a]

	for given compound (solvent)						
	1a (C_6D_6)	**1a** ($C_2D_2Cl_4$)	**1b** (C_7D_8)	**1c** (C_6D_6)	**1c** (C_7D_8)	**1d** (C_6D_6)	**1e**[b] (C_6D_6)
α-Bu	23.4	23.2	23.5	23.7	23.2	23.3	na
β-Bu	31.3	30.7	31.1	31.4	31.1	31.2	na
γ-Bu	27.2	27.0	27.2	27.4	27.2	27.2	na
δ-Bu	14.5	14.5	14.3	14.6	14.6	14.4	na
Cp	106.1	106.4	105.5	106.0	107.4	*c*	*c*
Cp	105.9	106.1	105.6	106.9	106.6	*c*	*c*
Cp*	na	na	na	11.8	11.9	na	na
Cp*	na	na	na	11.7	11.9	na	na
CH_2Si	na	na	27.4	na	na	na	na
o-Ph	135.2	135.2	nd	136.2	136.7	135.4	nd
m-Ph	128.0	129.1	nd	128.6	129.0	129.2	nd
p-Ph	128.9	130.9	nd	nd	130.7	130.9	nd
ipso-Ph	nd	135.6	nd	nd	nd	nd	nd
Si−H	105.9 (203.5, 32.2)	110.0 (203.0, nd)	110.9 (203.3, nd)	106.0 (nd)	106.2 (nd)	nd (nd)	101.5 (202.4, nd)

[a] The chemical shifts are in parts per million, and the figures in parentheses are J_{SiH} coupling constants in hertz. The multiplicity of the ^{29}Si resonance is unknown as the data were determined indirectly from a 2D ^{1}H−^{29}Si HMQC experiment. Abbreviations: nd, not determined; na, not applicable. All spectra were recorded at +25 °C (except for **1a** in $C_2D_2Cl_4$, which was recorded at −40 °C). [b] The borate counterion is $[HB(C_6F_5)_3]^-$. [c] The ^{1}H (Table 1) and ^{13}C (this table) resonances for the directly bonded H and C nuclei in MeCp ligands are reported in the same order. ^{13}C chemical shifts (ppm): for **1d**, 107.1, 105.2, 107.1, 104.3, 109.1, 107.5, 101.2, 113.1, 14.7, 14.4; for **1e**, 112.6, 100.4, 107.0, 109.2, 103.8, 105.0, 104.8, 104.8, 13.2, 13.2.

Table 3. ^{19}F NMR Chemical Shifts for $[BBu_n(C_6F_5)_{4-n}]^-$ Anion[a]

	for given compound (solvent)					
	1a (C_6D_6)	**1a** ($C_2D_2Cl_4$)	**1b** (C_7D_8)	**1c** (C_6D_6)	**1c** (C_7D_8)	**1d** (C_6D_6)
o-Ph$^F_2$	−139.7, br s	−141.2, br s	−139.5, br s	−139.0, br s	−139.1, br s	−139.6, br s
m-Ph$^F_2$	−166.0, t (20.7)	−167.3, t (19.8)	−166.1, br s	−166.2, br s	−165.4, t (20.5)	−166.1, t (20.0)
p-Ph$^F_2$	−161.7, t (19.5)	−163.5, t (20.3)	−162.0, br s	−162.0, br s	−161.8, t (20.7)	−161.8, t (20.7)
o-Ph$^F_3$	−134.4, d (24.5)	−136.5, d (23.0)	−134.3, br s		−135.7, d (21.2)	
m-Ph$^F_3$	−168.7, t (20.7)	−170.1, t (19.8)	−168.4, br s		−167.6, t (21.1)	
p-Ph$^F_3$	−166.3, t (21.4)	−167.6, t (20.5)	−166.1, br s		−165.2, t (20.5)	
o-Ph$^F_4$			−132.9, br s	−136.4, br s	−135.5, d (21.2)	−134.6, d (21.2)
m-Ph$^F_4$			nd	−167.6, br s	−167.8, t (21.1)	−168.7, t (20.7)
p-Ph$^F_4$			−165.1, br s	−165.3, br s	−165.4, t (20.5)	−166.3, t (20.7)

[a] The chemical shifts are reported in parts per million, and the figures in parentheses are the J_{FF} coupling constants in hertz. Abbreviations; d, doublet; t, triplet; br s, broad singlet; na, not applicable; nd, not determined. Ph$^F_2$, Ph$^F_3$, and Ph$^F_4$ stand for $[BBu_2(C_6F_5)_2]^-$, $[BBu_1(C_6F_5)_3]^-$, and $[B(C_6F_5)_4]^-$ anions, respectively. All spectra were recorded at +25 °C (except for **1a** in $C_2D_2Cl_4$, which was recorded at −40 °C).

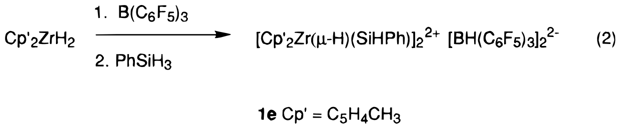
Table 4. ^{13}C NMR Chemical Shifts for the C_6F_5 Groups of the $[BBu_n(C_6F_5)_{4-n}]^-$ Anion[a]

	for given compound (solvent)		
	1a ($C_2D_2Cl_4$)	**1b** (C_7D_8)	**1c** (C_7D_8)
o-Ph$^F_2$	147.6, d m	149.0	148.4
m-Ph$^F_2$	nd	137.4	137.2
p-Ph$^F_2$	138.2, m	139.3	139.1
o-Ph$^F_3$	148.3, d m (236.7)	nd	149.2
m-Ph$^F_3$	136.1, d m (226.5)	nd	136.8
p-Ph$^F_3$	137.1, d m (244.9)	nd	138.0
ipso-Ph$^F_3$	135.3	nd	nd
o-Ph$^F_4$		nd	149.2
m-Ph$^F_4$		nd	136.8
p-Ph$^F_4$		nd	138.0

[a] The chemical shifts are reported in parts per million, and the figures in parentheses are the $^1J_{CF}$ coupling constants in hertz. Most of the $^1J_{CF}$ are unknown as the ^{13}C chemical shifts were determined indirectly from 2D ^{19}F−^{13}C HMQC experiments. Abbreviations: d, doublet; t, triplet; br s, broad singlet; m, multiplet; d m, doublet of multiplets; na, not applicable; nd, not determined. Ph$^F_2$, Ph$^F_3$, and Ph$^F_4$ stand for $[BBu_2(C_6F_5)_2]^-$, $[BBu_1(C_6F_5)_3]^-$, and $[B(C_6F_5)_4]^-$ anions, respectively. All spectra were recorded at +25 °C (except for **1a** in $C_2D_2Cl_4$, which was recorded at −40 °C).

