Metal-Promoted Oxidative π-Conjugation and Coupling of Substituted-Fulvalene-Type Ligands: Synthesis and Crystal Structures of π-Conjugated $C_{24}H_{12}(SiMe_3)_2$ and the Dimer $[C_{24}H_{13}(SiMe_3)_2]_2$

Dennis Malaba, Claire A. Tessier,* and Wiley J. Youngs*

Department of Chemistry, The University of Akron, Akron, Ohio 44325-3601

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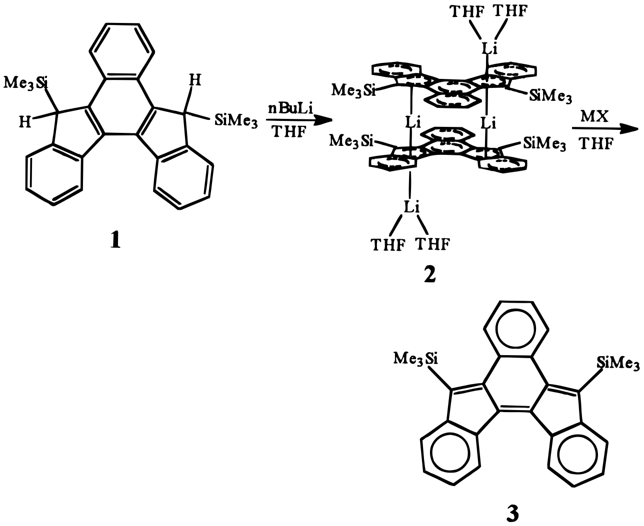
The oxidation of the substituted-fulvalene dianion with group 13 metal halides yields dark green crystals of the stable π-conjugated fulvalene $C_{24}H_{12}(SiMe_3)_2$. Reaction of the fulvalene monoanion with the metal halides results in the oxidative coupling of the ligand to give the dimer $[C_{24}H_{13}(SiMe_3)_2]_2$. These compounds, obtained rather unexpectedly during efforts to synthesize metal complexes of the fulvalene-type ligand, have been characterized by X-ray crystallography.

Introduction

Fulvalenes are attractive synthetic and theoretical[1] models for the spectroscopic studies[2] of π-bond delocalization and charge transfer distribution in conjugated systems. The unsubstituted fulvalene, pentafulvalene,[3,4] is an extremely unstable compound which can only be handled in very dilute solutions under an inert atmosphere at very low temperatures. Substituted pentafulvalenes are known to be stable at room temperature; however, only a few structures have been determined from X-ray analysis.[5] The synthesis of pentafulvalenes is achieved quite efficiently by the reaction of fulvalene dianions with transition metal species which act as oxidants. For instance, Ag(I) and Cu(II) salts have been used to prepare[6] pentafulvalenes in high yields. Other oxidants such as elemental oxygen and iodine[7] have been employed but are less efficient. These reagents have also been effective in inducing the oxidative coupling of cyclopentadienide anions.[4,6]

In general, the use of transition metal species to promote various reactions in synthetic organic chemistry is well-known and has now become a tool of major importance in synthetic chemistry.[8] Metal-mediated reactions are advantageous over many other types of reactions because they are usually stereospecific, making them highly valuable in preparative chemistry.

In this paper we report the application of main-group metals in the synthesis of a stable substituted fulvalene, $C_{24}H_{12}(SiMe_3)_2$, a compound with a π-conjugated system having strongly alternating bond lengths in the fulvalene moiety and a dimer, $[C_{24}H_{13}(SiMe_3)_2]_2$, obtained by oxidative coupling of "*Hückel anions*". Both compounds were obtained rather unexpectedly during the course of efforts to synthesize metal complexes of the fulvalene type ligand. The compound $C_{24}H_{12}(SiMe_3)_2$ is an electron deficient molecule which may serve as a π-type charge transfer acceptor toward aromatic hydrocarbons and as a precursor to conjugated polymeric materials with interesting electronic, magnetic, and conducting properties.



