Synthesis and Properties of Bridgehead-Functionalized Permethylbicyclo[2.2.2]octasilanes

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Supporting Information

ABSTRACT: A series of previously unknown bridgehead-functionalized bicyclo[2.2.2]octasilanes, Me2Si-SiMe12-X, X=SiMe12-Y [X, Y = –SiMe3, Ph, n (n = 1, 2) (2, 3, 10), –SiMe2Fc (Fc = ferroceny) (4, 11, 13, 14)], –COR (R = Me, iBu) (6, 7, 12), COOME (8), COOH (9), have been prepared by the reaction of the silanides Me2Si-SiMe12-K+ or K-SiMe2Fc (Fc = ferroceny) with proper electrophiles and fully characterized. The molecular structures of 2, 3, 4, 6, 8, 9, 10, and 13 as determined by single-crystal X-ray diffraction analysis exhibit a slightly twisted structure of the bicyclooctasilane cage. Endocyclic bond lengths, bond angles, and dihedral angles are not influenced considerably by the substituents attached to the bridgehead silicon atoms. Due to (SiMe3)/(Si(aryl)) conjugation, a 20–30 nm bathochromic shift of the longest wavelength UV absorption band relative to Me2Si-SiMe12-SiMe2 (1) is evident in the UV absorption spectra of the phenyl and ferrocenyl derivatives. Otherwise, UV absorption data do not support the assumption of aryl/aryl or aryl/C=O interaction via the (SiMe3) bicyclooctasilane framework.

INTRODUCTION

Oligo- and polysilanes have been extensively studied due to their chemical stability and due to their unique electronic properties, which more or less can be related to the extensive delocalization of σ-electrons along the silicon skeleton (σ-delicitation).1 σ-Delicitation within cyclic Si–Si frameworks is particularly well established,2 giving rise to pronounced substituent effects on the properties of the Si–Si backbone such as long-wavelength UV absorption up to the visible range,3 room-temperature photoluminescence,4 nonlinear optical behavior,5 and photochemical activity.6 Furthermore, σ-conjugated cyclopolysilane bridges have been shown to be better mediators for electronic effects in bichromophoric covalently linked donor–bridge–acceptor (D–br–A) compounds as compared to their open-chained counterparts.7 Wurtz-type coupling has also been applied to the synthesis of polysilanes with bicyclic or cage-like structures.6 In many cases, however, poor yields and severe problems in the course of the isolation of the desired reaction products were encountered. Thus, tetradecamethylbicyclo[2.2.2]octasilane (1-Me2) has been prepared for the first time in <5% yield by West using Na/K condensation of Me3SiCl2/MeSiCl3 mixtures.10 In order to enhance the selectivity of the coupling reaction Kira et al. reacted two equivalents of (ClMe2Si)2SiMe with lithium metal and obtained 1-Me2 in 19% yield.11 Recent achievements in the chemistry of α,ω-oligosilanylidianions mainly by Marschner et al.12 finally enabled the synthesis of bis(trimethylsilyl)dodecamethylbicyclo[2.2.2]octasilane (1) and a whole series of related oligosilane cycles and cages in excellent yields.13 Furthermore, it has been reported that 1-Me2 and 1 can be functionalized selectively at the bridgehead Si atoms to give 1-K, 1-K2, 1-MeX, and 1-X2 (X = Cl, Br) (compare Scheme 1), which represent valuable synths for further derivatization. In a small-scale experiment Kira et al. obtained 1-Ph from 1-MeCl and PhLi in 58% yield.13 Nucleophilic substitution reactions of 1-MeCl, however, turned out to be of limited scope because neither scale-up to preparative amounts nor the synthesis of bicyclo[2.2.2]octasilanes bearing functional aromatic side groups such as p-PhCN or p-PhCF3 could be accomplished successfully.14 The reaction of 1-K and 1-K2 with various C or Si electrophiles to the corresponding bridgehead-functionalized cages, on the other hand, gave quite satisfactory results.15

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For 1-Ph Kira et al. observed dual fluorescence from the locally excited (LE) and the intramolecular charge transfer (ICT) state even in nonpolar solvents and, thus, were able to demonstrate that bicyclo[2.2.2]octasilane cages can get involved in charge transfer processes. In contrast to cyclic and open-chained permethyloligosilanes, for which the first visible transition is of $\sigma \rightarrow \sigma^*$ character, TD-DFT calculations published by Marschner and Ottoson recently assigned the longest wavelength UV absorption band in 1 to $\sigma \rightarrow \pi^*$ type electron transitions. The authors of this study further suggest that the electronic structure within bicyclo[2.2.2]octasilane cages may result in charge transport characteristics that are different from those of linear oligosilanes. Therefore, we found it highly desirable to improve the understanding of the impact of various substituent groups on the properties of the Si–Si bond system within the bicyclo[2.2.2]octasilane cage. Herein we now would like to report on the synthesis of previously unknown bicyclo[2.2.2]octasilanes with phenyl, ferrocenyl, and carbonyl side groups and on the investigation of substituent effects within the target compounds using mainly UV absorption spectroscopy and X-ray crystallography.

