

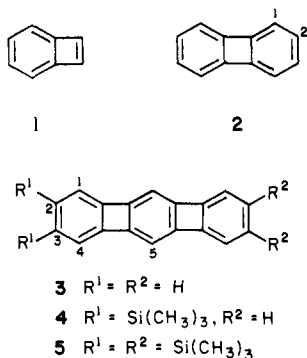
A New Approach to the Construction of Biphenylenes by the Cobalt-Catalyzed Cocyclization of *o*-Diethynylbenzenes with Alkynes. Application to an Iterative Approach to [3]Phenylene, the First Member of a Novel Class of Benzocyclobutadienoid Hydrocarbons

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Abstract: CpCo(CO)₂ has been found to catalyze the cocyclization of *o*-diethynylbenzenes with alkynes to give 2,3-disubstituted biphenylenes. This method has been applied to the total synthesis of [3]phenylene (3) and some silylated derivatives 4 and 5. The spectral, chemical, and structural data indicate this system to be a highly unusual "benzocyclobutadienoid" hydrocarbon framework containing $[4n + 2]$ π electrons. The central benzene ring is highly reactive to hydrogenation, alkyllithium addition, and transition-metal complexation. Reduction and oxidation furnishes the corresponding $4n$ dianions and dications. The nuclear magnetic resonance data of these ions show unexpected trends in comparison with the neutral parent system.

The study of benzenoid and nonbenzenoid conjugated molecules has experienced a renaissance because of the renewed interest in coal as a source of chemicals¹ and because of advances in the understanding of their carcinogenic potential.² Many compounds have been prepared consisting of annelated $(4n + 2)\pi$ -electron systems, such as naphthalene and the other acenes, as well as macrocyclic annulenoannulenes.³ Their properties generally reflect the stability of their component rings. Even more interesting molecules are those containing both $(4n)$ - and $(4n + 2)\pi$ -electron cycles (the $[4n]$ annuleno $[4n + 2]$ annulenes), because they incorporate individual and/or peripheral circuits which may make opposing (e.g., stabilizing and destabilizing) contributions to the resonance energy.⁴ A subgroup in this class of compounds, the "cyclobutadienoids",⁵ has shown especially unusual behavior. Two key compounds in this area are benzocyclobutadiene (1)⁶ and biphenylene (2) (dibenzocyclobutadiene)^{6a,7} in which the antiaromatic cyclobutadiene is juxtaposed to the classic aromatic ring of benzene. This paper deals with a new approach to the regioselective construction of the biphenylene nucleus and its extension to the preparation of a new polycyclic benzocyclobutadienoid, [3]phenylene (3).



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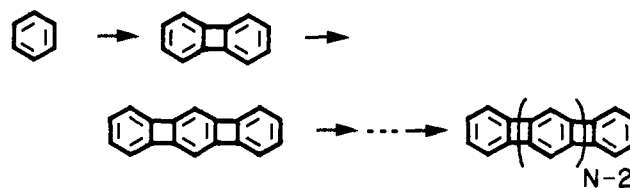
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Scheme I



Although in biphenylene the rings are linked by essentially single bonds (length 1.522 Å),⁸ there is strong electronic interaction between them. The ¹H NMR spectrum of 2 shows that the protons nearer to the four-membered ring (H-1) are shielded compared to H-2 and the hydrogens in benzene.⁹ This shielding seems to be due to both reduced diamagnetic and strong paramagnetic ring currents.^{9,10} The regioselectivity of the electrophilic substitution reactions of biphenylene further supports the idea that electronic effects are transmitted through the four-membered ring.¹¹ Binsch¹² concluded that, unlike cyclobutadiene, biphenylene (2) is aromatic on the basis of a bond length alternation criterion. In seeming accord with this conclusion, it appears that 2, even though destabilized by the strain and/or antiaromaticity of its four-membered ring, is relatively unreactive.

In light of the unusual physical and chemical properties of biphenylene (2) we deemed it of interest to prepare its benzocyclobutadienoid homologue 3. This molecule is a dibenzo derivative of 6, a highly unusual 10π -electron system of which a persubstituted example is known.¹³ It is also an isomer of the

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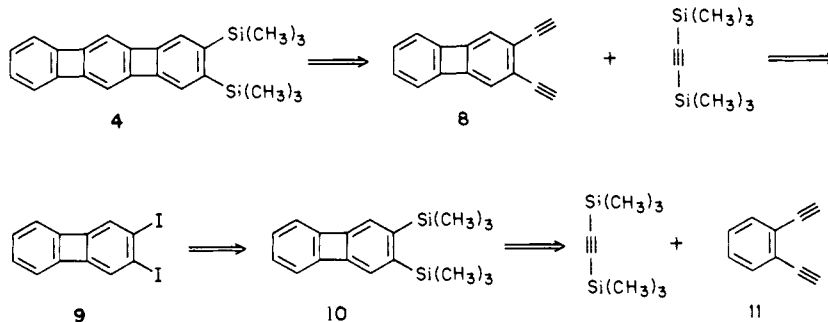
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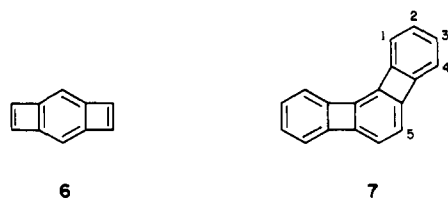
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Scheme II



angular system **7**, prepared by Barton in 1978 by a pyrolytic route in low yield.^{14a} The conjugated circuits theory¹⁵ (CC) predicts



a substantial resonance stabilization (+0.357 eV) of the linear **3**, while **7** is supposed to be destabilized by cyclic conjugation (-0.315 eV; cf. **2**: +0.330 eV). On the other hand, we have applied Hess and Schaad's version of the HMO theory¹⁶ (REPE) and found that it predicts a small stabilization for both isomers (**3**, +0.007 eV; **7**, +0.008 eV; cf. **2**: +0.027 eV). Both theories agree that biphenylene is stabilized by resonance. Using simple HMO theory, Barton and co-workers judged **7** to be marginally more stable than **3**,^{14b} whereas PMO theory¹⁷ suggests the strong opposite, in agreement with CC.

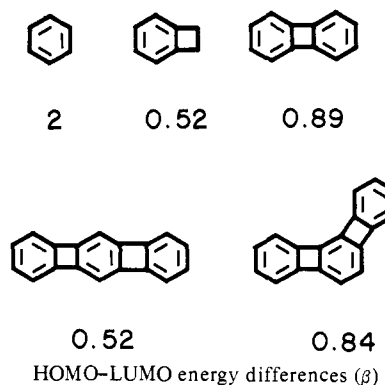
The preparation of **3** was thought to be important simply as a complement to the synthesis of **7**, because the properties of these isomers could then be compared. Furthermore, **3** itself was expected to exhibit interesting reactivity and spectra. Although it has $(4n + 2)$ π electrons, it also has two cyclobutadienoid rings, making predictions concerning its reactivity difficult.

Compound **3** is related to biphenylene, as biphenylene is to benzene, by a formal "cyclobutabenzannulation". Sequential annelation in this manner leads to a class of compounds which are composed of fused benzene rings linearly linked at the ortho positions as shown in Scheme I.

We term this novel series of benzenoid aromatics the *multi-phenylenes* (e.g., biphenylene, terphenylene, etc.) in analogy to the multiphenyls [biphenyl, terphenyl, etc.; IUPAC rule (blue book) A-52, A-54; specifically A-54.3] or "[N]phenylenes", where *N* indicates the number of benzene rings. Thus, biphenylene (**2**) would be the first member of the series $N = 2$, and **3** would be designated as [3]phenylene.

The class of [N]phenylenes has several interesting features. When *N* is odd, the π -electron count is $(4n + 2)$. On the other hand, when *N* is even, the π -electron count is $(4n)$. Therefore, an alternation of properties might be expected as a reflection of the total electron count, just as in the annulenes.¹⁸ The [N]-

phenylenes are predicted by HMO theory to have progressively smaller differences in energy between their HOMOs and LUMOs.