magnetically equivalent and do not exhibit scalar coupling. Although the SiH signal integrates for one H against two Cp groups, the actual number of protons attached to silicon could be higher as the peak is broad and the apparent integral intensity could be misleading. The possibility of a second proton being bonded to silicon was probed by investigating an analogue $[Cp_2Zr(\mu\text{-H})(SiHCH_2Ph)]_2^{2+}[BBu_n(C_6F_5)_{4-n}]_2^{2-}$ (**1b**) with a benzyl group on silicon instead of phenyl. The methylene protons in the former are clearly a doublet in the ^{1}H NMR spectrum as expected for a $=Si(H)CH_2Ph$ fragment as opposed to a triplet for a $-Si(H)_2CH_2Ph$ group, which proves that Y is not H. The last two possible candidates for Y, C and Si, are ruled out by 1D ^{29}Si NMR and long-range ^{1}H−^{13}C and ^{1}H−^{29}Si correlation (HMBC) experiments. The only H(Si) to C cross-peak is to the ipso-carbon of the phenyl ring, which also correlates to the ortho-protons, and the integral intensities confirm that there is only one phenyl group per zirconocene. Furthermore, there is only one peak in the ^{29}Si NMR spectrum, and it is already assigned. Neither are there any long-range H(Si) to Si cross-peaks other than those which belong to the $[Cp_2Zr(\mu\text{-H})(SiHPhY)]_x$ fragment. We have thus dismissed all available nuclei as possible candidates for substituent Y. On the other hand, the existence of a borate anion requires the presence of a positive charge somewhere in the molecule to balance the charge. The fourth "substituent Y" on silicon is then a positive charge, and the structure is proposed to be $[Cp_2Zr(\mu\text{-H})(SiHPh)]_x^{x+}[BBu_n(C_6F_5)_{4-n}]_x^{x-}$. The degree of association (x) can be measured directly from the NMR spectrum of $[CpCp^*Zr(\mu\text{-H})(SiHPh)]_x^{x+}[BBu_n(C_6F_5)_{4-n}]_x^{x-}$ (**1c**). The presence of chemically inequivalent cyclopentadienyl groups (Cp and Cp*) in **1c** results in a diastereotopic relationship between the bridging hydrides, which gives a characteristic *two spin* second order AX quartet. The number of bridging hydrides in **1c** is then two and so is the degree of association. The tendency to dimerize should be even more pronounced in the cases of the less sterically constrained **1a** and **1b**. The other important conclusion from the diastereotopy in **1c** is that there is at least one chiral center in the molecule. In fact, there are two of them, as the Cp rings in **1a** and **1b** are diastereotopic but the other groups are not. The necessary condition to have pairs of nondiastereotopically related groups in a chiral dimer is to have them related by a symmetry operation.[14] This proves that although the dimeric molecule possesses chirality, it is still a symmetric dimer and thus must have an even number of chiral centers.

To probe the validity of the structural analysis, a similar compound, $[MeCp_2Zr(\mu\text{-}H)(SiHPh)]_2^{2+}[BH(C_6F_5)_3]_2^{2-}$ (**1e**), was synthesized by an alternative procedure (eq 2) from $[MeCp_2Zr(\mu\text{-}H)H]_2$, $B(C_6F_5)_3$, and $PhSiH_3$. This synthetic route avoids ambiguities associated with the Cp_2ZrCl_2/2BuLi reagent[15] and furnishes a single borate anion, $[HB(C_6F_5)_3]^-$, which has been reported before.[16] The ^1H and ^{13}C NMR spectra of the zirconocene core of **1e** are almost identical with $[MeCp_2Zr(\mu\text{-}H)(SiHPh)]_2^{2+}[BBu_n(C_6F_5)_{4-n}]_2^{2-}$ (**1d**), which has been synthesized from a mixture of $MeCp_2ZrCl_2$, BuLi, $B(C_6F_5)_3$, and $PhSiH_3$.



$$Cp'_2ZrH_2 \xrightarrow[2.\ PhSiH_3]{1.\ B(C_6F_5)_3} [Cp'_2Zr(\mu\text{-}H)(SiHPh)]_2^{2+}\ [BH(C_6F_5)_3]_2^{2-} \qquad (2)$$

1e $Cp' = C_5H_4CH_3$

In view of the controversy surrounding the existence of cationic silylium in the condensed phase,[2−12] two caveats are offered with respect to the structure of **1**. Firstly, two mesomeric structures are possible (Figure 2), one of them having the positive charge on zirconium, **1′**, the other one on silicon, **1″**. Secondly, a stabilizing interaction with the borate ion and/or solvent cannot be excluded (mesomer **1‴**). The latter interactions, if they exist, must be weak since the solvent (toluene) can be completely removed upon long exposure to high vacuum, and no concentration dependence in the ion pairing in solution for **1a** was detected, *vide infra*.

In the IR spectrum of **1a** a peak is observed at 1216 cm^{-1}, which is absent from the spectrum of a sample of **1a** prepared with $PhSiD_3$. This peak is in the region expected for neutral[17−26] and cationic[27] zirconocene hydrides containing the $Zr_2(\mu\text{-}H)_2$ group. The ν_{SiH} mode appears at 2113 cm^{-1}, in good agreement with the assignment for mesomers **1a″** and **1a‴**.[28] If the structure is visualized in terms of mesomer **1a′**, the 2113 cm^{-1} stretch corresponds to a normal, unperturbed SiH. The low frequency for the other stretch reflects a considerable weakening of the second SiH bond. In the well-documented examples of an agostic SiH−Zr[29] the frequency is decreased by 100−200 cm^{-1}, whereas in **1a** it is shifted by about 900 cm^{-1}. The IR data thus favors mesomer **1a″** and **1a‴** over **1a′**.

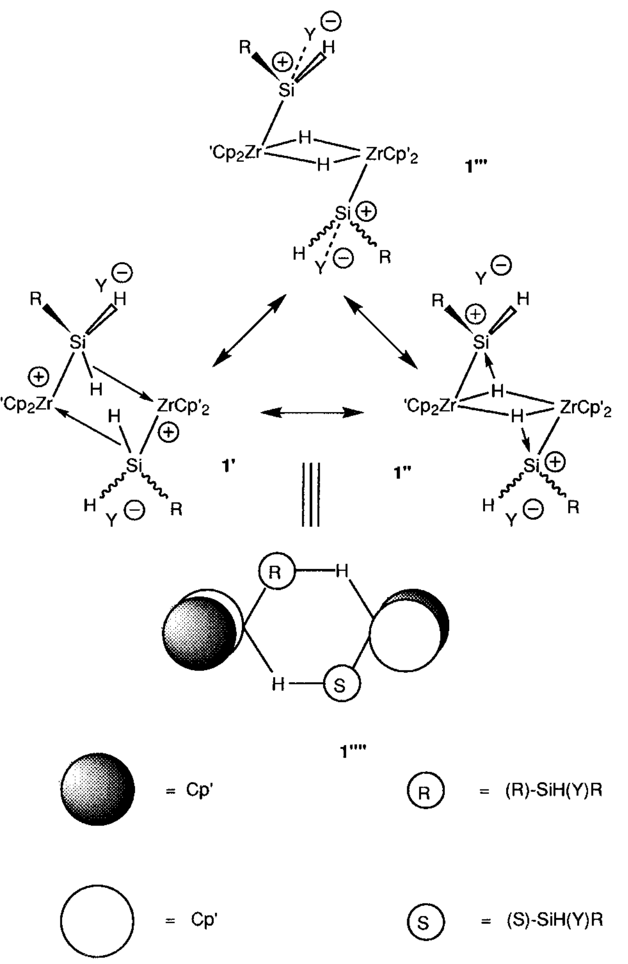


Figure 2. Proposed mesomer structures for **1a**−**e** and their topological representation.