## RESULTS AND DISCUSSION

It has been demonstrated earlier that polysilanyl alkali metal compounds such as (Me3Si)3SiM (M = K, Li) smoothly react with various electrophiles to give functional silanes (Me3Si)3SiX with substituents X such as H, alkyl, SiR3, GeR3, COR, COOR, or COOH attached to the central silicon atom. In the present study we used a similar approach to synthesize the corresponding bridgehead-functionalized bicyclo[2.2.2]octasilanes 2–12 starting from the potassium silanides 1-K and 1-K2.

As depicted in Scheme 2, 1-K can easily be silylated with PhMe2SiCl, Ph2MeSiCl, or FcMe2SiCl (Fc = ferrocenyl) in toluene solution at $-70^\circ$C to give the air-stable and crystalline compounds 2, 3, and 4, respectively, in yields of $>70\%$. With a 4-fold excess of Me2SiCl2 the SiMe2Cl-substituted product 5 was obtained, which may be used for further derivatization by nucleophilic substitution at the silicon–chlorine bond. Treatment of 1-K with equimolar amounts of CICOR (R = Me, tBu) or CICOOMe, furthermore, allowed for the synthesis of the acyl- and methylcarboxybicyclo[2.2.2]octasilanes 6–8. The corresponding carboxylic acid 9 finally could be obtained by carbonation of 1-K with CO2 followed by acid hydrolysis of the...
primarily formed potassium carboxylate. 6−9 are stable against air and moisture but slowly decompose within several weeks upon storage at room temperature under formation of polymeric products of unidentified composition, which also applies to the acyl and diacyl bicyclo[2.2.2]octasilanes 12 and 14 mentioned below.

The reaction of 1-K2 with two equivalents of PhMe2SiCl, FcMe2SiCl, or CICOtBu also proceeded straightforwardly and yielded the symmetrically disubstituted species 10, 11, and 12, respectively (Scheme 3).

If 4 was stirred with a 1.1 molar excess of KOtBu in DME for 40 min at room temperature, the Me3Si group was split off selectively and the potassium silanide 4-K was cleanly formed. The 29Si NMR spectrum of the resulting reaction solution exhibits a resonance line at −177.62 ppm, which is easily assigned to the negatively charged bridgehead silicon atom, while the signals of the ≡SiSiMe3 moiety at −6.11 (SiMe3) and −130.67 (SiSiMe3) had disappeared. Subsequent addition of 1.1 equivalents of PhMe2SiCl or CICOtBu at −70 °C finally afforded the asymmetrically disubstituted cages 13 and 14 (Scheme 4).

In a similar manner 7 reacted with KOtBu to give the silanide 7-K with \(\delta^{29}\text{Si} = -180.69\) ppm for the silicon atom bearing the negative charge, which could be converted to 12 by addition of another equivalent of CICOtBu (Scheme 5). The reaction of 8 with KOtBu finally afforded a product mixture of unidentified composition instead of the silanide 8-K. The 29Si NMR spectra of the resulting reaction solution showed numerous signals that could not be assigned unambiguously.

All previously unknown compounds were fully characterized by spectroscopic means and elemental analyses. Analytical data (compare Experimental Section) are consistent with the proposed structures in all cases. For compounds 3, 6, 7 and 12 elemental analyses did not give satisfactory results very likely due to incomplete combustion. In all cases, however, proper HRMS data were obtained. Additionally 1H- and 29Si NMR spectra of 3, 6, 7 and 12 are displayed in the Supporting Information in order to demonstrate the purity of the compounds.

29Si NMR chemical shift data of the bicyclooctasilane core are summarized in Table 1. The asymmetrically substituted compounds exhibit two 29Si resonance lines for the SiMe2 groups, while only one signal appears in the same range of the 29Si spectra of the symmetrical species 10−12. 29Si chemical shift values near −39 ppm were found for the SiMe2 groups, which are not significantly influenced by the nature of the substituents X.
Single crystals suitable for X-ray structure analysis could be grown from compounds 2, 3, 4, 6, 8, 9, 10, and 13. The obtained molecular structures are depicted in Figures 1–7 together with selected bond distances, bond angles, and dihedral angles.