Because of this trend, the larger [N]phenylenes may be expected to be materials capable of conductivity,¹⁹ perhaps by a mechanism similar to that of $(\text{CH})_x$.²⁰ Molecules of this type, with nearly degenerate HOMOs and LUMOs, might behave as organic ferromagnets.²¹

An analogy may be drawn between the [N]phenylenes and the well-known acenes, which are derived from benzene by sequential benzoannulation in a linear manner.²² In contrast to the [N]phenylenes, the acenes always have a π -electron count of $(4n + 2)$. The higher acenes, such as heptacene, are quite unstable and difficult to purify.²² In particular, their reactivity toward Diels-Alder cycloaddition increases with the number of rings.²³ However, it is expected that the [N]phenylenes would be resistant to this type of reaction because the products would have either strained double bonds or benzocyclobutadienoid structures (depending on the mode of addition). This leads to the surprising possibility that the [N]phenylenes, with their antiaromatic moieties, may be kinetically more stable than the aromatic acenes.

Synthetic Strategy

In order to prepare **3**, we needed to develop a new synthesis of biphenylene and its derivatives which would provide unsymmetrically substituted systems with appropriate functionality to allow for further annelation. Relatively few good methods for preparing biphenylenes exist,^{6a,7} presumably because of the incorporated large amount of strain and/or antiaromaticity, estimated to be at least 64 kcal mol⁻¹.²⁴ Among the several stra-

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Table I. Biphenylenes by Cocyclization of *o*-Diethynylbenzenes with Alkynes

biphenylene	R ¹	R ²	R ³	% yield ^a
10	Si(CH ₃) ₃	Si(CH ₃) ₃	H	96 ^b
12	Si(CH ₃) ₃	<i>n</i> -C ₅ H ₁₁	H	58
13	H	<i>n</i> -C ₅ H ₁₁	H	41
14	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	H	44
15	H	C ₆ H ₅	H	25
16	C ₆ H ₅	C ₆ H ₅	H	35
17	CO ₂ CH ₃	CO ₂ CH ₃	H	30
18	Si(CH ₃) ₃	Si(CH ₃) ₃	Cl	90 ^b

^a Yields were not optimized except for the preparation of 2,3-bis(trimethylsilyl)biphenylene (**10**). ^b Reactions were run with btmse as solvent.

gies,²⁵⁻²⁹ most notable in connection with the present work is the extrusion of nitrogen from cinnolines,³⁰ as applied by Barton and co-workers¹⁴ to the synthesis of **7**. After we had synthesized **3** and during an investigation of its chemistry, the same group reported the preparation of **3** by this technique and again in low yield.³¹ 2,3-Didehydrobiphenylene has been generated and trapped by pyrolysis of the corresponding diazonium carboxylate,³² although [4]phenylene was not detected.

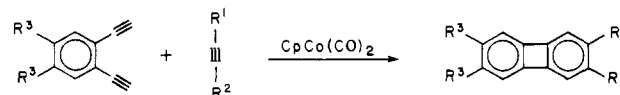
We envisaged a synthesis of **3** and its derivatives by the cocyclization of *o*-diethynylarenes with alkynes in the presence of (η^5 -cyclopentadienyl)dicarbonylcobalt [CpCo(CO)₂]^{33a,b} (Scheme II). In particular, utilization of bis(trimethylsilyl)ethyne (btmse) as a cocyclization partner³³ would allow the introduction of trimethylsilyl groups at strategic positions, to be further functionalized by iododesilylation,^{33,35} palladium-catalyzed ethynylation,³⁶ and renewed cyclization. The iterative nature of this strategy is an attractive advantage, allowing the possibility of synthesizing the higher [*N*]phenylenes. The only concerns surrounding the feasibility of the approach were the known sensitivity of *o*-diethynylbenzenes, their established propensity to be the source of a multitude of (mainly organometallic) products when exposed to metal carbonyls,^{34,37} and the fact that (η^4 -1,2-diethynylcyclobutadiene)(η^5 -cyclopentadienyl)cobalt did not lead to analogous cyclization products, but rather to complexed cyclobutadienes.³⁸

In this paper we detail the successful execution of Scheme II and an even shorter variant en route to **3**, **4**, and **5**, including a

general synthesis of 2,3-disubstituted biphenylenes, and an investigation of the structure and chemistry of the [3]phenylene system.³⁹

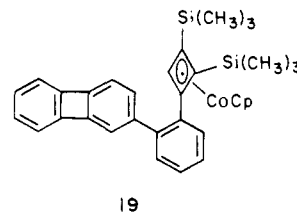
Results and Discussion

A Cobalt-Catalyzed Biphenylene Synthesis. The starting material 1,2-diethynylbenzene (**11**) was readily obtained in either of two ways by using published procedures.^{36a,40} We have found (Table I) that 2,3-disubstituted biphenylene derivatives are formed by cocyclization of **11** with alkynes in the presence of CpCo(CO)₂.^{39a} With btmse as solvent a virtually quantitative yield



of 2,3-bis(trimethylsilyl)biphenylene (**10**) was obtained on a small scale (ca. 1 mM) (see Experimental Section). On a larger scale, a lesser, but still good yield of crystallized product was realized.

The cyclobutadiene complex **19** was isolated in 44% yield (based on cobalt) in one reaction which was not carried out under high dilution conditions. The cyclizations leading to the new biphenylenes **12-17** were carried out by using nearly equimolar



amounts of starting materials (5% excess of monoalkyne) in irradiated and boiling *o*-xylene. The high yield of biphenylene **18** resulting from the cocyclization of 1,2-dichloro-4,5-bis(ethynyl)benzene with btmse is remarkable. We had noted previously that bromo- and iodoarenes decompose the catalyst, presumably because of facile oxidative addition processes.⁴¹ The preparation of **18** is the first successful cyclization involving a haloarene. The required diene precursor was obtained by converting first 4,5-dichloro-1,2-benzenediamine into the corresponding diiodide [(1) NaNO₂, H⁺; (2) KI, 42.5%], followed by palladium-catalyzed trimethylsilylethynylation (87%) and protodesilylation (75%), as in Scheme II.

In the case of silylated biphenylenes, electrophilic ipso substitution at C-2 and C-3 gives access to other derivatives, extending the scope of the method (see below). The trimethylsilyl groups in **10** could be protodesilylated by treatment with trifluoroacetic acid, giving the parent biphenylene in 72% yield. Monitoring of this reaction by ¹H NMR spectroscopy indicated that the first trimethylsilyl group was much more quickly removed than the second, in accord with similar observations in other systems.^{33a} However, in contrast to them, migration of the silyl groups was not apparent under these conditions. This may be due to the decreased relative reactivity of the 1-positions in biphenylene compared to benzocyclobutene.⁷ Because of the enhanced reactivity of one of the silyl groups, selective substitution should be a feasible way of preparing biphenylenes with different substituents on C-2 and C-3, a particularly attractive route to molecules not directly accessible by cocyclization.

The biphenylenes prepared by the above methods were all new and exhibited characteristic analytical and spectral data. For example, the ¹H NMR spectrum of **10** revealed an AA'BB' multiplet with chemical shifts of δ 6.71 and 6.64, assigned to the

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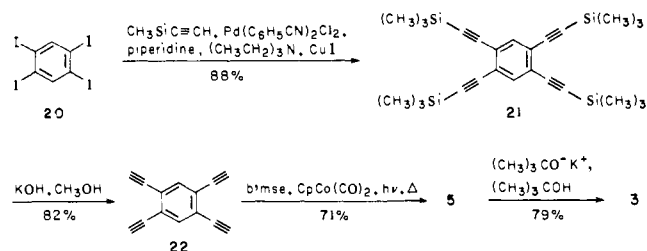
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Scheme III



unsubstituted benzene nucleus. These absorptions are upfield of those of benzene, and similar to those in biphenylene, due to the presence of the paratropic central ring.^{9,10} The proton on the silicon-substituted ring is shifted downfield compared to the parent system, absorbing at δ 6.94. This effect is apparently a result of steric compression. A similar trend is observed in the trimethylsilyl-substituted benzocycloalkenes.³³ The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10** exhibited 7 peaks in accord with the assigned structure. The UV spectrum was characteristic of the biphenylene chromophore and is very similar to the parent system.