The UV spectrum of **1a** exhibits a weak absorption in toluene at 430 nm ($\epsilon = 165\ dm^3\ mol^{-1}\ cm^{-1}$), similar to that observed previously for zirconocene silyl complexes and tentatively assigned as a silyl ligand-to-metal charge-transfer transition.[30]

From a topological point of view all of the mesomers are identical as they contain the same symmetry elements and can be schematically drawn as **1⁗** (Figure 2). The two chiral silicon atoms and the two possible (cis- and trans-) orientations of the Cp and Cp* ligands

---

[14] Mislow, K.; Raban, M. In *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley: New York, 1967; Vol. 1, pp 1−38.

[15] Dioumaev, V. K.; Harrod, J. F. Submitted for publication in *Organometallics*.

[16] Yang, X.; Stern, C.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375−1377.

[17] Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846−1855.

[18] Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889−2894.

[19] Weigold, H.; Bell, A. P.; Willing, R. I. *J. Organomet. Chem.* **1974**, *73*, C23−C24.

[20] Wailes, P. C.; Weigold, H. *J. Organomet. Chem.* **1970**, *24*, 405−411.

[21] Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933−6937.

[22] Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *43*, C29−C31.

[23] Kautzner, B.; Wailes, P. C.; Weilgold, H. *J. Chem. Soc., Chem. Commun.* **1969**, 1105−1105.

[24] Wailes, P. C.; Weilgold, H. *J. Organomet. Chem.* **1970**, *24*, 405−411.

[25] Wailes, P. C.; Weilgold, H.; Schwartz, J.; Jung, C. *Inorg. Synth.* **1979**, *19*, 223−227.

[26] Erker, G.; Kropp, K.; Kruger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 2447−2460.

[27] Luinstra, G. A.; Rief, U.; Prosenc, M. H. *Organometallics* **1995**, *14*, 1551−1552.

[28] Szymanski, H. A.; Erickson, R. E. *Infrared Band Handbook*, 2nd ed.; IFI/Plenum: New York, 1970; Vol. 1.

[29] Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 177−185.

[30] Woo, H.-G.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 5698−5707.

Table 5. Spacial Relationship of the Cp, Cp*, μ-H, and Si Ligands in 1a, 1b, and 1c

			Cp's		
diastereomer	μ-H	Si–H	diagonal	top/bottom	left/right
(S,S)- or (R,R)-*trans*-**1c**	ni[a] diast	ni diast	ni diast	chemically inequivalent	
(S,S)- or (R,R)-*cis*-**1c**	C_2 equiv	C_2 equiv	chemically inequivalent		C_2 equiv
(S,R)- or (R,S)-*trans*-**1c**	S_2 enant	S_2 enant	S_2 enant	chemically inequivalent	
(S,R)- or (R,S)-*cis*-**1c**	ni diast	ni diast	chemically inequivalent		ni diast
(S,S)- or (R,R)-**1a** or -**1b**	C_2 equiv	C_2 equiv	ni diast		C_2 equiv
(S,R)- or (R,S)-**1a** or -**1b**	S_2 enant	S_2 enant	S_2 enant	ni diast	
achiral[b] *trans*-**1c**	S_2 enant	S_2 enant	S_2 enant	chemically inequivalent	
achiral[b] *cis*-**1c**	C_2 equiv	C_2 equiv	chemically inequivalent		C_2 equiv

[a] Abbreviations: ni, not interchangeable by any symmetry operation; diast, diastereotopic; enant, enantiotopic; equiv, equivalent; C_2, axes of rotation; S_2, axes of rotation-inversion; cis, both Cp* ligands are on one side of the bisectorial plane; trans, on opposite sides. "Diagonal", "top/bottom", and "left/right" ligand labels are given with respect to the bisectorial plane. [b] Planar silicon cation with no chiral center on it.

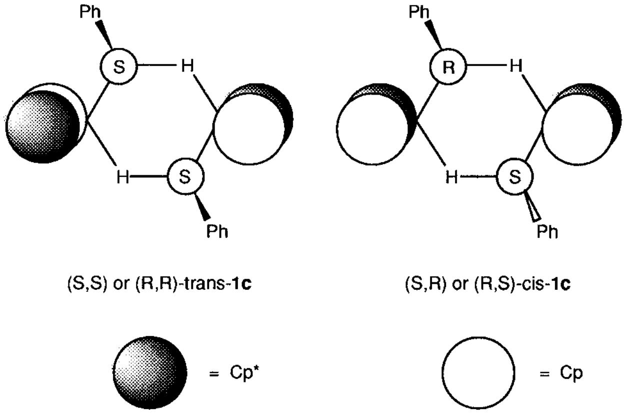


Figure 3. Topological representation of all isomers of **1c**, which agree with the results of the NOESY experiment. Cis stands for an arrangement of both Cp ligands on one side of the bisectorial plane; trans, on opposite sides.

give rise to four diastereomers for **1c** (Table 5). Compounds **1a** and **1b** can only form two diastereomers as all Cp groups are chemically equivalent. Table 5 summarizes the symmetry point groups for all diastereomers and the spatial relationships between potentially diastereotopic groups stemming from them.[14]

Both diastereomers of **1a** and **1b** have diastereotopic Cp groups as reflected in the observed NMR spectra. Unfortunately, it is not possible to establish which isomer is actually formed as the only difference between them is that the SiH and the bridging hydride fragments are enantiotopic in one of them and equivalent in the other. Both of these structures give rise to the same NMR multiplicity pattern. On the other hand the NMR spectrum of **1c** is more informative and can be assigned to only two out of four possible stereoisomers, as the other two do not possess diastereotopic groups (Table 5). One of the two diastereomers can be discarded on steric grounds (Figure 3, (S,R)- or (R,S)-*cis*-**1c**) as it has both Cp* groups on the same side of the bisectorial plane. The other diastereomer ((S,S)- or (R,R)-*trans*-**1c**) is almost identical with the structure of the neutral silyltitanocene dimer, which was studied earlier by single crystal X-ray diffraction.[31] It is not clear why the phenyl groups in this compound adopt a cis arrangement, but at least it proves that there is no significant repulsion between them. Besides, the larger covalent radius of zirconium should further reduce steric interactions between cis phenyl groups and between phenyl and cyclopentadienyl groups. Another possible explanation is that the structure of **1c** could be closer to the mesomeric form **1c**‴ (Figure 2), which has at least a restricted rotation about the Si–Zr axis and does not have to have the two phenyls in a cis arrangement to be (S,S)- or (R,R)-*trans*-**1c**. The ^{29}Si NMR chemical shift for **1c** is in good agreement with the nonplanar geometry of the silicon ligand of mesomer **1c**‴, as compared with the data for organic[2,3,32–34] and organometallic[35] "cation-like" silylium compounds reported previously. It is also favored by the J_{SiH} coupling constants, which differ by an order of magnitude for the Si–H and Si–(μ-H) bonds (203.5 and 32.2 Hz, respectively). The coupling constant of 32.2 Hz is very close to a normal HSi–Zr–H $^3J_{\mathrm{SiH}}$ value,[36,37] which would be expected for **1c**″ and **1c**‴. On the other hand, this value is also within the range for compounds containing nonclassical, or agostic, metal–SiH bonds.[38,39] This suggests that the mesomer structure **1c**′ is feasible as well, although most of the known nonclassical metal–SiH compounds exhibit much higher scalar coupling.[29,36,40–46]