The phenyl compounds 2 and 3 crystallize in the triclinic space group $P\bar{T}$ and orthorhombic space group $Pca2(1)$, respectively, with two independent molecules in the asymmetric unit. 2, 4, 10, and 13 exhibit a roughly perpendicular arrangement of the plane of the aromatic rings relative to the adjacent Si–Si bond with torsional angles $\psi$ not far from 90°. Deviation from perpendicularity is much larger in compound 3, which can be ascribed to the sterical bulk of the two phenyl rings attached to the same silicon atom. In general a perpendicular geometry is frequently observed within the fragment phenyl–Si–Si because it provides the basis for effective $\sigma(Si-Si)-\pi$(phenyl) overlap. A study of the absorption spectra of conformationally constrained arylsilanes thus demonstrated that a torsion angle between the phenyl ring plane and the Si–Si bond of 90° effects in maximum $\sigma-\pi$ conjugation.18 Similar conformational dependence of UV absorption and emission properties was also observed when the 1,2-diphenylsilane moiety was conformationally constrained by incorporation into cyclic structures.19

The sum of the bond angles around the carbonyl C atom in 6, 8, and 9 is close to 360° and reflects the trigonal planar geometry within the SiRC=O moiety. Carbonyl C=O bond lengths between 1.19 and 1.23 Å were measured, approximately the same as that found in simple organic ketones, carboxylic acids, and esters.20 Silicon carbonyl group bond lengths at

Table 1. $\delta^{29}$Si Chemical Shift Data of the Bicyclo[2.2.2]octasilane Core in 1–14 (CDCl$_3$ solution, vs ext. TMS, ppm)

<table>
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<th></th>
<th>$SiMe_2$</th>
<th>$\equiv SiMe_2-R_5$</th>
<th>$\equiv SiC=O$</th>
<th>$\equiv Si^\prime K$</th>
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<td>-38.10</td>
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</table>

$^a$Taken from ref 12h, $^b$Measured in DME.
C(30) 3
Si(15) C bond distances in acyl silanes have been observed earlier,22
The crystals contain two independent molecules (3, 3′) in the asymmetric unit. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: 3: Si−Si (mean) 2.355, Si(1)−C(2) 1.889(3), Si(1)−C(8) 1.876(3), Si−Cmethyl (mean) 1.887, Si−Si−Si (mean) 109.6, C(2)−Si(1)−Si(2) 112.30(9), C(8)−Si(1)−Si(2) 113.60(9), Si(2)−Si(3)−Si(4)−Si(5) −17.22(5), Si(2)−Si(7)−Si(6)−Si(5) −19.85(5), Si(2)−Si(8)−Si(9)−Si(5) −18.59(5), Si(2)−Si(1)−C(2)−C(3) −55.5(5), Si(2)−Si(1)−C(2)−C(7) −128.1(2), Si(2)−Si(1)−C(8)−C(9) −123.3(2), Si(2)−Si(1)−C(8)−C(15) 60.1(3). 3′: Si−Si (mean) 2.354, Si(11)−C(30) 1.890(3), Si(11)−C(36) 1.881(3), Si−Cmethyl (mean) 1.888, Si−Si−Si (mean) 109.8, C(30)−Si(11)−Si(12) 113.33(9), C(36)−Si(11)−Si(12) 109.3(1), Si(15)−Si(14)−Si(13)−Si(12) −14.11(5), Si(15)−Si(16)−Si(17)−Si(12) −18.43(6), Si(15)−Si(19)−Si(18)−Si(12) −17.16(6), Si(12)−Si(11)−C(30)−C(31) −68.7(2), Si(12)−Si(11)−C(30)−C(35) 114.6(2), Si(12)−Si(11)−C(36)−C(37) 117.7(3), Si(12)−Si(11)−C(36)−C(41) −61.1(3).

The silacarboxylic acid 9 afforded crystals of proper quality only from 2-propanol. The resulting crystals belong to the triclinic space group P1 with two molecules in the unit cell, which are connected to dimers via hydrogen bridges by two molecules of 2-propanol (compare Figure 7).

There is only a minor impact of the substituents attached to the bridgehead silicon on the structure of the bicyclooctasilane core. In line with structural data of bicyclo[2,2,2]octasilanes published earlier13,15,16 the compounds investigated in this study exhibit a slightly twisted structure of the bicyclooctasilane cage with nonparallel −SiMe2− bridges in order to minimize steric repulsion. Endocyclic dihedral angles \( \Phi_{bridgehead} \) range from 14.1° to 22.4°. Si−Si−Si bond angles close to the ideal tetrahedral angle between 105.8° and 111.5° and Si−Si bond lengths between 2.34 and 2.37 Å were

1.92−1.94 Å are considerably elongated, the average Si−C(sp^3) bond length was calculated from 19 169 individual XRD experimental values to be 1.860 Å.21 Significantly elongated Si−C bond distances in acyl silanes have been observed earlier,22 and it has been suggested that this shortening of the silicon carbonyl group bond can be ascribed not only to contributions of canonical forms with single C−O bonds (Scheme 6, structure A), but also to a resonance structure without a formal bond between the metalloid atom and the carbonyl carbon (Scheme 6, structure B).23 According to a more recent study, finally, the situation is best described by structure C with a dative bond between a negatively charged carbon and a positively charged silicon atom.24