The cobalt-catalyzed approach to biphenylenes described in this section has found application in the literature in the construction of the 1,3-diazabiphenylene nucleus.⁴²

Synthesis and Physical Properties of [3]Phenylene. The ready availability of **10** suggested the iterative Scheme II as a route to the next higher phenylene **4** and ultimately **3**. Thus, treatment of **10** with ICl resulted in a 63% yield of 2,3-diiodobiphenylene (**9**). Interestingly, similar exposure of the parent biphenylene to ICl gives 2-chlorobiphenylene rather than iodine-containing products.⁴³ Moreover, the bromination of substituted biphenylenes is known to furnish ring-opened structures.⁴⁴ 2,3-Bis(trimethylsilylethynyl)biphenylene was obtained in 75% yield by the palladium-mediated coupling of tmse and **9**. Desilylation with basic methanol gave **8** quantitatively. Gratifyingly, reaction of **8** with btmsc in the presence of $\text{CpCo}(\text{CO})_2$ gave the intensely red-colored [3]phenylene derivative **4** in 36% yield. The relatively lower yield of this compound is probably due to the fact that high dilution conditions were not employed for solubility reasons, and because its preparation was not optimized (see Experimental Section) due to the simultaneously developed more efficient approach to **5** to be described below.

The structural assignment of **4** rests on its physical and chemical behavior. Thus, the high-resolution mass spectrum confirmed the molecular formula. The ^1H NMR spectrum (C_6D_6) exhibited an AA'BB' multiplet with chemical shifts of δ 6.45 and 6.19. The upfield part was assigned to H-6 by analogy with biphenylene.^{9,10} The coupling constants were determined by spectral simulation ($J_{6,7} = 6.7$ Hz, $J_{7,8} = 8.4$ Hz). In addition to these signals, a singlet absorption at δ 6.84 was assigned to H-1. This assignment is aided by reference to the spectrum of **10**, in which the singlet absorption due to the proton nearer the silyl group is *downfield* of its counterpart on the unsubstituted ring. The remaining "aromatic" absorption was a singlet at δ 6.07 due to H-5 by comparison with the spectrum of the parent **3** (see below). The UV-vis spectrum was similar to that of **3** (see below). The IR spectrum exhibited the expected absorptions. Especially characteristic were two peaks at 736 and 758 cm^{-1} , observed in the spectra of typical biphenylene derivatives.^{6a,7}

In order to obtain the parent system, it was necessary to desilylate **4**. This transformation proved to be unexpectedly troublesome because trifluoroacetic acid treatment of **4** resulted in what appeared (by ^1H NMR spectroscopy) to be a mixture of

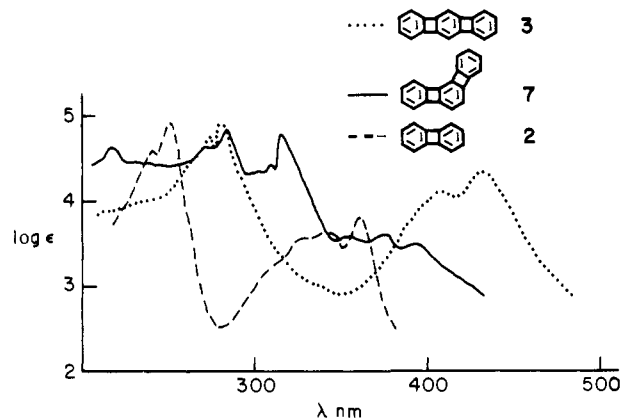
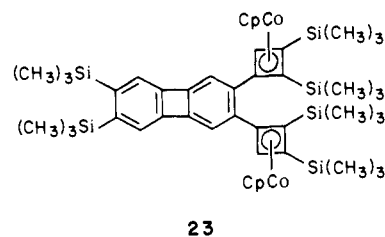


Figure 1. UV-visible absorption spectra of **2**, **3**, and **7**.

partly desilylated material and other unidentified products, but none of **3**. At this point a more efficient route into the [3]-phenylene nucleus was developed which led to the tetrasilyl derivative **5**. Most of the chemistry to be reported was carried out with this system, including its base-mediated transformation into **3**.

The improved approach to **3** started with the readily available 1,2,4,5-tetraiodobenzene (**20**)⁴⁵ which was converted (Scheme III) into the stable, protected tetraethynylbenzene **21** in 88% yield. Protodesilylation under basic conditions gave **22** (82%), an unstable molecule which detonated with inflammation when heated in air or on attempted vacuum sublimation! Despite its sensitivity, **22** efficiently coccyclized with toluene and DMF as co-solvents to give 2,3,7,8-tetrakis(trimethylsilyl)terphenylene (**5**) in a reaction which makes four rings and six carbon-carbon bonds in one operation. This molecule is stable at room temperature and in hydrocarbon solvents but was found to decompose under the influence of light in halogenated solvents (e.g., CHCl_3 , CH_2Cl_2). Also obtained in the cyclization reaction was the cyclopentadienylcobalt complex **23** (stereochemistry unknown) in 94% yield (based on cobalt). Because of the problems encountered in the acid treatment of **4**, base-mediated removal of the silyl



groups was explored. It had been reported that arylsilanes could be desilylated by aqueous KOH in Me_2SO solution.⁴⁶ However, **5** was found to be insoluble in Me_2SO , and no reaction took place in this solvent. On the other hand, both **4** and **5** were desilylated by potassium *tert*-butoxide in a mixture of Me_2SO , *tert*-butyl alcohol, and THF in 6 h at 85 °C. The parent [3]phenylene, similar to its precursor, is deep red, forming very thin crystalline flakes, mp 275–280 °C dec. Once crystallized, it dissolves only very slowly in hot solvents. Like **4** and **5**, it is stable to air, but it decomposes overnight in chloroform.

The structural assignment of **3** was supported by analytical and spectral data. The elemental analysis and HRMS confirmed the molecular formula. The mass spectrum was notable for its intense parent ion signal and a lack of fragmentation ion peaks. In the ^1H NMR spectrum (C_6D_6) the proton on the central ring, H-5, gave rise to a singlet absorption at unusually high field, δ 5.91. The protons on the outer rings, H-1 through H-4 and H-6 through H-9, absorb as an AA'BB' pattern with chemical shifts of δ 6.45

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and 6.19. The upfield portion of this multiplet was assigned to H-1,4,6,9 by analogy with biphenylene. The coupling constants ($J_{1,2} = 6.6$ Hz, $J_{2,3} = 8.6$ Hz) were obtained by spectral simulation. The ^{13}C NMR spectrum exhibited only five lines, the carbons α to the strained rings being relatively shielded (116.0 and 111.2 ppm) and exhibiting relatively large $J_{\text{C-H}}$ values (158 and 165 Hz, measured on the more soluble **5**) as expected for such systems.⁴⁷ The UV spectrum of **3** is shown in Figure 1 and compared with that of biphenylene **2** and the angular isomer **7** (reconstructed from literature data).^{14a} The spectrum of **3** shows two major absorption bands (λ_{max} 436 and 290 nm) with large extinction coefficients and some fine structure. The fact that **3** has peaks at much longer wavelengths than **7** supports HMO calculations which predict that the HOMO-LUMO energy gap of the former is less than that of the latter. This will be pertinent to the discussion of the ring current properties of these molecules. An unusual feature of this spectrum is the relatively large separation between these absorptions (146 nm) compared to **7**, and also to biphenylene (110 nm).