Experimental Section

General Procedures. Unless otherwise stated, all manipulations were performed under argon or vacuum by using

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

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standard inert-atmosphere techniques.[9,10] Solvents were distilled from appropriate drying agents under nitrogen prior to use. Thallium chloride and indium chloride were obtained from Strem Chemicals, Inc., and used without further purification. Compound **1** was prepared as reported[11] elsewhere. *n*-Butyllithium (Aldrich) was standardized with diphenylacetic acid prior to use.[12] ^1H and ^{13}C NMR spectra were recorded at ambient temperatures on a Gemini-300 NMR spectrometer at 300 MHz. Microanalytical determinations were performed at the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Synthesis of $C_{24}H_{12}(SiMe_3)_2$ (3). Compound **1** (0.20 g, 0.44 mmol) was dissolved in THF (30 mL) to give a yellow solution which was cooled to −78 °C followed by addition of *n*-BuLi in hexanes (0.36 mL, 0.89 mmol, 2.5 M). The solution immediately turned red. The cold bath was removed, and the mixture was allowed to slowly warm to room temperature. Stirring was continued for 1 h at room temperature after which TlCl (0.21 g, 0.89 mmol) was added. The solution immediately turned purple and then blue within a few minutes. After 2 h the solution turned dark green. No further color changes were observed after stirring overnight. The solvent was removed under vacuum. The product was taken up in hexane followed by filtration through a medium frit to remove lithium chloride and metallic thallium. Hexane was removed in vacuo to give a very dark green (almost black) powder of **3**. Yield: 0.18 g, 96%. ^1H NMR (C_6D_6, δ): 0.36 (s, $SiMe_3$, 18H), 6.93 (td, J_1 = 7.1 Hz, J_2 = 7.37 Hz, 2 H), 6.99−7.07 (m, 4 H), 7.33 (d, J = 7.14 Hz, 2 H), 7.65 (m, 2 H), 8.18 (d, J = 7.14 Hz, 2). ^{13}C NMR (C_6D_6, δ): 1.45, 21.40, 123.41, 123.86, 124.47, 124.78, 126.73, 128.21, 132.90, 141.21, 142.83. Anal. Calcd: C, 80.67; H, 6.77. Found: C, 80.74; H, 6.61.

Synthesis of $[C_{24}H_{13}(SiMe_3)_2]_2$ (8). Compound **1** (0.10 g, 0.22 mmol) was dissolved in THF (40 mL) to give a yellow solution. Upon addition of *n*-BuLi in hexanes (0.14 mL, 0.22 mmol, 1.6 M), the solution immediately turned red. This solution was stirred at room temperature for 1 h after which TlCl (0.06 g, 0.25 mmol) was added. The solution immediately turned dark blue. After stirring of the reaction mixture at room temperature for 16 h, no further color changes were observed. The solvent was removed under vacuum. The product was taken up in toluene followed by filtration through a medium frit to remove lithium chloride, metallic thallium, and excess thallium chloride. The solvent was removed *in vacuo* to give a bluish powder. ^1H NMR of this powder showed a complex mixture of products which could not be separated by chromatography. Repeated recrystallizations of the product from toluene/hexane produced a small amount of colorless crystals suitable for X-ray analysis.

X-ray Crystallographic Analysis. X-ray intensity data were collected at 130 K with the use of graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation on a Syntex $P2_1$ diffractometer equipped with a Molecular Structure Corp. low-temperature setup. Background measurements were made at the beginning and end of each scan, equal to a quarter of the total scan time. Crystal stability was monitored by measuring three standard reflections every 97 measurements. Data were corrected for Lorentz and polarization factors. Crystallographic calculations were performed by using the Siemens SHELXTL PLUS (PC Version)[13] program library. Crystal data, data collection and reduction, and structure refinement details for $C_{24}H_{12}(SiMe_3)_2$ (**3**) and $[C_{24}H_{13}(SiMe_3)_2]_2$ **(8)** are listed in Table 1.