Figure 2. ORTEP diagram for compound 3. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: Si−Si (mean) 2.355, Si(1)−C(2) 1.889(3), Si(1)−C(8) 1.876(3), Si−Cmethyl (mean) 1.887, Si−Si−Si (mean) 109.6, C(2)−Si(1)−Si(2) 112.30(9), C(8)−Si(1)−Si(2) 113.60(9), Si(2)−Si(3)−Si(4)−Si(5) −17.22(5), Si(2)−Si(7)−Si(6)−Si(5) −19.85(5), Si(2)−Si(8)−Si(9)−Si(5) −18.59(5), Si(2)−Si(1)−C(2)−C(3) −55.5(5), Si(2)−Si(1)−C(2)−C(7) −128.1(2), Si(2)−Si(1)−C(8)−C(9) −123.3(2), Si(2)−Si(1)−C(8)−C(15) 60.1(3). 3′: Si−Si (mean) 2.354, Si(11)−C(30) 1.890(3), Si(11)−C(36) 1.881(3), Si−Cmethyl (mean) 1.888, Si−Si−Si (mean) 109.8, C(30)−Si(11)−Si(12) 113.33(9), C(36)−Si(11)−Si(12) 109.3(1), Si(15)−Si(14)−Si(13)−Si(12) −14.11(5), Si(15)−Si(16)−Si(17)−Si(12) −18.43(6), Si(15)−Si(19)−Si(18)−Si(12) −17.16(6), Si(12)−Si(11)−C(30)−C(31) −68.7(2), Si(12)−Si(11)−C(30)−C(35) 114.6(2), Si(12)−Si(11)−C(36)−C(37) 117.7(3), Si(12)−Si(11)−C(36)−C(41) −61.1(3).
observed. The average Si–Si bond distance of 2.35 Å is typical for Si–Si single bonds in cyclopolsilanes and agrees well with the Si–Si covalent bond length of 2.34 Å.

UV absorption spectra of 1–14 have been recorded in order to estimate the extent of interactions between the bridgehead substituents with the bicyclooctasilane Si–Si bond system. UV absorption data are summarized in Table 2.

Figure 8 compares the absorption spectrum of 1 with the spectra of the phenyl- and ferrocenyl-substituted compounds 2, 3, 4, 10, 11, and 13. The ferrocenylsilanes 4, 11, and 13 show characteristic weak absorption bands near 460 and 330 nm, which arise from local transitions within ferrocene. All spectra exhibit additional bands in the near UV region. For 1 a typical shoulder appears at 240 nm, which previously has been assigned to 4 type electron transitions involving the σ-SiSi skeleton. In the spectra of 2 and 4 this band is shifted considerably to the red by 20 and 30 nm, respectively. This behavior is usually observed when aromatic side groups are attached to permethylated oligosilane frameworks and is easily rationalized if one assumes σ–π type hyperconjugative interactions between the aromatic π- and the SiSi σ-electrons. In the case of open-chained permethyloligosilanes the most striking red shift was found upon introduction of the first phenyl group, while a second phenyl substituent is much less effective. Thus, Me3SiSiMe3SiMe3 exhibits a first absorption maximum at 216 nm, which is shifted to 240 nm in PhMe3SiSiMe3SiMe3 and to 243 nm in PhMe3SiSiMe3SiMe3Ph. In line with this observation the absorption spectrum of 3 displays a 5 nm red shift of the first absorption maximum relative to 2, while 10 and 11 show identical λmax values as compared to 2 and 4, respectively. Apparently the σ–π conjugated bond system within 2 and 4 is not extended further by the presence of the second aryl group, which makes any electronic coupling of the aromatic substituents via the bicyclooctasilane cage rather unlikely.

UV absorption spectra of the carbonyl derivatives 6–7 and 12 are depicted in Figure 9. The weak low-energy absorption bands in the spectra of compounds 6, 7, and 12 centered near 370 nm are typical for acylsilanes and can be assigned to symmetry-forbidden local n→π* transitions within the C=O group. The position and intensity of these absorption maxima are nearly unaffected by the structure of the attached oligosilanyl moiety and compare closely with the values estimated for (Me3Si)3SiCOR or Me3SiCOR. In general it is well established that β-silyl groups exert only little influence on the energies of n→π* transitions in acyl silanes. Otherwise the spectra are rather featureless. In the UV part strong maxima around 210 nm appear, which cannot be assigned without ambiguity either to carbonyl π→π* or electron transitions within the polysilane skeleton. The silyl carboxylate 8 and the silyl carboxylic acid 9 exhibit a continuously rising absorption below 300 nm without any detectable maxima above 205 nm, which is characteristic for related systems. Obviously in these cases the carbonyl n→π* absorption band that is found at 245 and 243 nm in the spectra of Me3SiCOOMe and Me3SiCOOH, respectively, is completely masked by the polysilanyl absorption in the near-UV region.