The ^1H NMR spectra of **3**, its derivatives, and **7** are quite unusual for arene structures. Thus, all of the absorptions appear upfield of the signal for benzene at δ 7.15. These upfield shifts suggest either the presence of paramagnetic ring currents, the quenching of diatropicity due to increased bond alternation compared to benzene, or a combination of both. It has been shown that increasing bond alternation is associated with diminishing ring currents; paratropism is more strongly influenced by bond alternation.⁴⁸

The following discussion pertains to NMR spectra determined in CDCl_3 , in order to allow for comparison with the literature data. The central ring protons H-5 of both compounds **3** and **7** have the most unusual chemical shifts, δ 6.24 in **3** and at δ 6.13 in **7**. Thus, they are nearly isochronous though H-5 in the former is adjacent to two four-membered rings and in **7** only to one. There must be another factor which compensates for the differing proximity effects⁴⁷ which would otherwise be expected to shield H-5 in **3** more than in **7**. Either **3** has a stronger diamagnetic component ring current than **7** or it has a weaker paramagnetic contribution. The former possibility is quite reasonable considering the fact that **3** has little bond alternation in the central ring (see below), while **7** probably has more (expected on simple valence structure terms). Thus, the large shielding of H-5 in **7** may be the result of bond localization. On the basis of an examination of the most stable resonance structures in these molecules, it can be argued that **3** has a greater π -bond order in its four-membered rings than **7** and should therefore have a stronger paramagnetic component ring current. This idea is also supported by the smaller calculated HOMO-LUMO energy gap for **3** which should impart stronger paratropism.⁴⁹ As a result, the outer-ring protons of **3** are shielded more strongly than those of **7** (δ 6.51 vs. 6.92). Indeed, these protons in **7** appear to be nearly unaffected by paramagnetic ring currents since their ^1H NMR resonances are only 0.20 ppm upfield of that of benzene. This may be an indication of a lack of bond alternation in these rings, as expected on the basis of an examination of resonance structures. The variation in chemical shifts of the outer-ring protons also supports the claim that **3** has a stronger paramagnetic component ring currents. H-1, -2, -3, and -4 in **7** have quite similar chemical shifts, giving rise to a broad single absorption. On the other hand, the chemical shifts of the two portions of the AA'BB' multiplet in the spectrum of **3** differ by 0.21 ppm. For comparison, the protons in biphenylene have chemical shifts which differ by only 0.10 ppm. In sum, the high-field chemical shift of H-5 in **3** may be explained by the existence of paramagnetic ring current effects. Compound **7**, on the other hand, may exhibit predominant bond localization in the central ring, also shielding the central ring proton.^{14c}

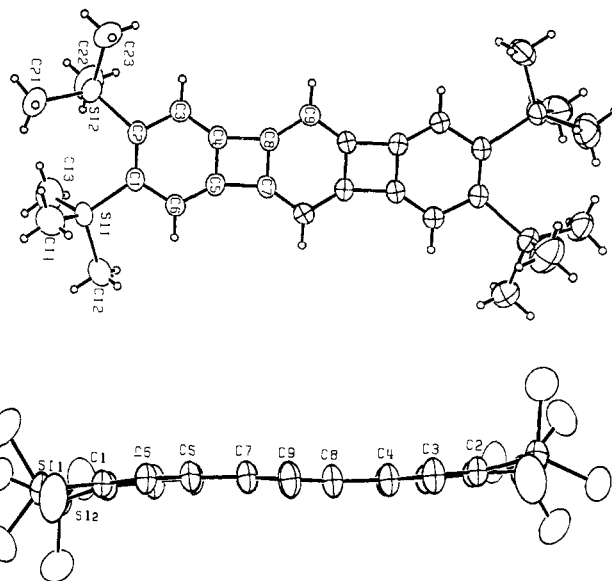


Figure 2. ORTEP drawing of **5** with labeling scheme: top, frontal view; bottom, side view. The hydrogens are shown as arbitrarily small spheres for clarity. The other ellipsoids represent the 50% probability surface.

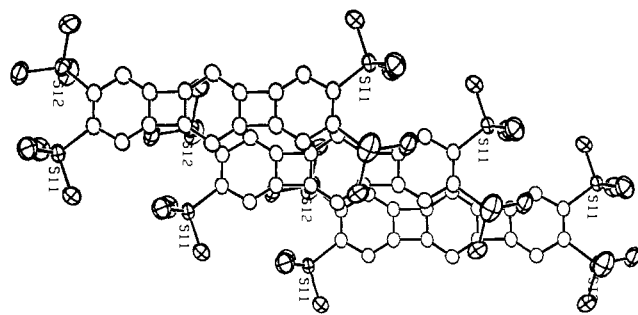


Figure 3. View of the packing in the unit cell of **5**. The c axis is vertical and the b axis is horizontal. The direction of view is approximately down the a axis. The ellipsoids are scaled to represent the 20% probability surface.

An alternative explanation for the difference in the chemical shifts in the two [3]phenylene isomers is proposed by Barton.³¹ He has chosen to focus on the outer-ring protons because their chemical shifts will not be complicated by differences in proximity to the four-membered rings. He points out that HMO calculations predict lesser resonance stabilization for the linear isomer, resulting in stronger paratropism. However, resonance energy may not be an indicator to the magnitude of paramagnetic ring currents.^{49,50}

The X-ray Structure of 5. Although crystals of **3** suitable for an X-ray structure determination could not be obtained, the structure of the tetrasilylated derivative **5** was solved by this method. Figure 2 shows two views of the individual molecule, Figure 3 reveals aspects of the crystal packing.

The individual molecules of the compound are packed very compactly along the a axis so that the bulky trimethylsilyl groups are slipped into the "hollow" on the back of the planar part of a neighboring molecule. The compact chains are congregated in layers in the a - b plane. These layers are stacked in the c direction so that the only contacts are between methyl groups of the silyl moieties. There are no abnormally short distances between any of the molecules.

The [3]phenylene frame of **5** is basically flat, but it deviates significantly from complete planarity. Each molecule contains a crystallographic inversion center in the middle of the central ring, and in addition each possesses near mirror symmetry about a plane normal to the plane of the molecule and running its length (Figure 2). This mirror symmetry is broken only by the torsion

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Table II. Selected Bond Distances (Å) and Angles (deg)^a in 5

Intramolecular Distances														
atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance			
Si1	C1	1.891 (1)	C1	C2	1.397 (2)	C3	C4	1.359 (2)	C7	C8	1.407 (2)			
Si1	C11	1.855 (2)				C5	C6	1.356 (2)						
Si1	C12	1.868 (2)	C2	C3	1.436 (2)				C8	C9	1.385 (2)			
Si1	C13	1.861 (2)	C1	C6	1.441 (2)	C4	C5	1.397 (2)	C7	C9'	1.385 (2)			
Si2	C2	1.907 (1)				C4	C8	1.513 (2)						
Si2	C21	1.859 (2)				C5	C7	1.512 (2)						
Si2	C22	1.865 (2)												
Si2	C23	1.864 (2)												
Nonbonding Intramolecular Contacts between Methyl Carbons														
	atom 1	atom 2	distance											
			C21...C11	3.606 (3)										
			C21...C13	3.568 (3)										
			C22...C13	3.699 (3)										
Intramolecular Angles														
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle			
C1	Si1	C11	110.16 (8)	C2	C3	C4	118.07 (12)							
C1	Si1	C12	109.96 (6)	C1	C6	C5	118.32 (11)							
C1	Si1	C13	113.48 (7)											
C11	Si1	C12	106.13 (9)	C3	C4	C5	122.01 (11)							
C11	Si1	C13	111.72 (10)	C4	C5	C6	121.74 (11)							
C12	Si1	C13	105.01 (9)											
				C5	C4	C8	90.22 (10)							
C2	Si2	C21	117.76 (7)	C4	C5	C7	90.14 (10)							
C2	Si2	C22	106.75 (7)	C5	C7	C8	89.89 (10)							
C2	Si2	C23	109.37 (7)	C4	C8	C7	89.72 (10)							
C21	Si2	C22	110.93 (8)											
C21	Si2	C23	104.31 (9)	C7	C8	C9	124.02 (12)							
C22	Si2	C23	107.31 (10)	C8	C7	C9'	124.04 (11)							
Si1	C1	C2	127.73 (9)	C8	C9	C7'	111.94 (12)							
Si1	C1	C6	112.52 (9)											
				C3	C4	C8	147.58 (13)							
Si2	C2	C1	128.46 (9)	C6	C5	C7	147.91 (12)							
Si2	C2	C3	111.06 (9)	C4	C8	C9	146.10 (12)							
				C5	C7	C9'	145.96 (12)							
C2	C1	C6	119.75 (11)											
C1	C2	C3	120.05 (11)											
Torsional Angles (deg)														
atom 1	atom 2	atom 3	atom 4	angle	atom 1	atom 2	atom 3	atom 4	angle	atom 1	atom 2	atom 3	atom 4	angle
C2	C1	Si1	C11	-75.3	C1	C2	Si2	C22	-82.6					
C2	C1	Si1	C12	168.1	C1	C2	Si2	C23	161.6					
C2	C1	Si1	C13	50.8	C3	C2	C1	Si1	179.8					
C1	C2	Si2	C21	42.8	C6	C1	C2	Si2	170.7					

^aIn this and subsequent tables, the esds, given in parentheses right-adjusted to the least significant digit(s) shown, were calculated including the correlation terms derived from the inverted least-squares matrix. Distances and angles are not corrected for thermal motion.

angles about the C-Si bonds and by the deviation of Si-2 from the plane of the six-carbon ring to which it is attached.