Table 1. Summary of Crystallographic Data for the Compounds $C_{24}H_{12}(SiMe_3)_2$ (3) and $[C_{24}H_{13}(SiMe_3)_2]_2$ (8)

	3	**8**
formula	$C_{60}H_{60}Si_4$	$C_{60}H_{62}Si_4$
fw	893.4	895.5
color, habit	dark green, chunk	colorless,
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	Cc
a, Å	11.600(2)	13.821(3)
b, Å	16.508(3)	26.901(3)
c, Å	25.690(5)	14.705(3)
β, deg	96.98(3)	113.56(3)
V, Å^3; Z	4883.0(15); 4	5012(2); 4
D_{calc}, g cm^{-3}	1.215	1.187
abs coeff, mm^{-1}	0.155	0.151
temp, K	130	130
2θ range, deg	3.5−45.0	3.5−45.0
scan type	ω	ω
scan speed, deg min^{-1}	constant; 8.37 in ω	constant; 8.37 in ω
scan range, deg	1.60 (ω)	1.80 (ω)
no. of data collcd	8057	3924
no. of unique data	6380 (R_{int} = 3.93%)	3758 (R_{int} = 1.07%)
no. of obsd data, $F > 4\sigma(F)$	3347	2570
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0018F^2$	$w^{-1} = \sigma^2(F) + 0.0008F^2$
R, R_w	0.065, 0.0738	0.0511, 0.0492

X-ray Analysis for $C_{24}H_{12}(SiMe_3)_2$ (3). Crystals of compound **3** were grown from a solution of hexane by slow evaporation of the solvent. A dark green crystal measuring approximately 0.25 × 0.50 × 0.55 mm was mounted on a glass fiber and aligned on the diffractometer in a stream of cold nitrogen. Unit cell parameters were determined using 15 photographic data and refined using an additional 25 reflections with 20.0° ≤ 2θ ≤ 30.0°. The diffraction symmetry was $2/m$ with systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$), and the structure was successfully solved in $P2_1/c$ (No. 14) with a = 11.600(2) Å, b = 16.508(3) Å, c = 25.690(5) Å, β = 96.98(3)°, V = 4883.0(15) Å^3, and Z = 4. The positions of C and Si atoms were determined by direct methods and refined anisotropically by use of full matrix least-squares methods. All H atoms were included using a riding model with isotropic thermal parameters fixed at 0.08 Å^2. The refinement on 3876 unique reflections with $|F_o| > 4.0\sigma(|F_o|)$ from 3.5 to 45° in 2θ converged to R = 6.50% and R_w = 7.38%; all 6380 unique data gave R = 13.18%, R_w = 9.43%, and GOF = 1.17 for 577 parameters.

X-ray Analysis for $[C_{24}H_{13}(SiMe_3)_2]_2$ (8). Crystals of compound **8** were grown from a mixture of THF/hexane. A colorless crystal with the dimensions 0.15 × 0.25 × 0.50 mm was mounted on a glass fiber and aligned on the diffractometer in a stream of cold nitrogen. Unit cell parameters were determined using 12 photographic data and refined using an additional 25 reflections with 20.0° ≤ 2θ ≤ 30.0°. A careful survey of the preliminary data set revealed the systematic absences (hkl, $h + k = 2n + 1$; $h0l$, h, $l = 2n + 1$; $0kl$, $k = 2n + 1$; $hk0$, $h + k = 2n + 1$; $0k0$, $k = 2n + 1$; $h00$, $h = 2n + 1$; $00l$, $l = 2n + 1$) indicating the space group $C2/c$ or Cc. The space group Cc was later determined to be the correct choice by successful solution of the structure with a = 13.821(3) Å, b = 26.901(5) Å, c = 14.705(3) Å, β = 113.56(3)°, V = 5012.0(2) Å^3, and Z = 4. All H atoms were included using a riding model with isotropic thermal parameters fixed at 0.08 Å^2. The refinement on 2776 unique reflections with $|F_o| > 4.0\sigma(|F_o|)$ from 3.5 to 45° in 2θ converged to R = 5.11% and R_w = 4.92%; all 3758 unique data gave R = 8.79%, R_w = 5.73%, and GOF = 1.06 for 575 parameters.