As shown in Figure 10, finally, the absorption spectrum of 14 resembles the calculated sum spectrum of compounds 4 and 7, which contain the separate chromophores. The spectrum of 14,

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**Figure 5. ORTEP diagram for compound 13.** Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: Si–Si (mean) 2.353, C(1)–O(1) 1.231(4), Si(1)–C(1) 1.917(4), Si–Caryl (mean) 1.880, Si–Si–Si (mean) 109.1, O(1)–C(1)–O(2) 116.4(4), O(1)–C(1)–Si(1) 121.3(3), C(2)–C(1)–Si(1) 122.1(3), Si(1)–Si(2)–Si(3)–Si(4) –22.38(6), Si(4)–Si(5)–Si(6)–Si(1) –19.06(6), Si(4)–Si(8)–Si(7)–Si(1) –19.00(6), Si–Si–Si (mean) 2.354, C(1)–O(1) 1.201(2), C(2)–O(2) 1.447(2), C(1)–O(2) 1.357(2), Si(1)–C(1) 1.935(2), Si–Caryl (mean) 1.885, Si–Si–Si (mean) 109.0, O(1)–C(1)–O(2) 121.5(1), O(1)–C(1)–Si(1) 126.9(1), O(2)–C(1)–Si(1) 111.6(1), Si(1)–Si(2)–Si(3)–Si(4) 19.15(3), Si(4)–Si(5)–Si(6)–Si(1) 21.61(3), Si(4)–Si(8)–Si(7)–Si(1) 18.49(3), Si(1)–C(1)–O(2)–C(2) –178.7(1).

**Figure 6. ORTEP diagram for compounds 6 and 8.** Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond and torsional angles [deg] with estimated standard deviations: 6: Si–Si (mean) 2.353, C(1)–O(1) 1.231(4), Si(1)–C(1) 1.917(4), Si–Caryl (mean) 1.880, Si–Si–Si (mean) 109.1, O(1)–C(1)–O(2) 116.4(4), O(1)–C(1)–Si(1) 121.3(3), C(2)–C(1)–Si(1) 122.1(3), Si(1)–Si(2)–Si(3)–Si(4) –22.38(6), Si(4)–Si(5)–Si(6)–Si(1) –19.06(6), Si(4)–Si(8)–Si(7)–Si(1) –19.00(6), Si–Si–Si (mean) 2.354, C(1)–O(1) 1.201(2), C(2)–O(2) 1.447(2), C(1)–O(2) 1.357(2), Si(1)–C(1) 1.935(2), Si–Caryl (mean) 1.885, Si–Si–Si (mean) 109.0, O(1)–C(1)–O(2) 121.5(1), O(1)–C(1)–Si(1) 126.9(1), O(2)–C(1)–Si(1) 111.6(1), Si(1)–Si(2)–Si(3)–Si(4) 19.15(3), Si(4)–Si(5)–Si(6)–Si(1) 21.61(3), Si(4)–Si(8)–Si(7)–Si(1) 18.49(3), Si(1)–C(1)–O(2)–C(2) –178.7(1).
therefore, seems to fulfill the classical expectation for nonconjugatively connected chromophores.

**CONCLUSIONS**

In summary, we have elaborated synthetic approaches toward bridgehead-functionalized permethylbicyclo[2,2,2]octasilanes. Starting from the corresponding 1-potassium and 1,4-dipotassium silanides previously unknown mono- and difunctional derivatives with COR, COOR, COOH, and SiMe_3R (R = Ph, Fc) attached to the bridgehead silicon atoms have been prepared successfully and fully characterized. In the crystalline state all compounds investigated in this study exhibit a slightly twisted structure of the bicyclooctasilane cage, which turned out to be remarkably insensitive toward the nature of the substituents attached to the bridgehead silicon atoms.

Except for the n→π* absorption bands of the acyl silanes 6 and 7 centered near 370 nm, which exhibit nearly constant excitation energies as compared to Me_3SiCOR or (Me_3Si)_2SiCOR, the UV absorption spectra of the C=O derivatives 6–9 are rather featureless and, thus, do not allow drawing even qualitative conclusions concerning interactions between σ(SiSi) and C=O group orbitals. Due to σ(SiSi)/π(aryl) conjugation, the absorption spectra of the phenyl and ferrocenyl derivatives show the expected bathochromic shift of the first UV absorption band relative to 1. Attachment of another aryl substituent to the second terminal MeSi group, however, did not lead to further bathochromic shifts as observed in open-chained systems of comparable size. This allows us to conclude that there is no direct conjugational type interaction of the two aryl groups via the bicyclo[2,2,2]octasilane skeleton, which can be rationalized using steric arguments. It has earlier been shown that cisoid conformations do not extend the conjugation within the σ(SiSi) oligosilanes. Because the conjugation path going from one aryl group to the other via the octasilane cage contains one cisoid fragment, it is not surprising that conjugation between the two aryl groups leading to an extended conjugated system does not occur. This assumption is further supported by the observation
that the absorption spectrum of 14 resembles the calculated sum spectrum of compounds 4 and 7 and, thus, seems to fulfill the classical expectation for nonconjugatively connected chromophores.