The molecule can be described in terms of five planes, of which two are related to two others by the inversion center. The three unique planes are (1) C1-C6, (2) C4-C5-C7-C8, and (3) C7-C9 plus C7'-C9', the latter passing through the center of inversion. Each of these planes is flat to ± 0.01 Å. Si-1 lies in plane 1, but Si-2, due to inter- and intramolecular interactions, is located 0.27 Å out of plane on the same side as C7, C8, and C9. Plane 1 is bent 4.7° with respect to plane 2 and 8.1° with respect to plane 3. The bending lines essentially coincide with the C4-C5 and the C7-C8 vectors.

The bond distances and angles in the molecule are given in Table II. In comparison with the structures of 4,5-bis(trimethylsilyl)benzocyclobutene⁵¹ and biphenylene⁸ several features are noteworthy. The outer rings show considerably more pronounced bond alternation than the model compounds and are

similar to that in the antiaromatic 1,2-di-*tert*-butyl-3,4,5,6-tetramethylbenzocyclobutadiene.⁵² The validity of this comparison is reinforced on comparing the Q value⁵³ for the outer rings in 3 ($Q = 0.74$) with that calculated for benzocyclobutadiene ($Q = 0.78$). There appears to be little doubt regarding the bond-fixing nature of the four-membered rings. While the bond lengths of the central benzene ring are not all equal, they do not alternate to the same degree as the outer rings and, because of symmetry, not in a "Kekule" sense, involving consecutive short and long bonds. Rather, the central ring resembles two strongly interacting allyl fragments. The cyclobutadienoid bonds are remarkably short, particularly compared to those in biphenylene, and are very similar in length to those found in benzene itself.

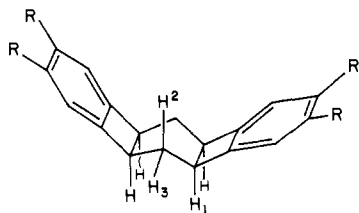
The trimethylsilyl groups at the ends of the molecule interact strongly with each other. A listing of the shorter methyl-methyl contacts is given in Table II. The resulting steric strain is relaxed in part by the deviation of Si-2 from the plane of the ring and

(51) Moder, K. P.; Duesler, E. N.; Leonard, N. J. *Acta Crystallogr., Sect. B* 1981, B37, 1524.

(52) Winter, W.; Butters, T. *Acta Crystallogr., Sect. B* 1981, B37, 1524.
(53) Cremer, D.; Günther, H. *Liebigs Ann. Chem.* 1972, 763, 87. Günther, H.; Shyokh, A.; Cremer, D.; Frisch, K. H. *Tetrahedron Lett.* 1974, 781.

by the different conformation of the silyl group on C-1 in comparison to that on C-2. In the packing diagrams, it is the second silyl substituent which is in close proximity to the flat plane of the nearest molecule and its distortion from the plane is away from it. C-21, in particular, has distances of 3.75 Å from C-5 and 3.81 Å from C-6 in the nearest molecule.

The Reactivity of the Central Benzene Ring in 3 and 5. The [3]phenylenes **3** and **5** exhibit remarkable reactivity of the central "benzene" ring. Thus, both compounds when exposed to hydrogen in THF over palladium on charcoal underwent rapid and unusually stereospecific⁵⁵ hydrogenation of the *all-cis* hexahydrogenated products **24** or **25** in good yield. No other stereoisomers were detectable by ¹H NMR spectroscopy or GLC analysis of the crude



24 R = H
25 R = Si(CH₃)₃

reaction mixtures. However, in the case of **3**, traces of two other products were detected by GC, tentatively identified as *m*- and *p*-terphenyl by coinjection with authentic samples. The hydrogenolysis of biphenylene rings to give biphenyls is known.^{6a}

The stereochemistry of the hydrogenation products **24** and **25** was established by examination of their 250-MHz ¹H NMR spectra. In the case of **25** the aromatic protons gave rise to a singlet at δ 7.64 (4 H), a multiplet at δ 3.40 (4 H) was assigned to H-1, a doublet of triplets at δ 2.24 (*J* = 6, 13 Hz, 2 H) was judged to be due to H-3, and a doublet of triplets at δ 1.51 (*J* = 12, 13 Hz, 2 H) was associated with H-2. The coupling constants and assignments were verified by double-irradiation experiments. Irradiation of the multiplet at δ 3.47 simplified the doublet of triplets due to H₂ and H₃ and caused the multiplet at δ 3.47 to become a doublet (*J* = 12 Hz) and the signal at δ 1.52 to collapse into a broad triplet (*J* ~ 12 Hz). Irradiation of the signal at δ 1.52 assigned to H-2 simplified the multiplet at δ 3.47 into a doublet (*J* = 6.8 Hz) and caused the collapse of the signal at δ 2.40 into a broad triplet (*J* ~ 7 Hz).

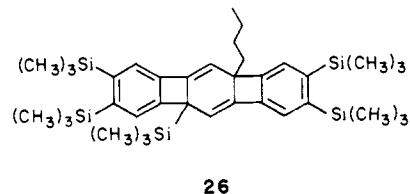
The syn relationship between the two benzocyclobutene rings was established by the fact that there are three multiplets in the aliphatic part of the spectrum. The anti isomer would be expected to display only two such patterns because H-2 and H-3 are equivalent in this structure. The ¹H NMR spectrum also strongly implicates the conformer shown in the drawings for **24** and **25** as the predominant species in solution, as might be expected on steric grounds. Thus, the upfield absorption at δ 1.51 is assigned to an axial position, as in H-2 and as observed in other cyclohexane derivatives.⁵⁴ The two large couplings are then readily identified as a geminal and a *trans*-diaxial interaction.

To obtain a qualitative measure of the relative reactivity of **3**, it was subjected to hydrogenation in competition with cycloheptene. It was found that hydrogenation of **3** over Pd takes place selectively in the presence of *unreacted* cycloheptene. Thus, only a trace of cycloheptene was observable (GC) after over 90% of **3** (UV) had been converted. Therefore, the central ring of **3** is more reactive than a simple cycloalkene!

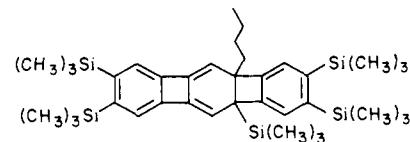
The relative reactivity of the central ring in **3** (and perhaps also **5**, although the trimethylsilyl substituents constitute a considerable steric perturbation) is also of interest when taking into consideration the considerably larger extent of bond alternation in the outside rings. Bond alternation is usually taken as an indication

of lesser aromaticity and higher reactivity.⁵⁶ Polycyclic benzenoid hydrocarbons typically hydrogenate at "bond-fixed" K-regions.⁵⁷ It is possible that the unique "bisallyl" structure of the reactive ring in **3** and **5** allows for particularly strong surface complexation. This ring certainly functions as a good ligand to homogeneous transition metals (see below).