Results and Discussion

In our earlier reports,[11] we described the synthesis of a tetralithium complex, the dimeric $\{Li_2(THF)_2[\eta^5:\eta^5,\eta^5\text{-}C_{24}H_{12}](SiMe_3)_2\}_2$ (**2**). Structural studies of com-

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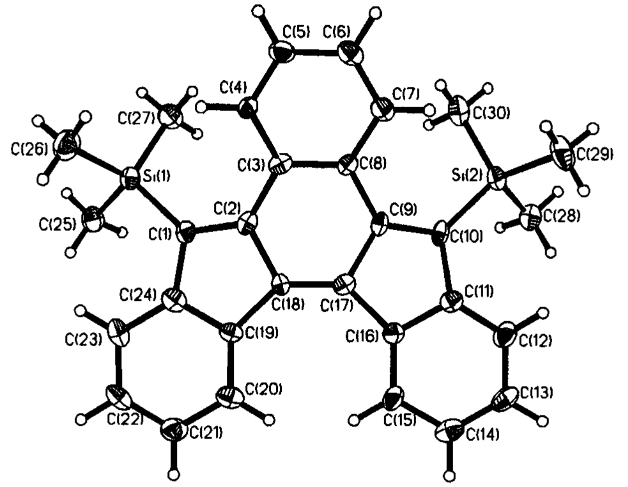

Figure 1. Molecular labeling diagram of $C_{24}H_{12}(SiMe_3)_2$ (**3**), showing one of the two crystallographically independent molecules. The thermal ellipsoids are drawn at the 50% probability level except for the hydrogen atoms which are drawn arbitrarily small for clarity.

pound **2** showed that two of the four lithium atoms were found on the same side of each ligand in a *cis* fashion with each sandwiched between two Cp rings. In light of the above structural features of **2** we became interested in the possibility of synthesizing bimetallic main-group complexes with nonclassical metal−metal interactions. Our ligand system seemed to be ideally suited for this purpose. We therefore set out to synthesize thallium and indium complexes from **2**.

Compound **1** in THF was treated with 2 equiv of *n*-butyllithium at −78 °C to give a red solution of **2**. Addition of 2 equiv of thallium chloride to the solution of **2** at room temperature resulted in a dark green solution which was presumed to contain a thallium complex of the substituted-fulvalene ligand. On workup of the reaction mixture, a dark green (almost black) powder of **3** was isolated in high yield. A similar product was obtained when indium chloride was used in place of thallium chloride. A close examination of the ^1H NMR spectra revealed the presence of a single product. The same product was observed regardless of the metal species used in the reaction. The structure of **3** which contained neither thallium nor indium metal was confirmed by X-ray crystal structure analysis.

An attempt to run the reaction in ether or noncoordinating solvents such as hexane and toluene instead of THF produced the same results. Compound **3**, which is soluble in most common organic solvents, is air stable in the solid state but decomposes in solution to unidentified products.

The compound $C_{24}H_{12}(SiMe_3)_2$ (**3**) crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent molecules in the asymmetric unit. A thermal ellipsoid labeling diagram of one of the molecules is shown in Figure 1, and selected bond distances and bond angles are listed in Table 2. The two molecules are arranged in a head-to-tail fashion and are positioned in such a way that the two external benzene rings fused to Cp rings stack over the Cp of the next molecule (Figure 2a). The distance between the closest two atoms of the two molecules is approximately 3.5 Å. Figure 2 shows two views of the arrangement of two of the molecules in **3** clearly revealing the overlapping nature and bending of the molecules. As can be seen from the packing diagram (Figure 3), eight molecules are packed in the unit cell and the paired molecules are stacked forming diagonal columns which are mutually oriented at approximately 90°.