A NOESY experiment is in excellent agreement with the proposed mesomer structures **1c**′ and **1c**″. Each of the bridging hydrides exhibits a cross-correlation to a different pair of Cp and Cp* ligands (Figure 4), which can be rationalized in terms of distorted Zr–H–Zr or inherently asymmetrical Zr–Si–H–Zr bridges. Indeed, the frontier orbitals of zirconocene are in the bisectorial

---

(31) Aitken, C. T.; Harrod, J. F.; Samuel, E. *J. Am. Chem. Soc.* **1986**, *108*, 4059–4066.

(32) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430–2443.

(33) Xie, Z.; Liston, D. J.; Jelinec, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384–386.

(34) Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383–384.

(35) Choe, S.-B.; Kanai, H.; Klabunde, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 2875–2882.

(36) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151–187.

(37) Tilley, T. D. In *Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; pp 246–364.

(38) Spaltenstein, E.; Palma, P.; Kreutzer, K. A.; Willoughby, C. A.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 10308–10309.

(39) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159–1160.

(40) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686–5694.

(41) Scharrer, E.; Brookhart, M. *J. Organomet. Chem.* **1995**, *497*, 61–71.

(42) Ohff, A.; Kosse, P.; Baumann, W.; Tillack, A.; Kempe, R.; Gorls, H.; Burlakov, V. V.; Rosenthal, U. *J. Am. Chem. Soc.* **1995**, *117*, 10399–10400.

(43) Lemke, F. R. *J. Am. Chem. Soc.* **1994**, *116*, 11183–11184.

(44) Luo, X.-L.; Kubas, G. J.; Bryan, J. C.; Burns, C. J.; Unkefer, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 10312–10313.

(45) Schubert, U.; Scholz, G.; Muller, J.; Ackermann, K.; Worle, B. J. *J. Organomet. Chem.* **1986**, *306*, 303–326.

(46) Colomer, E.; Corriu, R. J. P.; Marzin, C.; Vioux, A. *Inorg. Chem.* **1982**, *21*, 368–373.

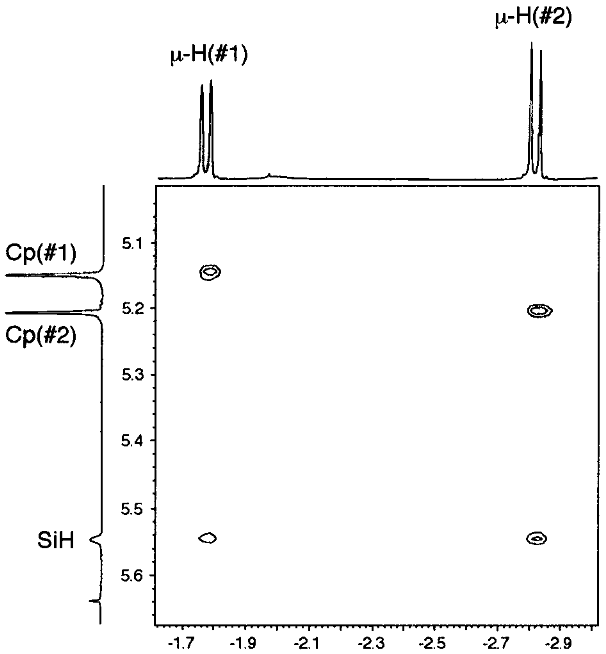


Figure 4. Fragment of an ^{1}H NOESY plot for **1c** which shows that each of the bridging hydrides exhibits a cross-correlation to a different Cp ligand, which can be rationalized in terms of distorted Zr−H−Zr or inherently asymmetric Zr−Si−H−Zr bridges.

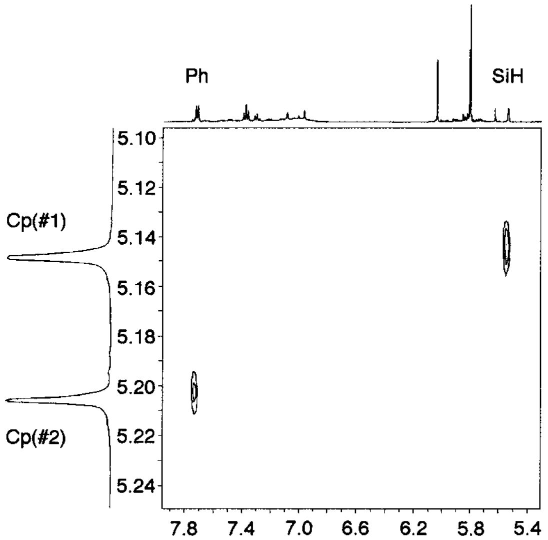


Figure 5. Fragment of an ^{1}H NOESY plot for **1c** which shows that the SiH and Ph groups have NOEs with different Cp ligands, confirming that they appear on different sides of the bisectorial plane (Figure 3, (*S*,*S*)- or (*R*,*R*)-*trans*-**1c** structure).

plane of the sandwich. The bridging hydrides are thus constrained to be in close proximity to that plane, so that the NOEs between μ-H and the cyclopentadienyl groups of the same CpCp*Zr moiety are approximately equal. Experimentally observed pairs of NOE cross-peaks (μ-H(#1) to Cp(#1) and Cp*(#1); μ-H(#2) to Cp(#2) and Cp*(#2)) thus represent the left and the right sides of the bridged dimer with respect to the (μ-H)−(μ-H) axis. The SiH and Ph groups have NOEs with other pairs of Cp and Cp* (Figure 5), confirming that they appear on different sides of the bisectorial plane as predicted from the topological analysis.

No NOE was detected between the butyl group of the borate anion and any proton of the cation, although the relaxation times for the butyl protons (except for the α-CH_2) are of the same order as those for the SiH and μ-H protons, which makes any short cation−anion contacts in **1c‴** (Figure 2) unlikely. There is no evidence for any cation−anion interactions in the ^{19}F NMR spectra either, which casts further doubt on the structure **1c‴**. Although the number of ^{19}F resonances is doubled when a sample of **1c** in C_7D_8 is cooled to −20 °C, it is not due to coordination. If a borate really coordinates through one of the F atoms, a significant upfield shift is expected for the latter[47] and the ratio of integrals for the coordinated/free pentafluorophenyl groups $[(C_6F_5)_{coord}BBu_n(C_6F_5)_{3-n}]^-$ should be strictly $1/(3 - n)$. Besides, if the coordination occurs through ortho or meta fluorines,[16] the pentafluorophenyl group loses C_2 symmetry and the spin system changes from AA′MM′X to ABMNX. None of these changes occur in the cooled samples of **1c**. The multiplicity of the spectrum indicates that all pentafluorophenyls within the borate are C_2 symmetrical and equivalent in a broad temperature range (−40 to +40 °C for $C_2D_2Cl_4$ and −90 to +40 °C for C_7D_8). Careful inspection of the sample revealed that the spectral changes are due to the formation of a second liquid phase (**1c**−C_7D_8 liquid clathrate[48]) upon cooling below −10 °C. The second phase solidifies upon further cooling to −60 to −90 °C, and the ^{19}F spectrum simplifies accordingly (Figure 6).