The aromatic hydrogens H-5 located α to the two activating strained rings were anticipated to exhibit unusual acidity.⁴⁷ However, treatment of **5** with methylolithium or lithium diisopropyl amide in THF at 0 °C followed by quenching with chlorotrimethylsilane gave only starting material. Remarkably, however, when butyllithium (1 equiv, in hexane) was added to a solution of **5** in THF at -78 °C, a deep blue color developed which disappeared immediately upon quenching with the silylating agent. After workup and chromatography, a single pure colorless crystalline product was obtained in 84% yield. Surprisingly, UV spectroscopy indicated (λ_{max} 331 nm) that conjugation in the product was not as extensive as in the starting material. The molecular ion in the mass spectrum showed that the product had incorporated both a trimethylsilyl and a butyl group. The 250-MHz ¹H NMR spectrum exhibited four regions: four aromatic doublets (*J* ~ 0.9 Hz) between δ 7.90 and 7.70, a set of vinyl peaks at δ 6.27 and 6.14 (d, *J* = 0.6 Hz), an aliphatic region at δ 2.37-0.94 (*n*-butyl group), and five trimethylsilyl singlets (δ 0.54-0.29). The ¹³C NMR spectrum revealed the presence of four new aliphatic carbons assigned to the butyl group, two new quaternary signals, six vinyl (aromatic) carbons bearing hydrogens, and eight (not ten) peaks assignable to quaternary sp²-hybridized nuclei. On the basis of this evidence, a structure **26** or **27** can be assigned in which the central ring has been both alkylated and silylated. Unfortunately, the data do not allow for an unambiguous distinction between these two alternatives, nor for a stereochemical assignment.



26



27

In order to reduce the potential for asymmetry in products of this type, the reaction was repeated but with 1-iodobutane as the alkylating agent. Again, only one crystalline product formed (81%) with mass spectral and analytical properties consistent with dibutylation. The carbon spectrum showed only 14 carbon resonances, confirming the symmetry of the adduct. Proof of the regioselectivity of the reaction came from an inspection of the ¹H NMR spectrum of the product. The aromatic hydrogens resonated as two doublets at δ 7.95 and 7.78 (*J* = 0.9 Hz). Only in a 1,4-adduct of the type **26** are the aromatic hydrogens on one ring nonequivalent and expected to exhibit spin-spin splitting. The observed coupling constant of 0.9 Hz is consistent with *para* coupling.

Because of the novelty of the reaction and because the spectral data still could not provide us with a stereochemical assignment, a single-crystal X-ray diffraction study of the dibutyl adduct was undertaken which revealed the formation of **28** (the *cis*-dibutyl analogue of **26**). There are two independent molecules of the compound in the asymmetric unit of the crystal structure (Figure

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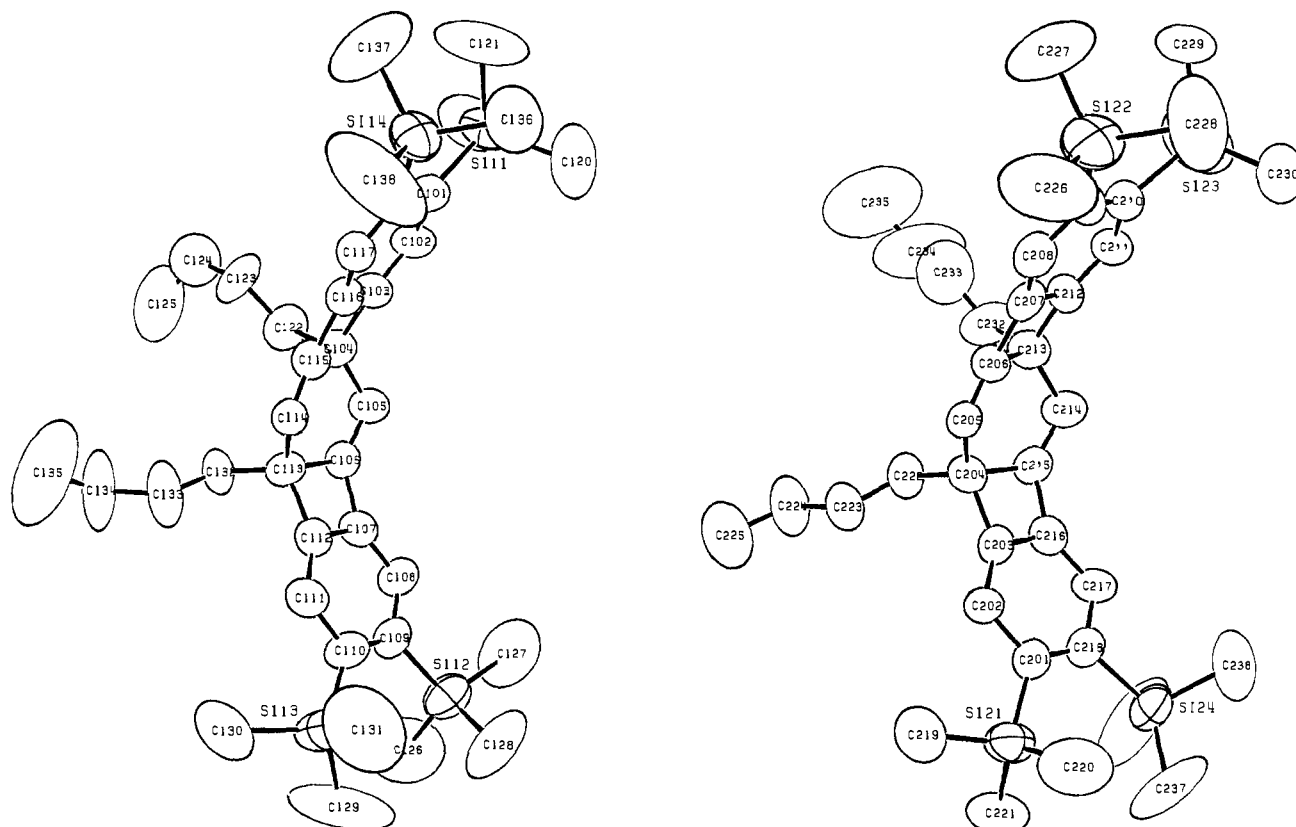


Figure 4. ORTEP drawing of **28** with labeling schemes. The ellipsoids represent 50% probability surface. Given are the two molecules in the orientation which shows the closest relationship between the two. Note the differences in thermal parameters and in the conformation of the butyl groups.

4). The atoms of molecule 1 have numbers beginning with 1 and those of molecule 2 have numbers beginning with 2.

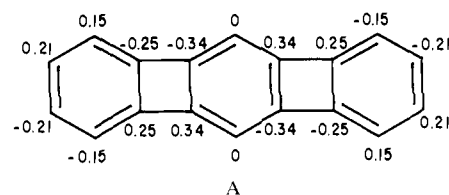
The features of the two molecules are very similar but not identical. The major differences are the conformation of the butyl groups, the twist angles of the trimethylsilyl groups involving Si-12 and Si-13 compared to those involving Si-24 and Si-21, and the overall degree of bending of the molecule away from planarity. In molecule 1 the two terminal benzene rings form an angle of 56.4° , while molecule 2 is bent so that they form an angle of 65.7° .

The two butyl groups on each molecule are on its same side, attached to para carbons on the central six-membered ring. This ring has a diplanar configuration, being folded around the line C104...C113 (C204...C213) by about 40° . The strained double bonds are localized. The fused four- and six-membered rings in the periphery of the molecule are essentially planar and approximately coplanar. The entire framework has approximate C_2 symmetry.

Systematic effects due to thermal motion limit the accuracy of distances in the periphery of the molecule to large multiples of the esds, reported based on inversion of the least-squares matrix. The distance table (Table III) is given first in a conventional form and then with the chemically equivalent bonds grouped to show the spread of values. The structure as a whole, due to the rapid fall-off of intensity at high angle, should be regarded as a low-resolution structure and not much weight given to differences in bond distances of less than 0.02 \AA .