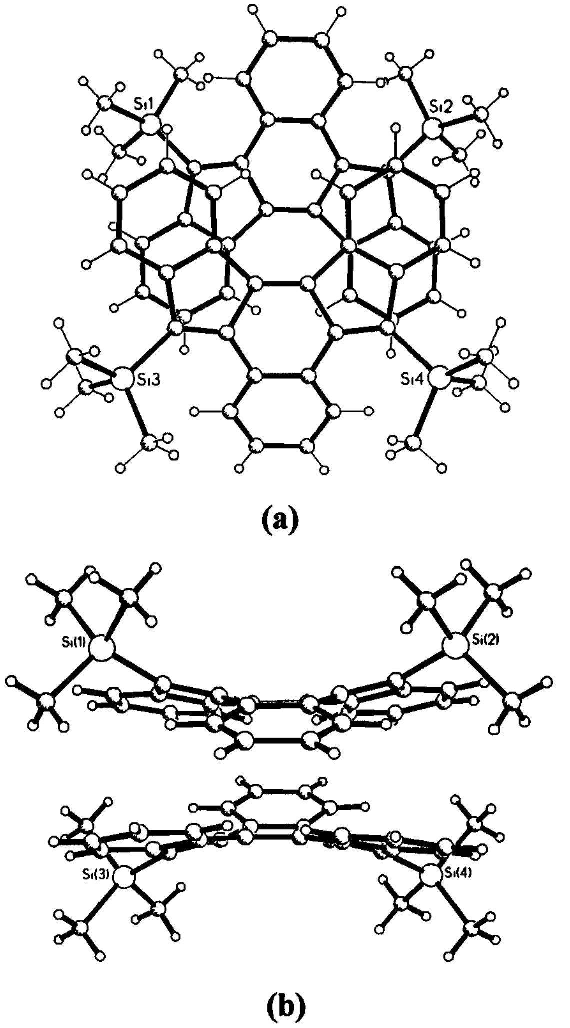

Figure 2. Perspective views of the arrangements of the two molecules in the asymmetric unit of $C_{24}H_{12}(SiMe_3)_2$ (**3**).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 3

Si(1)−C(1)	1.884(7)	Si(2)−C(28)	1.859(9)
Si(1)−C(25)	1.878(8)	Si(2)−C(29)	1.868(8)
Si(1)−C(26)	1.863(8)	Si(2)−C(30)	1.880(7)
Si(1)−C(27)	1.867(8)	C(10)−C(11)	1.482(10)
C(1)−C(2)	1.381(10)	C(11)−C(16)	1.440(10)
C(1)−C(24)	1.477(10)	C(16)−C(17)	1.487(10)
C(2)−C(18)	1.483(9)	C(17)−C(18)	1.353(10)
C(9)−C(10)	1.374(10)	C(18)−C(19)	1.474(10)
C(9)−C(17)	1.483(10)	C(19)−C(24)	1.419(10)
Si(2)−C(10)	1.881(7)		
Si(1)−C(1)−C(2)	131.1(5)	Si(2)−C(10)−C(9)	130.8(5)
Si(1)−C(1)−C(24)	121.4(5)	Si(2)−C(10)−C(11)	121.6(5)
C(2)−C(1)−C(24)	106.4(6)	C(9)−C(10)−C(11)	106.8(6)

The overall geometry of each molecule is essentially nonplanar with the benzene ring fused to an internal benzene ring bending away from the plane of the molecule pointing inward toward a second molecule. The actual bending occurs in the internal benzene ring at carbons C(2) and C(9). This bending is clearly caused by steric repulsion of the fairly large trimethylsilyl groups attached to the sp^2 carbons C(1) and C(10) with

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(14) The *cis* assignment is made relative to the least-squares plane of the fused cyclic portion of the molecule.