It can thus be concluded that **1c** is a racemic mixture of (*S*,*S*)- and (*R*,*R*)-*trans*-**1c** isomers, which can be best visualized either as mesomer **1c′** or **1c″**. The SiH coupling constants and the IR data for **1a** suggest that **1c″** corresponds most closely to the true structure of **1c**. The real structure, however, might be a hybrid of both mesomeric extremes, with the positive charge shared between Zr and Si atoms, as indicated by the NMR data.

This charge delocalization can be the source of the surprising stability of the “silylium-like” cation in this case. High-level *ab initio* calculations show that the poor stability of silylium ions in the condensed phase is mainly due to the inefficiency of the hyperconjugative and inductive stabilization of Si^+ by hydrocarbon substituents (Me) as compared to the same effects for C^+. The hyperconjugation is decreased because the energy difference and spatial separation between the pseudo-π(Me) and $2p\pi(Si^+)$ orbitals results in poor overlap. The inductive effect of the alkyl groups destabilizes R_3Si^+ as C is more electronegative than Si.[49−52] On the other hand, the mesomeric form **1″** can have a much better stabilization than trialkylsilylium because of the inductive effect of Zr, which is more electropositive than C and Si, and because of the better hyperconjugation between a Zr−H bond and an unoccupied Si^+ orbital. The latter should be facilitated by the larger size of the Zr- compared to C-centered orbitals. Such hyperconjugation leads to an increase in the Zr−Si bond order, and it is of interest to note that recent calculations on $(CO)_5Cr{=}SiR_2$ (R_2 = H_2, Me_2, F_2, Cl_2, Me(OMe)) com-

---

(47) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910−3918.

(48) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; pp 197−232.

(49) Olsson, L.; Ottosson, C.-H.; Cremer, D. *J. Am. Chem. Soc.* **1995**, *117*, 7460−7479.

(50) Cremer, D.; Olsson, L.; Ottosson, C.-H. *J. Mol. Struct. (THEOCHEM)* **1994**, *313*, 91−109.

(51) Olsson, L.; Cremer, D. *Chem. Phys. Lett.* **1993**, *215*, 433−443.

(52) Schleyer, P. v. R.; Buzek, P.; Muller, T.; Apeloig, Y.; Siehl, H.-U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1471−1473.

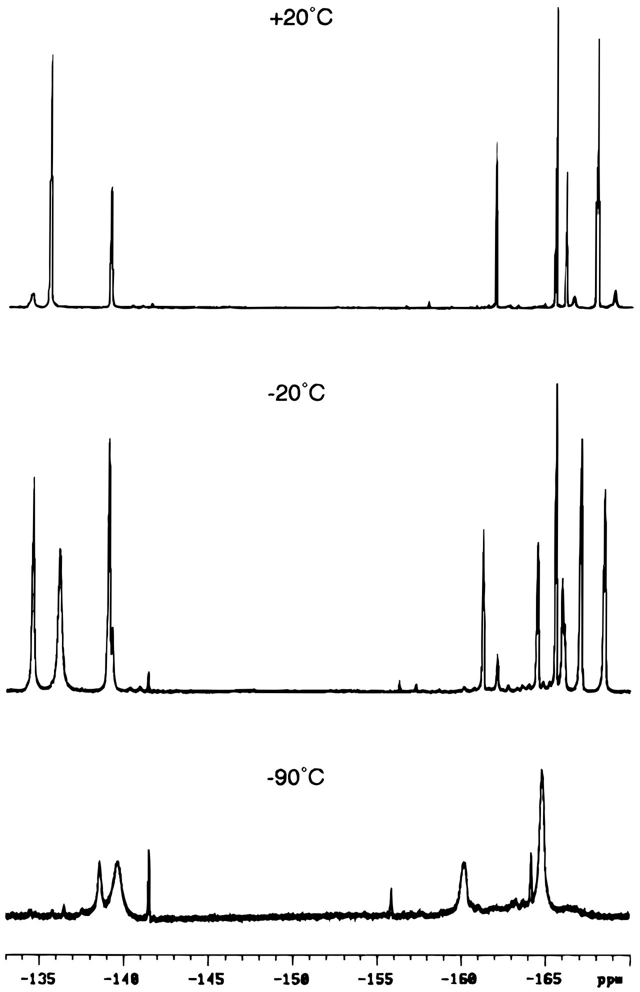


Figure 6. Variable temperature ^{19}F NMR spectra for compound **1c** in C_7D_8. The number of ^{19}F resonances is doubled when the sample is cooled to −20 °C, due to the formation of a second liquid phase (**1c**−C_7D_8 clathrate). The clathrate phase solidifies upon further decrease of temperature (−90 °C), and the ^{19}F spectrum simplifies accordingly.

pounds indicate that substantial contributions to bonding can arise from π-overlaps in transition metal−silicon bonds.[53] Indeed, stable metal−silylene complexes with strong M=Si double bonds are well-known,[54] and their electronic structure can be described adequately.[55] In the cases of Tilley's base-stabilized[56-61] and base-free[62-68] cationic silylene compounds, the π-bond is weaker due to the positive charge on the metal, and the structure could be a hybrid of two mesomers, [M^+=Si] and [M−Si^+]. It should be emphasized that in compounds **1a**−**e** there are no d-electrons on the metal, as opposed to cationic silylene complexes, and there is no posibility of multiple bonding.

II. ^{29}Si NMR Studies of Ion Pairs in Solution. Perhaps the most useful tool for studying the share of the silicon atom in positive charge delocalization is ^{29}Si NMR spectroscopy;[69,70] at the same time it is the source of the most controversial discussions.[8-10,71-73] If there is a partial positive charge on silicon and it exists as an ion pair in solution, then the ^{29}Si chemical shift and $^1J_{SiH}$ coupling constant should be sensitive to the tightness of the ion pair, which in turn is concentration dependent. This type of concentration dependence study requires high dilution, which usually leads to contamination with traces of moisture and oxygen from the solvents. The silylium cation can then degrade, forming Si−O bonds giving rise to deceptively low field chemical shifts. These can then be misinterpreted as less tightly bonded ion pairs or free ions.