**EXPERIMENTAL SECTION**

All experiments were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried using a column solvent purification system. KOBu (97%), MeCOCl (99%), fBuCOCl (99%), and CICOOMe (98%) were used as purchased; Me3SiCl (98%) was distilled prior to use. Commercial CO2 was dried by passing through P2O5, PhMe3SiCl, Ph3MeSiCl, FeMe3SiCl, 1-K, and 1-K3Cl. 1H (299.95 MHz), 13C (75.43 MHz), and 29Si (59.59 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer in C6D6 solution and referenced versus TMS using the internal 2H-lock signal of the solvent. Mass spectra were run either on an HP 5971A/S890-II GC/MS coupling (HP 1 capillary column, length 25 m, diameter 0.2 mm, 0.33 μm poly(dimethylsiloxane)) or on a Kratos Profile mass spectrometer equipped with a solid probe inlet. Infrared spectra were obtained on a Bruker AlphA-P Diamond ATR spectrometer from the solid sample. UV-visible spectra were recorded in n-hexane solution, ε = 4 × 10^4 and 10^5 mol·L^-1, respectively, on a Perkin-Elmer Lambda 35 spectrophotometer. Positions of absorption maxima and shoulders were obtained directly from the experimental spectra; absorptivity values ε were determined at the position of the maxima using Lambert–Beer’s law. Melting points were determined using a Büchi 535 apparatus and are uncorrected. Elemental analyses were carried out on a Hanau Vario Elementar EL apparatus.

**Synthesis of Dodecamethyl-4-(trimethylsilyl)-1-(dimethylphenylsilyl)bicyclo[2.2.2]octasilanes (2).** A solution of 1-K in 5 mL of DME was freshly prepared from 275 mg (0.5 mmol) of 1 and 62 mg (0.55 mmol) of KOBu. After removal of the volatile components in vacuo at room temperature the resulting residue was taken up in 10 mL of toluene, cooled to −70 °C, and slowly added to a solution of 102 mg (0.6 mmol) of PhMe3SiCl in 20 mL of toluene. Subsequently the mixture was stirred for another 30 min and finally allowed to warm to room temperature. After aqueous workup with 100 mL of 10% sulfuric acid the organic layer was separated and dried over Na2SO4, and the solvent was stripped off with a rotary evaporator. Drying in vacuo (0.02 mbar) and crystallization from pentane by evaporation of the solvent at room temperature afforded 210 mg (69%) of white and crystalline 2.

**Synthesis of Dodecamethyl-4-(trimethylsilyl)-1-(methyldiphenylsilyl)bicyclo[2.2.2]octasilanes (3).** The procedure followed was that used for 2 with 715 mg (1.3 mmol) of 1, 160 mg (1.4 mmol) of KOBu, and 333 mg (1.4 mmol) of Ph3MeSiCl. Crystallization of the crude product from diethyl ether/ethanol (1:1) by evaporation of the solvents at room temperature afforded 670 mg (76%) of white and crystalline 3.

**Synthesis of 1-(Ferrocenyldimethylsilyl)dodecamethyl-4-(trimethylsilyl)bicyclo[2.2.2]octasilanes (4).** To a solution of 1-K in 10 mL of DME (freshly prepared from 2.76 g (5 mmol) of 1 and 0.62 g (5.5 mmol) of KOBu) was slowly added a solution of 1.45 g (5.2 mmol) of Fe3SiMeCl in 50 mL of DME at −50 °C. Subsequently the mixture was stirred for another 30 min and finally allowed to warm to room temperature. After aqueous workup with 10% sulfuric acid the organic layer was separated and dried over Na2SO4 and the volatile components were stripped off with a rotary evaporator. Drying in vacuo (0.02 mbar) and crystallization from diethyl ether/acetone (1:1) by evaporation of the solvents at room temperature afforded 2.83 g (78%) of white and crystalline 4.