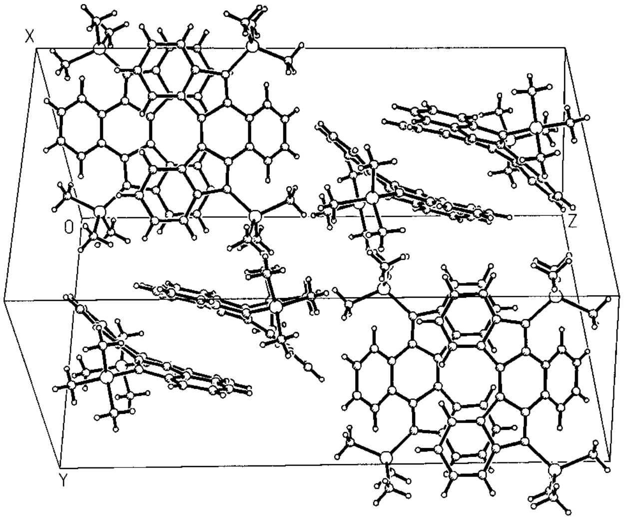


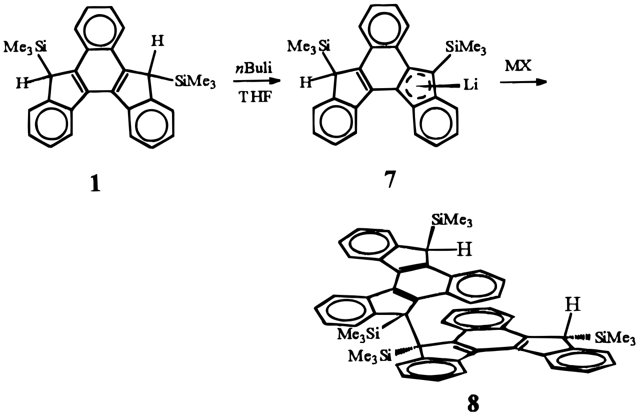
Figure 3. Packing diagram of $C_{24}H_{12}(SiMe_3)_2$ (**3**), showing eight molecules packed in the unit cell.

the hydrogen atoms on the external benzene ring. The trimethylsilyl groups slightly point away from the plane of the molecule and are arranged in a *cis*[14] fashion. The structure shows very little helical character, which arises in part from the steric interactions of hydrogen atoms on external benzene rings attached to the Cp moieties. The distance of the hydrogen−hydrogen interaction is 1.800 Å, and the dihedral angle between the two rings is only 12.6°. These values compare well with those of a similar *cis* structure also with very little helical character but with sp^3 carbons at C(1) and C(10) which was determined earlier by us.[11]

It is readily apparent from crystallographic analysis that the C−C bond lengths in the conjugated fulvalene moiety of **3** alternate between long and short and there is significant double-bond localization between C(1)−C(2), C(17)−C(18), and C(9)−C(10). This pattern is similar to that found in other π-conjugated fulvalene structures.[5] The Cp rings are reasonably planar while the trimethylsilyl groups deviate slightly from the plane of the Cp rings. The C−C bond distances within the Cp rings are typical for $C(sp^2)$−$C(sp^2)$ single and double bonds and are comparable with those found in other fulvalene structures and those obtained from a microwave study[15] of pentafulvene. The central C═C bond of the fulvalene moiety, C(17)═C(18), in **3** has an average value of 1.359(10) Å for the two crystallographically independent molecules in the asymmetric unit and is only slightly larger than the standard 1.34 Å expected for the C═C in ethylene[16] and planar fulvalenes.[17] The lengthening of the central C═C bond in other pentafulvalenes[5] has been attributed to the twisting[1] of the bond which inevitably lead to the loss of π-bond character. However, the structure of **3** shows no twisting of the central C═C so that the bond lengthening in **3** can only be attributed to other electronic factors such as dipolar[18] or diradical character[19] or hybridization effects.

Our current working hypothesis for the mechanism of this reaction is similar to the one proposed[20] by Beachley and co-workers. In this mechanism (Scheme 1), an initial formation of a complex **4** in which the metal atoms are bound to the Cp moiety in an η^5 fashion takes place. Both *cis* and *trans* isomers with respect to the plane of the molecule would be present at this stage. This is followed by coordination of the base (solvent molecules) to a Lewis acid site on the metal in **4** forcing ring slippage[21] of the Cp ring from η^5 to η^1 to form an intermediate **5**. This intermediate then immediately decomposes through a homolytic cleavage of the metal−carbon σ-bond resulting in a diradical **6** and metal atoms (Tl^0 or In^0). Electron rearrangement then leads in almost quantitative yield to the observed product **3**. Whereas Beachley and co-workers isolated their desired metal complexes in addition to decamethyl-1,1′-dihydrofulvalene,[20] we have not been able to observe or isolate corresponding metal complexes.