In contrast to the reactions with *n*-butyllithium, *tert*-butyllithium led to addition-alkylations to give what appeared to be isomeric mixtures of diadducts, which, however, were not characterized beyond mass determinations and ^1H NMR. It is nevertheless clear that certain alkyllithium reagents in the presence of **5** initiate a sequence of steps which ultimately allows diaddition of alkyl (silyl) groups to the central ring. The facility with which this occurs is extraordinary. Anionic alkylation of easily reducible arenes has been observed by using organomagnesium⁵⁸ and organo-

lithium⁵⁹ compounds. In the case of perylene,^{59b} treatment with methyllithium-TMEDA led to the isolation of methyldihydroperylene which upon dehydrogenation gave 1-methylperylene. Nucleophilic aromatic methylation with methylsulfinyl carbanion of some polycyclic aromatic molecules⁶⁰ has also been reported and shown to proceed via initial nucleophilic attack of the methylsulfinyl carbanion. Recently,⁶¹ the alkylation of anthracene with alkyllithium reagents followed by photolysis of the resulting adducts was found to give products of net nucleophilic substitution. Isolation of dimeric products in the latter alkylation led the investigators to propose a mechanism involving single electron transfer. To our knowledge, the alkylation of **5** is the first which proceeds by initial nucleophilic attack at an ipso position. We cannot say whether the latter occurs directly or through electron-transfer mechanisms, but we note that the deep blue color generated on addition of the alkyllithium is probably not that of the radical anion of **5** which is emerald green (vide infra). With respect to the regioselectivity of this step, it is in accord with expectations based on a simple HMO estimate of the properties of the LUMO of **3**, as shown in A (labels are the coefficients).



The largest coefficients are found at the positions which are subject to attack. It is possible that the subsequent alkylation of the

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Table III. Selected Bond Distances (Å) and Angles (deg)^a in 28

Equivalent Bonds					
atom 1	atom 2	distance	atom 1	atom 2	distance
C101	C118	1.428 (5)	C103	C104	1.566 (6)
C109	C110	1.430 (6)	C112	C113	1.529 (5)
C201	C218	1.447 (6)	C203	C204	1.548 (5)
C209	C210	1.442 (6)	C212	C213	1.534 (5)
C101	C102	1.447 (5)	C115	C116	1.519 (6)
C108	C109	1.410 (6)	C106	C107	1.493 (5)
C110	C111	1.427 (5)	C215	C216	1.485 (6)
C117	C118	1.407 (5)	C206	C207	1.504 (5)
C201	C202	1.440 (5)	C104	C115	1.566 (5)
C208	C209	1.379 (6)	C106	C113	1.560 (5)
C210	C211	1.424 (6)	C204	C215	1.561 (5)
C217	C218	1.403 (6)	C206	C213	1.594 (6)
C102	C103	1.373 (5)	C104	C105	1.492 (5)
C107	C108	1.411 (5)	C113	C114	1.520 (5)
C111	C112	1.389 (5)	C204	C205	1.522 (5)
C116	C117	1.385 (5)	C213	C214	1.491 (5)
C202	C203	1.391 (5)	C105	C106	1.336 (5)
C207	C208	1.436 (5)	C114	C115	1.354 (5)
C211	C212	1.330 (5)	C205	C206	1.299 (5)
C216	C217	1.405 (6)	C214	C215	1.347 (5)
C103	C116	1.378 (5)			
C107	C112	1.378 (5)			
C203	C216	1.371 (5)			
C207	C212	1.395 (5)			
Intramolecular Distances					
Si11	C101	1.895 (5)	Si21	C201	1.865 (4)
Si11	C119	1.886 (6)	Si21	C219	1.893 (5)
Si11	C120	1.919 (6)	Si21	C220	1.862 (5)
Si11	C121	1.821 (7)	Si21	C221	1.909 (5)
Si12	C109	1.894 (4)	Si22	C209	1.870 (5)
Si12	C126	1.835 (7)	Si22	C226	1.884 (6)
Si12	C127	1.891 (7)	Si22	C227	1.854 (6)
Si12	C128	1.856 (7)	Si22	C228	1.962 (7)
Si13	C110	1.886 (5)	Si23	C210	1.923 (5)
Si13	C129	1.780 (8)	Si23	C229	1.840 (5)
Si13	C130	2.025 (7)	Si23	C230	1.805 (7)
Si13	C131	1.909 (8)	Si23	C231	1.997 (7)
Si14	C118	1.891 (4)	Si24	C218	1.908 (4)
Si14	C136	1.914 (6)	Si24	C236	1.816 (7)
Si14	C137	1.899 (6)	Si24	C237	1.821 (7)
Si14	C138	1.888 (7)	Si24	C238	1.859 (7)
C101	C102	1.447 (5)	C201	C202	1.440 (5)
C102	C103	1.373 (5)	C202	C203	1.391 (5)
C103	C104	1.566 (6)	C203	C204	1.548 (5)
C103	C116	1.378 (5)	C203	C216	1.371 (5)
C104	C105	1.492 (5)	C204	C205	1.522 (5)
C104	C115	1.566 (5)	C204	C215	1.561 (5)
C104	C122	1.581 (5)	C204	C222	1.575 (5)
C105	C106	1.336 (5)	C205	C206	1.299 (5)
C106	C107	1.493 (5)	C206	C207	1.504 (5)
C106	C113	1.560 (5)	C206	C213	1.594 (6)
C107	C108	1.411 (5)	C207	C208	1.436 (5)
C107	C112	1.378 (5)	C207	C212	1.395 (5)
C108	C109	1.410 (6)	C208	C209	1.379 (6)
C109	C110	1.430 (6)	C209	C210	1.442 (6)
C110	C111	1.427 (5)	C210	C211	1.424 (6)
C111	C112	1.389 (5)	C211	C212	1.330 (5)
C112	C113	1.529 (5)	C212	C213	1.534 (5)
C113	C114	1.520 (5)	C213	C214	1.491 (5)
C113	C132	1.567 (5)	C213	C232	1.599 (6)
C114	C115	1.354 (5)	C214	C215	1.347 (5)
C115	C116	1.519 (6)	C215	C216	1.485 (6)
C116	C117	1.385 (5)	C216	C217	1.405 (6)
C117	C118	1.407 (5)	C217	C218	1.403 (6)
C118	C101	1.428 (5)	C218	C201	1.447 (6)
C122	C123	1.547 (6)	C222	C223	1.557 (6)
C123	C124	1.536 (8)	C223	C224	1.551 (6)
C124	C125	1.334 (10)	C224	C225	1.472 (7)
C132	C133	1.530 (6)	C232	C233	1.426 (8)
C133	C134	1.533 (7)	C233	C234	1.636 (10)
C134	C135	1.338 (10)	C234	C235	1.490 (14)

Table III (Continued)