**Synthesis of 1-(Ferrocenyldimethylsilyl)dodecamethyl-4-(trimethylsilyl)bicyclo[2.2.2]octasilanes (4).** To a solution of 1-K in 10 mL of DME (freshly prepared from 2.76 g (5 mmol) of 1 and 0.62 g (5.5 mmol) of KOBu) was slowly added a solution of 1.45 g (5.2 mmol) of Fe3SiMeCl in 50 mL of DME at −50 °C. Subsequently the mixture was stirred for another 30 min and finally allowed to warm to room temperature. After aqueous workup with 10% sulfuric acid the organic layer was separated and dried over Na2SO4 and the volatile components were stripped off with a rotary evaporator. Drying in vacuo (0.02 mbar) and crystallization from diethyl ether/acetone (1:1) by evaporation of the solvents at room temperature afforded 2.83 g (78%) of white and crystalline 4.
Synthesis of 1-(Chlorodimethylsilyl)dodecamethyl-4-(trimethylsilyl)bicyclo[2.2.2]octasilane (5).
A solution of 1-K in 5 mL of DME was freshly prepared from 2.21 g (4 mmol) of 1 and 0.42 g (4.2 mmol) of KO[Bu]. After removal of the volatile components in vacuo at room temperature the resulting residue was taken up in 5 mL of toluene, cooled to −70 °C, and slowly added to a solution of 2.06 g (16 mmol) of MeSiCl in 20 mL of toluene. Subsequently the mixture was stirred for another 30 min and finally allowed to warm to room temperature. After removal of the volatile components in vacuo (0.02 mbar) the solid residue was taken up with 20 mL of heptane and filtered over Celite. Removal of the solvent from the filtrate and drying in vacuo at room temperature afforded 2.13 g (93%) of pure 5 as colorless crystals.

Mp: 155–157 °C (dec). Anal. Found: C, 35.72; H, 8.89. Calcd for C17H38Si9: C, 38.00; H, 9.00. MS: calcd for [C17H36O2Si10]+ (M+) 570.2; found 570.3.

Synthesis of Dodecamethyl-4-(trimethylsilyl)bicyclo[2.2.2]octasilane-1-carboxylic Acid (9). A solution of 1-K in 10 mL of DME (freshly prepared from 3.31 g (6 mmol) of 1 and 740 mg (6.6 mmol) of KO[Bu]) was slowly added at −70 °C to a saturated solution of CO2 in diethyl ether, which has been obtained by slowly bubbling thoroughly dried CO2 through 150 mL of diethyl ether at −70 °C for 20 min. Subsequently the mixture was stirred for another 30 min at −70 °C and finally allowed to warm to room temperature. After aqueous workup with 100 mL of 2% sulfuric acid the organic layer was separated and dried over Na2SO4, and the solvent was stripped off with a rotary evaporator. Subsequent drying at 0.02 mbar afforded 301 mg (96%) of pure 9 as a white, moderately air-stable powder. Crystals suitable for X-ray structure analysis were obtained after recrystallization from 2-propanol by evaporation of the solvent at room temperature.

Mp: 163–165 °C (dec). Anal. Found: C, 36.08; H, 8.28. Calcd for C16H32O2Si9: C, 36.72; H, 8.86. 29Si NMR (CDCl3, TMS, ppm): −5.49 (SiMe3); −38.12, −39.22 (SiMe3); −76.72 (SiOCH3); −129.61 ppm (SiMe3). 13C NMR (CDCl3, TMS, ppm): 193.10 (COOH); 3.58 (Si(CH3)2); −1.31, −0.07 (Si(CH3)3). 1H NMR (CDCl3, TMS, ppm, rel int): 1.64 (3H, t, J = 8 Hz, s, Si(CH3)3); 0.32 (18H, s, Si(CH3)2); 0.25 (9H, s, Si(CH3)2); IR (neat): ν(CO) = 1631 (m) cm−1. HRMS: calcd for [C16H31O2Si9]+ ([M − H]+) 521.1343; found 521.1346.

Synthesis of 1,4-Bis(dimethylphenylsilyl)dodecamethylbicyclo[2.2.2]octasilane (10). A solution of 1-K in 10 mL of toluene (freshly prepared from 276 mg (0.5 mmol) of 1, 123 mg (1.1 mmol) of KO[Bu], and 291 mg (1.1 mmol) of 18-crown-6) was slowly added to a solution of 170 mg (1.0 mmol) of PhMe2SiCl in 40 mL of toluene at −70 °C. Subsequently the mixture was stirred for another 30 min at −70 °C and finally allowed to warm to room temperature. After aqueous workup with 100 mL of 3% sulfuric acid the organic layer was separated and dried over Na2SO4 and the solvent was stripped off with a rotary evaporator. Drying in vacuo (0.02 mbar) and crystallization from pentane by evaporation of the solvent at room temperature afforded 220 mg (65%) of colorless and crystalline 10.

Mp: 181–182 °C (dec). Anal. Found: C, 49.72; H, 8.17. Calcd for C28H58Si9: C, 49.78; H, 8.65. 29Si NMR (CDCl3, TMS, ppm): −10.60 (SiMe3); −37.90 (SiMe3); −129.73 (SiMe2Ph). 13C NMR (CDCl3, TMS, ppm, rel int): 132.89, 127.61 (Si(CH3)2); −1.64 (Si(CH3)3). HRMS: calcd for [C28H57Si9O]+ (M+) 720.1628; found 720.1653.