In our experiments we used a technique designed to keep the amount of hydrolysis products relative to the sample very low (see Experimental Section). To enhance the ^{29}Si NMR signals, an inverse detection (HMQC) was used, which improved the detection limit by 2 orders of magnitude. This allowed coverage of a concentration range in which up to 98% of the free ions of $R_3Si^+ClO_4^-$ (R = Ph, Me) were previously claimed to exist.[74] It was impossible to test this concentration range by direct detection ^{29}Si NMR techniques due to the low receptivity.[73] As can be seen from the results (Figure 7), neither the ^{29}Si chemical shift nor the $^1J_{SiH}$ coupling constant is significantly dependent on concentration. This suggests that **1a** either exists as free ions in the whole range of concentrations studied or as completely associated tight ion pairs. The former is incompatible with anion stabilized silylium **1a‴** but compatible with the zirconium cation **1a′**, or the internally stabilized silylium **1a″**. The latter is unlikely since even more polarizing cationic titanocene complexes, with the more coordinative $AlCl_4^-$ counterion, ionize extensively in chloroalkane solutions.[75] Still further evidence in favor of negligible bonding between anion and cation is the identity of the NMR parameters for the anion in **1a** to those of $[Ph_3C]^+[BBu_2(C_6F_5)_2]^-$ and

---

(53) Jacobsen, H.; Ziegler, T. *Organometallics* **1995**, *14*, 224−230.

(54) Zybill, C. E.; Liu, C. *Synlett* **1995**, *7*, 687−699, and references cited therein.

(55) Cundary, T. R.; Gordon, M. S. *Organometallics* **1992**, *11*, 3122−3129.

(56) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872−5873.

(57) Zhang, C.; Grumbine, S. D.; Tilley, T. D. *Polyhedron* **1991**, *10*, 1173−1176.

(58) Grumbine, S. D.; Chadha, R. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1518−1520.

(59) Kawano, Y.; Tobita, H.; Shimoi, M.; Ogino, H. *J. Am. Chem. Soc.* **1994**, *116*, 8575−8581.

(60) Kobayashi, H.; Ueno, K.; Ogino, H. *Organometallics* **1995**, *14*, 5490−5492.

(61) Grumbine, S. K.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 127−148.

(62) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801−7802.

(63) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673−2681.

(64) Lee, K. E.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 309−320.

(65) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358−360.

(66) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884−7885.

(67) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 5495−5496.

(68) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951−6952.

(69) Olah, G. A.; Rasul, G.; Heiliger, L.; Bausch, J.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 7737−7742.

(70) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485−1487.

(71) Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H.-K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123−5126.

(72) Olah, G. A.; Heiliger, L.; Li, X.-Y.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1990**, *112*, 5991−5995.

(73) Lambert, J. B.; Kania, L.; Schilf, W.; McConnell, J. A. *Organometallics* **1991**, *10*, 2578−2584.

(74) Lambert, J. B.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 6364−6367.

(75) Eisch, J. J.; Pombrik, S. I.; Zheng, G.-X. *Organometallics* **1993**, *12*, 3856−3863.

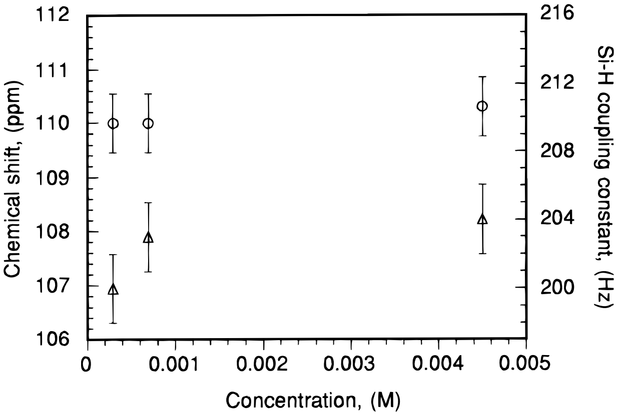


Figure 7. ^{29}Si chemical shift (○) and the $^1J_{SiH}$ coupling constant (△) versus concentration plots for **1a**. The sample does not exhibit any ion pairing effects in the studied range of concentrations.

of the parameters for the anion in **1e** to those of [Cp*$_2$-ZrH][BH(C$_6$F$_5$)$_3$].[16]

The very existence of silylium compounds has been challenged[4,5] as, in all the known examples, there are weak bonding contacts between R$_3$Si$^+$ and another group (S)[2,3,10,32−34] and the positive charge was calculated to be localized mainly on that group rather than on Si.[4,49−52] However, the ability of compounds [R$_3$Si···(S)]$^+$[X]$^-$ to ionize in halocarbon solvents is beyond any doubt,[2,10,32,34] and even if the resulting [R$_3$Si···(S)]$^+$ ions have no silylium character, the ^{29}Si NMR chemical shifts should still be sensitive to that type of ion pairing.[49]

III. Ion Exchange Reaction. An attempt to probe the charge delocalization between Zr and Si in **1** by reaction with CsF did not give a clear result. Reaction of **1a** and CsF in THF proceeded vigorously, and a number of unidentified products were formed (at least six major peaks in the Cp region). However, an ^{1}H−^{29}Si coupled HMQC experiment revealed only one Si-containing product in the reaction mixture ($\delta = -42.5$ ppm, $^1J_{SiH} = 172.5$ Hz, $J_{FH} = 14.2$ Hz). The concentration was not high enough to obtain a 1D ^{29}Si NMR spectrum, and the resolution in the ^{1}H−^{29}Si HMQC experiment was not high enough to resolve the F−Si coupling constant. Failure to resolve this peak places an upper limit of 20 Hz on any J_{FH}. Even though, the information was insufficient to identify the full structure of this product, the values for J_{FH} and J_{SiF} are characteristic enough to favor a structure containing HSi−[Zr]F rather than [Zr]−Si(H)F ($^2J_{HSiF}$ coupling constants are usually in the range of 45−65 Hz,[76] and $^1J_{SiF}$ are never as low as 20 Hz [77]).

Other attempted ion exchange reactions, with MeLi or with [NBu$_4$]F, gave even more inconclusive results.

Conclusions

Novel zirconocene complexes **1a**−**e** were isolated from silane dehydropolymerization reaction mixtures catalyzed by Cp′$_2$ZrCl$_2$/2BuLi/B(C$_6$F$_5$)$_3$ or by [Cp′$_2$Zr(μ-H)H]$_2$/2B(C$_6$F$_5$)$_3$ combination catalysts. In the absence of X-ray quality crystals, a total structure analysis of these compounds was performed by multinuclear, multidimensional NMR spectroscopy. A 3D structure, unambiguously determined by a set of homo- (COSY, TOCSY, and NOESY) and heterocorrelation (HMQC and HMBC) experiments, shows that each zirconocene fragment bears a positive charge, which is delocalized between the metal center and the hydrosilane ligand. Ion exchange reactions with CsF indicate that much of the positive charge is localized on Zr. However, it is likely that the positive charge is really delocalized between Zr and Si and cannot be assigned to only one particular atom. The structures of **1a**−**e** are best visualized as a hybrid of two mesomeric forms **1′** and **1″**, which can be formally described either as zirconocene with an internally stabilized silylium ligand or cationic zirconocene with an α-agostic (or nonclassically bonded) Si−H. A lack of concentration dependence for the ^{29}Si NMR chemical shifts and $^1J_{SiH}$ coupling constants is in agreement with this interpretation.