In order to test the hypothesis that a diradical is an intermediate immediately leading to formation of our product, we ran a similar reaction involving a monoanion (**7**) of compound **1** with the metal species in the hope of inducing coupling of the resulting radical to form a dimer. The monoanion **7** was generated by treatment of a solution of **1** in THF with 1 equiv of *n*-butyllithium. Indeed, reaction of **7** with thallium chloride produced an oxidatively coupled dimer $[C_{24}H_{13}(SiMe_3)_2]_2$ (**8**) in low yield. A similar result was observed by Okuda and coworkers who recently reported[22] an oxidative coupling of a trimethylsilyl-substituted cyclopentadienide anion by iron(III) chloride. These results are consistent with the coupling of two cyclopentadienyl radicals.



Evidence that a cyclopentadienyl radical is a key intermediate in oxidative coupling was provided by Sitzmann and co-workers, who recently reported[23] the isolation and crystal structure of a pentasubstituted cyclopentadienyl radical. This Cp radical which was prepared by reaction of its corresponding anion with

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[18] Ammon, H. L.; Wheeler, G. L. *J. Am. Chem. Soc.*, **1975**, *97*, 2326−2336.

[19] Bailey et al. reported a C═C twist with an average value of 40° and length of 1.39 Å for 1,1′-bis(isopropoxycarbonyl)-9,9′-bis-(fluorenylidene) and ascribed a diradical character to the bond (see ref 5d).

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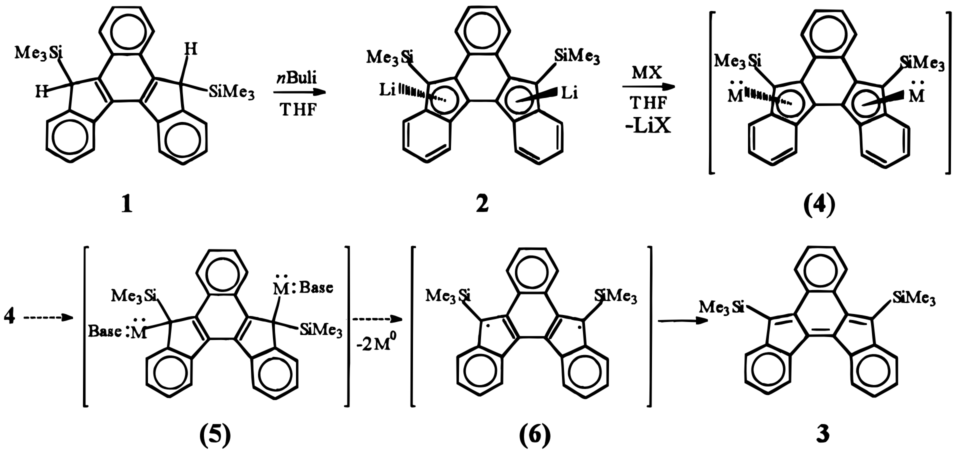
Scheme 1



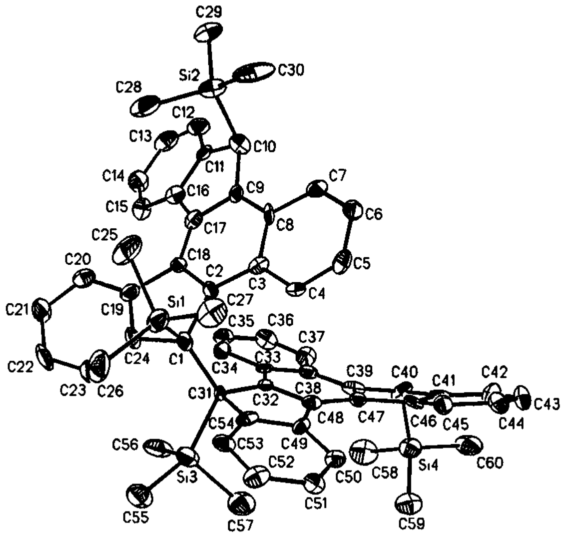


Figure 4. Molecular structure of $[C_{24}H_{13}(SiMe_3)_2]_2$ (**8**). The thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) for Compound 8