Synthesis of 1,4-Bis(ferroacenyldimethylsilyl)dodecamethylbicyclo[2.2.2]octasilane (11). The procedure followed was that used for 10 with 1.00 g (1.8 mmol) of 1, 0.43 g (3.8 mmol) of KO[Bu], 1.15 g (3.8 mmol) of 18-crown-6, and 1.15 g (4.1 mmol) of FeMe2SiCl. Crystallization of the crude product from diethyl ether by evaporation of the solvent at room temperature afforded 230 mg (20%) of orange and crystalline 11.

Mp: 290 °C (dec). Anal. Found: C, 47.92; H, 7.02. Calcd for C49H34Fe2Si10: C, 48.39; H, 7.67. 29Si NMR (CDCl3, TMS, ppm): −11.40 (SiMe3Fe); −38.14 (SiMe2); −129.12 (SiMe3Fe). 13C NMR (CDCl3, TMS, ppm): 74.61, 73.16, 70.51 (C5H3SiMe5), 67.92 (C19H26); 1.92 (Si(CH3)2Fe); −1.39 (Si(CH3)3). 1H NMR (CDCl3, TMS, ppm, rel int): 4.31, 4.05 (8H, s, Si(CH3)2Fe); 4.14 (10H, s, C3H2); 0.51 (12H, s, Si(CH3)2Fe); 0.13 (36H, s, Si(CH3)2). HRMS: calcd for [C49H34Fe2Si10]− (M−Fe) 890.1561; found 890.0459.

Synthesis of a 1,4-Bis(trimethylcarbonyl)dodecamethylbicyclo[2.2.2]octasilane (12). Method a: The procedure followed was that used for 10 with 276 mg (0.5 mmol) of 1, 123 mg (1.1 mmol) of KO[Bu], and 18-crown-6.
6, and 132 mg (1.1 mmol) of CICOBu. Crystallization of the crude product from acetone at −30 °C afforded 140 mg (48%) of white and crystalline 12.

Method b: 282 mg (0.5 mmol) of 7 was stirred with 62 mg (1.1 mmol) of KOtBu in 10 mL of DME at room temperature. At this time 29Si NMR analysis revealed quantitative formation of the silane 4-K. The resulting red solution was slowly added to a solution of 66 mg (0.55 mmol) of CICOBu in 10 mL of diethyl ether at −70 °C. Subsequently the mixture was stirred for another 30 min at −70 °C and finally allowed to warm to room temperature. After stirring for an additional 2 h aqueous workup was accomplished by addition of 100 mL of 3% sulfuric acid, separation of the organic layer, drying over Na2SO4, and removal of the solvent with a rotary evaporator. Crystallization of the oily residue from acetone/pentane (1:1) by evaporation of the solvents at room temperature afforded 90 mg (32%) of 12.

7-K. 29Si NMR (DME/D2O, TMS, ppm): −33.05; −40.06 (SiMe2); −73.86 (Si(CMe3)2); −178.04 (Si(CMe3)3); 0.52 (6H, s, Si(CH3)2). IR (neat): ν(C≡O) = 1621 cm−1 (m). HRMS: calcd for [C5H3FeSi8]+ (M+) 732.1919; found 732.1945.

X-ray Crystallography. For X-ray structure analysis suitable crystals were mounted onto the tip of glass fibers using mineral oil. Data collection was performed on a Bruker Kappa Apex II CCD diffractometer at 100 K for compounds 2, 3, 4, 6, 8, 10, and 13 and 200 K for compound 9 using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Details of the crystal data and structure refinement are provided as Supporting Information. The SHELX version 6.1 program package was used for the structure solution and refinement.8 All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the refinement at calculated positions using a riding model as implemented in the SHELXTL program. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-923021 (2), CCDC-923023 (3), CCDC-923024 (4), CCDC-923018 (6), CCDC-923020 (8), CCDC-923019 (9), CCDC-923017 (10), and CCDC-923016 (13). Copies of the data can be obtained free of charge via The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax internat.) +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk.

ASSOCIATED CONTENT

1H and 29Si NMR spectra of 3, 6, 7, and 12. Tables and CIF files giving crystal, collection, and refinement data for the structures of compounds 2, 3, 4, 6, 8, 10, and 13. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Ref 1c contains an up-to-date compilation of known methods for polysilane synthesis including extensive bibliography.

(9) Ref 1i, p 319 ff.


(14) Kira, M. Personal unpublished communication.


(25) Ref 21, p 197f.


(27) An extensive discussion on the topic including bibliography can be found in ref 1c, p 319 ff.


(41) SHELX and SHELXL PC, version 5.03, Bruker AXS Inc.; Madison, WI, 1994.