Experimental Section

Materials and Methods. All operations were performed in Schlenk-type glassware on a dual-manifold Schlenk line, equipped with flexible stainless steel tubing, or in an argon-filled M. Braun Labmaster 130 glovebox (<0.05 ppm H$_2$O). Argon was purchased from Matheson (prepurified for the glovebox and ultrahigh purity (UHP) for the vacuum line) and was used as received. Hydrocarbon solvents (protio- and deuteriobenzene, and toluene, pentane, and hexanes) were dried and stored over Na/K alloy, benzophenone, and 18-crown-6 in Teflon-valved bulbs and were vacuum transferred prior to use. THF was vacuum transferred from sodium benzophenone ketyl. Halogenated solvents and silanes (1,1,2,2-tetrachloroethane-d_2, C$_6$F$_5$Br, PhSiH$_3$, and PhCH$_2$SiH$_3$) were degassed and stored over molecular sieves. Cp$_2$ZrCl$_2$, Me$_5$C$_5$H, ZrCl$_4$, C$_6$D$_6$, C$_7$D$_8$, 1,1,2,2-tetrachloroethane-d_2, C$_6$F$_5$Br, CsF, PhC(O)Ph, 18-crown-6, BCl$_3$ (1.0 M in heptane), n-BuLi (1.6 M in hexanes), CpNa (2.0 M solution in THF), and CDCl$_3$ were purchased from Aldrich and used as received unless stated otherwise.

The compounds (MeCp)$_2$ZrCl$_2$,[78] [(MeCp)Zr(μ-H)H]$_2$,[18] CpCp*ZrCl$_2$,[79] B(C$_6$F$_5$)$_3$,[80] and RSiH$_3$ (R = Ph and PhCH$_2$)[81] were prepared according to literature procedures.

Physical and Analytical Measurements. NMR spectra were recorded on a Varian Unity 500 (FT, 500 MHz for ^{1}H), Varian XL-200, or Varian Gemini-200 (FT, 200 MHz for ^{1}H) spectrometers. Chemical shifts for ^{1}H and ^{13}C spectra were referenced using internal solvent references and are reported relative to tetramethylsilane. ^{11}B, ^{19}F, and ^{29}Si spectra were referenced to external Et$_2$O·BF$_3$, CF$_3$COOH, and Si(CH$_3$)$_4$, respectively. Quantitative NMR measurements were performed using residual solvent protons as internal references. IR and UV spectra were recorded on Brucker IFS-48 (FT) and HP-8452A (FT) spectrometers, respectively. Elemental analyses were performed by Oneida Research Services, Inc., Whitesboro, New York.

All NMR samples were prepared in an NMR-tube assembly, consisting of one or more 2 mL round-bottom flasks fitted with a Teflon valve to which an NMR tube was fused at an angle of 45°. Components of an NMR sample were loaded separately, when necessary, in each of the flasks and were mixed in appropriate order by transferring from one flask of choice to the other by tilting of the entire apparatus. A sample was

---

(76) Frankiss, S. G. *J. Phys. Chem.* **1967**, *71*, 3418−3421.

(77) *Recent Advances in Silicon-29 NMR Spectroscopy*; Williams, E. A., Ed.; Academic: London, 1983; Vol. 15, p 276.

(78) Samuel, E. *Bull. Soc. Chim. Fr.* **1966**, 3548−3564.

(79) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793−799.

(80) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250.

(81) Finholt, A. E.; Bond, A. C. J.; Wilzbach, K. E.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1947**, *69*, 2692−2696.

treated with small quantities (0.1–0.2 mL) of a deuterated solvent of choice. The solvent was then evaporated, and the evaporation–vacuum transfer cycle was repeated to remove any residual traces of nondeuterated solvent. A fresh portion of the same deuterated solvent (0.6–0.7 mL) was then vacuum transferred into the assembly, and the solution was carefully decanted into the side NMR tube. The top part of the tube was washed by touching it with a swab of cotton wool soaked with liquid nitrogen, which causes condensation of the solvent vapors on the inner walls. The sample was then frozen and flame sealed.

$[Cp_2Zr(\mu\text{-}H)(SiHPh)]_2^{2+}[BBu_n(C_6F_5)_{4-n}]_2^{2-}$ (1a),[1] Low-Temperature Synthesis. Part A. Cp_2ZrCl_2 (0.219 g, 0.75 mmol) and $(C_6F_5)_3B$ (0.384 g, 0.75 mmol) were loaded into separate Schlenk tubes in the glovebox. On the vacuum line, toluene was vacuum transferred into both tubes (8 mL each). The Cp_2ZrCl_2 was suspended in toluene at −41 °C (CH_3CN–dry ice bath), and a 2.5 M solution of BuLi in hexanes (0.6 mL, 1.50 mmol) was added. The mixture was stirred at −41 °C for 1 h. The color gradually changed from white to light yellow. The toluene solution of $(C_6F_5)_3B$ was cooled to −41 °C and was slowly transferred by cannula into the butylated zirconocene solution. A brown-red oil was formed almost instantaneously. The reaction mixture was protected from light with aluminum foil and was left stirring for 30 min. $PhSiH_3$ (0.56 mL, 4.50 mmol) was then added, and the stirring was continued for a further 3 h while the solution was allowed to warm gradually to room temperature. The solvent was partially evaporated (leaving 1–2 mL), and pentane was vacuum transferred into the tube, causing precipitation of a yellow slurry. The brown mother liquor was removed, and the bright yellow residue was washed with two additional portions of pentane (2 × 10 mL) and dried under vacuum to furnish a yellow microcrystalline powder.

Part B. The yellow solid was redissolved in toluene (300 mL) and was left standing for 3 days in the dark to allow precipitation of LiCl. The brownish-yellow mother liquor was carefully separated from the white precipitate and evaporated almost to dryness. The resulting slurry was washed with a 5% solution of toluene in pentane (2 × 10 mL) and with pure pentane (2 × 10 mL). The resulting yellow powder was dried under high vacuum for 2 days; yield 57%. IR (powder, cm^{-1}): 1216 (ν_{ZrH}), 2113 (ν_{SiH}). UV–vis (toluene, nm ($dm^3\ mol^{-1}\ cm^{-1}$)): λ (ϵ) 335 (3190), 430 (165). Anal. Calcd for $C_{76}H_{52}B_2F_{30}Si_2Zr_2$: C, 50.84; H, 2.92, N, 0.00; Cl, 0.00. Found: C, 50.45; H, 2.77; N, 0.00; Cl, 0.00. ^{11}B-NMR (C_6D_6, 25 °C): δ −24.3 and −24.8 (s, $[BBu_n(C_6F_5)_{4-n}]^-$, $n = 0, 2$); ^{11}B-NMR ($C_2D_2Cl_4$, −40 °C): δ −25.2 (s, $[BBu(C_6F_5)_3]^-$).

$[Cp_2Zr(\mu\text{-}H)(SiHPh)]_2^{2+}[BBu_n(C_6F_5)_{4-n}]_2^{2-}$ (1a), Room Temperature Synthesis. The title complex was synthesized using the same procedure as that for **1a** (part A), but all reactions were done at room temperature. The product was dark purple and was contaminated by poly(phenylsilane) and unidentified paramagnetic compounds (crude yield ~75%).