Si(1)−C(1)	1.993(8)	Si(3)−C(31)	1.976(11)
Si(1)−C(25)	1.876(13)	Si(3)−C(55)	1.878(10)
Si(1)−C(26)	1.881(11)	Si(3)−C(56)	1.861(10)
Si(1)−C(27)	1.873(9)	Si(3)−C(57)	1.876(12)
Si(2)−C(10)	1.916(10)	Si(4)−C(40)	1.904(11)
Si(2)−C(28)	1.869(11)	Si(4)−C(58)	1.873(10)
Si(2)−(29)	1.875(14)	Si(4)−C(59)	1.873(12)
Si(2)−(30)	1.836(11)	Si(4)−C(60)	1.877(11)
C(1)−C(2)	1.535(15)	C(19)−C(24)	1.394(16)
C(1)−C(24)	1.537(11)	C(31)−C(32)	1.533(11)
C(1)−C(31)	1.617(15)	C(31)−C(50)	1.520(12)
C(2)−C(18)	1.377(13)	C(32)−C(48)	1.386(12)
C(8)−C(9)	1.402(12)	C(39)−C(40)	1.484(12)
C(9)−C(10)	1.521(15)	C(39)−C(47)	1.388(11)
C(9)−C(17)	1.384(13)	C(40)−C(41)	1.518(12)
C(10)−C(11)	1.507(11)	C(41)−C(46)	1.394(12)
C(11)−C(16)	1.408(15)	C(46)−C(47)	1.482(12)
C(16)−C(17)	1.487(13)	C(48)−C(49)	1.487(11)
C(18)−C(19)	1.467(13)	C(49)−C(50)	1.397(13)

ferrous chloride has the sterically hindering isopropyl substituents which prevent it from coupling.

Compound **8** crystallizes in the monoclinic space group *Cc* with one molecule in the asymmetric unit. The molecular structure of **8** is shown in Figure 4, and selected bond distances are given in Table 3. The structure of **8** shows that it consists of two substituted-fulvalene moieties coupled through a carbon−carbon bond on the Cp rings with a distance of 1.617 Å. The entire molecule has a V-like shape, and the dihedral angle between the least-squares plane[24] of each of the substituted-fulvalene fragment is 39.6°. The trimethylsilyl groups are arranged in a *cis* fashion with respect to the least-squares plane of the substituted-fulvalene ligand to which they are attached and point away from the cone of the molecule.

Although the Cp and benzene rings are strictly planar, the molecule has a helical geometry which is clearly evident from the crystal structure. This helical character arises from the steric interactions of the hydrogen atoms on C(15) and C(45) with those on C(20) and C(54), respectively. The average hydrogen−hydrogen interaction is 1.917 Å, and the pitch of the helical interaction or the dihedral angle measured between the external benzene rings fused to the fulvalene moieties has an average value of 31.4°. These values are similar to those in the *trans* isomer of compound **1** which was reported[11] earlier but are considerably smaller than the values found in the *cis* and *trans* isomers of a bis((trimethylsilyl)indeno)chrysene.[25]

Conclusion

This work establishes that the concept of main-group-promoted oxidative π-conjugation and coupling is applicable as a synthetic tool for constructing pentafulvalenes and coupled fulvalenes particularly those that are highly fused. It remains to be seen whether this can be extended to the synthesis of oligomers of substituted fulvalenes and to π-conjugated systems of larger polycyclics such as bis((trimethylsilyl)indeno)chrysene.[25]

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Supporting Information Available: Complete listings of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond angles and bond lengths for **3** and **8** (24 pages). Ordering information is given on any current masthead page.

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[24] The trimethylsilyl groups were not included in the determination of the best least-squares plane of each of the substituted-fulvalene fragments.

[25] Bradshaw, J. D.; Solooki, D.; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1994**, *116*, 3177−3179.