$[Cp_2Zr(\mu\text{-}H)(SiHCH_2Ph)]_2^{2+}[BBu_n(C_6F_5)_{4-n}]_2^{2-}$ (1b). The title complex was synthesized using the same procedure as that for **1a** (part A) by the reaction of Cp_2ZrCl_2 (0.073 g, 0.25 mmol), BuLi in hexanes (0.2 mL, 0.50 mmol), $(C_6F_5)_3B$ (0.128 g, 0.25 mmol), and $PhCH_2SiH_3$ (0.139 mL, 1.0 mmol) (crude yield ~70%).

$[Cp'Cp''Zr(\mu\text{-}H)(SiHPh)]_2^{2+}[BBu_n(C_6F_5)_{4-n}]_2^{2-}$ ($Cp'Cp'' = CpCp^*$, $(MeCp)_2$) (1c,[1] 1d). The title compounds were synthesized using the same procedure as that for **1a** (part A) by the reaction of $CpCp^*ZrCl_2$ (0.136 g, 0.375 mmol) or $(MeCp)_2ZrCl_2$ (0.120 g, 0.375 mmol) with BuLi in hexanes (0.3 mL, 0.75 mmol), $(C_6F_5)_3B$ (0.202 g, 0.39 mmol), and $PhSiH_3$ (0.185 mL, 1.5 mmol) (crude yield ~70%). ^{11}B-NMR (C_6D_6, 25 °C): for **1c**, δ −24.4 (s, $[B(C_6F_5)_4]^-$), δ −24.5 (br s, $[BBu_n(C_6F_5)_{4-n}]^-$, $n = 0, 1, 2$); for **1d**, δ −24.6 (br s, $[BBu_n(C_6F_5)_{4-n}]^-$, $n = 0, 2$).

$[(MeCp)_2Zr(\mu\text{-}H)(SiHPh)]_2^{2+}[BH(C_6F_5)_3]_2^{2-}$ (1e). $[(MeCp)_2Zr(\mu\text{-}H)H]_2$ (0.025 g, 0.05 mmol) and $(C_6F_5)_3B$ (0.056 g, 0.11 mmol) were loaded into separate flasks of the double flask NMR assembly, *vide supra*, in the glovebox, and toluene was then vacuum transferred into both flasks (2 mL each). The apparatus was immersed in an acetone–dry ice bath (−78 °C), the reagents were mixed together, and the mixture was stirred for 30 min at −78 °C and for 3 h at room temperature. The color gradually changed from white to light yellow and light purple. The solvent was removed under vacuum, and the residue was washed with pentane (2 × 5 mL). A fresh portion of toluene (5 mL) was vacuum transferred into the flask, and $PhSiH_3$ (0.05 mL, 0.40 mmol) was added. The reaction mixture was protected from light with aluminum foil and was left stirring overnight. The solvent was partially removed (leaving 0.5–1 mL), and pentane was vacuum transferred into the flask, causing precipitation of a yellow solid. The clear mother liquor was removed, and the residue was washed with an additional portion of pentane (5 mL). The sample was dried under high vacuum, and an NMR sample was prepared as described above.

NMR data for $[BH(C_6F_5)_3]^-$ (C_6D_6, 25 °C). ^{11}B-NMR: δ −25.6 (s). ^{13}C-NMR: δ 148.2 (o-C_6F_5), 138.6 (p-C_6F_5), 136.8 (m-C_6F_5). ^{19}F-NMR: δ −139.1 (d, $J_{FF} = 15$ Hz, o-C_6F_5), −163.1 (t, $J_{FF} = 20.5$ Hz, p-C_6F_5), −167.2 (br t, m-C_6F_5). The rest of the NMR data for **1e** are reported in Tables 1 and 2.

^{29}Si NMR Studies of Ion Pairing in Solution. In the drybox, **1a** (0.0045 g, 0.0025 mmol) and 1,1,2,2-tetrachloroethane-d_2 (0.55 mL) were loaded in an NMR container, attached to a Teflon valve, and flame sealed under vacuum. To minimize the danger of side reactions, the measurements were performed at −40 °C immediately after the preparation of the sample.

A special NMR tube with a small, pendant bulb at the top was used to prepare highly diluted samples. The shape of the apparatus allowed it to be inserted in the standard 5 mm probe of the NMR spectrometer. Most of the original sample was poured into the bulb by tilting the NMR tube. The solvent was then vacuum transferred back into the tube, leaving the nonvolatile materials in the bulb. A single tilting-vacuum transfer cycle allowed at least a 10-fold dilution. No new impurities were introduced no matter how many dilution cycles were done, since the apparatus was flame sealed. The concentration changes were readily estimated by comparison of the residual solvent proton integrals (constant throughout the experiment) with those of the Cp ligands of **1a**. The dilution–measurement cycles were done until the detection limit for ^{29}Si nuclei was reached.

Reaction of 1a with CsF. CsF (0.003 g, 0.02 mmol) and **1a** (0.009 g, 0.005 mmol) were charged in the NMR assembly, *vide supra*, in the glovebox. On the vacuum line, THF was then vacuum transferred (1 mL) and the mixture was left stirring for 3 h. The color of the reaction mixture changed from yellow to black. The solvent was evaporated under vacuum, and an NMR sample was prepared in C_6D_6.

NMR (C_6D_6, 25 °C). ^{1}H-NMR: δ 7.85 (m, Ph), 7.35 (m, Ph) 7.20 (m, Ph), 6.00 (s, Cp), 5.28 (s, Cp), 5.27 (s, Cp), 5.15 (s, Cp), 4.94 (s, Cp), 4.93 (s, Cp), 4.85 (d, $J_{HF} = 14.2$ Hz, SiH), 1.83 (m, α-Bu), 1.68 (m, γ-Bu), 1.44 (m, β-Bu), 1.08 (t, $^2J_{HH} = 7.3$ Hz, δ-Bu), −5.55 (s, μ-H). ^{19}F-NMR for $[BBu_2(C_6F_5)_2]^-$, δ −135.8 (d, $J_{FF} = 20.2$ Hz, o-C_6F_5), −164.0 (t, $J_{FF} = 20.5$ Hz, p-C_6F_5), −167.8 (t, $J_{FF} = 20.5$ Hz, m-C_6F_5); for $[BBu_1(C_6F_5)_3]^-$, δ −134.0 (d, $J_{FF} = 20.2$ Hz, o-C_6F_5), −165.7 (t, $J_{FF} = 20.4$ Hz, p-C_6F_5), −168.4 (t, $J_{FF} = 20.5$ Hz, m-C_6F_5); for $[B(C_6F_5)_4]^-$, δ −132.5 (d, $J_{FF} = 20.2$ Hz, o-C_6F_5), −165.9 (t, $J_{FF} = 20.6$ Hz, p-C_6F_5), −168.6 (t, $J_{FF} = 20.5$ Hz, m-C_6F_5), −133.2 (d, $J_{FF} = 20.2$ Hz). ^{29}Si-NMR: δ −42.5 ($J_{HSi} = 172.5$ Hz, SiH).

No reaction occurred when CsF and **1a** were mixed in C_6D_6.

Acknowledgment. Financial support for this work from the NSERC of Canada and Fonds FCAR du Québec is gratefully acknowledged.

OM960254M