Intramolecular Angles							
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C101	Si11	C119	111.4 (2)	C107	C112	C111	121.1 (4)
C101	Si11	C120	105.4 (2)	C107	C112	C113	94.3 (3)
C101	Si11	C121	116.9 (3)	C111	C112	C113	144.5 (4)
C119	Si11	C120	107.7 (3)	C106	C113	C112	84.1 (3)
C119	Si11	C121	106.6 (3)	C106	C113	C114	108.8 (3)
C120	Si11	C121	108.5 (4)	C106	C113	C132	114.6 (3)
				C112	C113	C114	122.1 (3)
C109	Si12	C126	112.8 (3)	C112	C113	C132	111.0 (3)
C109	Si12	C127	108.7 (3)	C114	C113	C132	113.0 (3)
C109	Si12	C128	112.1 (3)	C113	C114	C115	112.2 (4)
C126	Si12	C127	110.5 (4)	C104	C115	C114	126.8 (4)
C126	Si12	C128	109.1 (5)	C104	C115	C116	89.8 (3)
C127	Si12	C128	103.3 (4)	C114	C115	C116	139.2 (4)
				C103	C116	C115	91.4 (4)
C110	Si13	C129	121.8 (4)	C103	C116	C117	123.8 (4)
C110	Si13	C130	106.2 (3)	C115	C116	C117	144.7 (4)
C110	Si13	C131	107.3 (3)	C116	C117	C118	116.2 (4)
C129	Si13	C130	103.3 (5)	Si14	C118	C101	127.1 (3)
C129	Si13	C131	111.4 (6)	Si14	C118	C117	111.9 (3)
C130	Si13	C131	105.6 (4)	C101	C118	C117	121.0 (4)
				C104	C122	C123	112.1 (4)
C118	Si14	C136	114.5 (2)	C122	C123	C124	109.4 (5)
C118	Si14	C137	113.6 (3)	C123	C124	C125	116.0 (7)
C118	Si14	C138	107.6 (3)	C113	C132	C133	110.2 (4)
C136	Si14	C137	107.9 (3)	C132	C133	C134	110.4 (5)
C136	Si14	C138	104.9 (4)	C133	C134	C135	118.9 (7)
C137	Si14	C138	107.9 (5)				
C201	Si21	C219	109.3 (2)	Si21	C201	C202	113.4 (3)
C201	Si21	C220	112.5 (2)	Si21	C201	C218	127.7 (3)
C201	Si21	C221	111.6 (2)	C202	C201	C218	118.9 (4)
C219	Si21	C220	106.3 (3)	C201	C202	C203	116.5 (4)
C219	Si21	C221	103.8 (3)	C202	C203	C204	143.0 (4)
C220	Si21	C221	112.8 (3)	C202	C203	C216	123.4 (4)
				C204	C203	C216	93.5 (4)
C209	Si22	C226	109.2 (3)	C203	C204	C205	120.3 (3)
C209	Si22	C227	112.9 (3)	C203	C204	C215	83.7 (3)
C209	Si22	C228	109.4 (3)	C203	C204	C222	113.0 (3)
C226	Si22	C227	110.6 (4)	C205	C204	C215	108.4 (3)
C226	Si22	C228	107.6 (4)	C205	C204	C222	114.5 (3)
C227	Si22	C228	107.0 (4)	C215	C204	C222	112.7 (3)
				C204	C205	C206	114.3 (4)
C210	Si23	C229	118.3 (3)	C205	C206	C207	140.7 (4)
C210	Si23	C230	109.7 (3)	C205	C206	C213	127.4 (4)
C210	Si23	C231	105.8 (3)	C207	C206	C213	86.6 (3)
C229	Si23	C230	116.2 (3)	C206	C207	C208	144.0 (5)
C229	Si23	C231	99.8 (3)	C206	C207	C212	94.3 (4)
C230	Si23	C231	105.0 (4)	C208	C207	C212	121.5 (4)
				C207	C208	C209	117.8 (4)
C218	Si24	C236	108.8 (3)	Si22	C209	C208	112.8 (4)
C218	Si24	C237	120.7 (3)	Si22	C209	C210	128.4 (4)
C218	Si24	C238	108.0 (3)	C208	C209	C210	118.8 (4)
C236	Si24	C237	107.7 (5)	Si23	C210	C209	127.3 (4)
C236	Si24	C238	107.7 (5)	Si23	C210	C211	110.9 (4)
C237	Si24	C238	103.3 (5)	C209	C210	C211	121.7 (4)
				C210	C211	C212	118.0 (4)
Si11	C101	C102	110.2 (3)	C207	C212	C211	122.2 (4)
Si11	C101	C118	129.5 (3)	C207	C212	C213	92.9 (3)
C102	C101	C118	120.3 (4)	C211	C212	C213	144.9 (4)
C101	C102	C103	116.4 (4)	C206	C213	C212	85.6 (3)
C102	C103	C104	142.4 (4)	C206	C213	C214	108.4 (3)
C102	C103	C116	122.2 (4)	C206	C213	C232	118.9 (4)
C104	C103	C116	95.2 (4)	C212	C213	C214	120.3 (4)
C103	C104	C105	122.9 (4)	C212	C213	C232	112.3 (3)
C103	C104	C115	83.0 (3)	C214	C213	C232	109.9 (4)
C103	C104	C122	112.7 (3)	C213	C214	C215	114.2 (4)
C105	C104	C115	109.3 (3)	C204	C215	C214	126.8 (4)
C105	C104	C122	109.4 (3)	C204	C215	C216	88.7 (3)
C115	C104	C122	117.7 (3)	C214	C215	C216	139.7 (4)
C104	C105	C106	113.4 (4)	C203	C216	C215	93.1 (4)
C105	C106	C107	140.9 (4)	C203	C216	C217	122.9 (4)
C105	C106	C113	127.1 (4)	C215	C216	C217	143.6 (4)
C107	C106	C113	88.6 (3)	C216	C217	C218	115.7 (4)
C106	C107	C108	143.9 (4)	Si24	C218	C201	128.6 (4)
C106	C107	C112	92.2 (3)	Si24	C218	C217	108.8 (4)
C108	C107	C112	123.9 (4)	C201	C218	C217	122.6 (4)
C107	C108	C109	115.4 (4)	C204	C222	C223	110.1 (4)

Table III (Continued)

Intramolecular Angles									
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle		
Si12	C109	C108	112.3 (4)	C222	C223	C224	106.3 (4)		
Si12	C109	C110	125.8 (3)	C223	C224	C225	112.8 (5)		
C108	C109	C110	121.9 (4)	C213	C232	C233	112.8 (5)		
Si13	C110	C109	130.2 (3)	C232	C233	C234	103.5 (7)		
Si13	C110	C111	110.2 (3)	C233	C234	C235	101.0 (9)		
C109	C110	C111	119.6 (4)						
C110	C111	C112	118.0 (4)						
Torsional Angles (deg)									
atom 1	atom 2	atom 3	atom 4	angle	atom 1	atom 2	atom 3	atom 4	angle
C118	C101	Si11	C119	150.8	C209	C210	Si23	C229	-48.1
C118	C101	Si11	C120	-92.6	C209	C210	Si23	C230	88.4
C118	C101	Si11	C121	28.0	C209	C210	Si23	C231	-158.8
C101	C118	Si14	C136	52.2	C210	C209	Si22	C226	-162.5
C101	C118	Si14	C137	-72.4	C210	C209	Si22	C227	74.1
C101	C118	Si14	C138	168.3	C210	C209	Si22	C228	-44.9
C110	C109	Si12	C126	-73.9	C201	C218	Si24	C236	111.8
C110	C109	Si12	C127	163.1	C201	C218	Si24	C237	-13.2
C110	C109	Si12	C128	49.6	C201	C218	Si24	C238	-131.6
C109	C110	Si13	C129	23.6	C218	C201	Si21	C219	-169.8
C109	C110	Si13	C130	141.1	C218	C201	Si21	C220	72.4
C109	C110	Si13	C131	-106.3	C218	C201	Si21	C221	-55.6
C115	C104	C122	C123	-41.3	C206	C203	C232	C233	-46.7
C104	C122	C123	C124	-178.1	C203	C232	C233	C234	-134.7
C122	C123	C124	C125	-65.0	C232	C233	C234	C235	176.1
C106	C113	C132	C133	-169.0	C215	C204	C222	C223	162.1
C113	C132	C133	C134	-174.8	C204	C222	C223	C224	-179.7
C132	C133	C134	C135	142.9	C222	C223	C224	C225	178.7
C115	C104	C105	C106	-36.9	C206	C213	C214	C215	35.4
C104	C105	C106	C113	6.0	C213	C214	C215	C204	-6.1
C105	C106	C113	C114	34.5	C214	C215	C204	C205	-32.4
C106	C113	C114	C115	-37.7	C215	C204	C205	C206	35.7
C113	C114	C115	C104	7.5	C204	C205	C206	C213	-6.2
C114	C115	C104	C105	32.9	C205	C206	C213	C214	-32.4

^aSee footnote to Table II.

resulting anion is similarly orbital controlled. However, the stereoselectivity of the reaction is not understood and may in fact not be general considering the results obtained with *tert*-butyllithium.

Reduction and Oxidation of [3]Phenylene. Preliminary cyclic voltammetry data reveal that **3** and **5** are readily reduced and oxidized by one-electron processes to the corresponding mono- and dications and mono- and dianions. This is interesting considering that the system has an aromatic π -electron count. Removal or addition of two electrons results in a formally antiaromatic system which would be expected to exhibit increased paratropism. In the case of the dianion this effect should manifest itself in strong shielding, reinforced by the negative charge (approximately a cumulative increment of 10 ppm per charge).⁶² In the dication, charge and ring current effects might cancel each other's influence.

The dianions **3**²⁻ and **5**²⁻ were prepared in NMR tubes by reduction of the neutrals with K in THF-*d*₈. Potassium was present as a highly active mirror in the upper part of the NMR tube generated by repeated sublimation in vacuo. The ¹H NMR spectra of the starting materials in THF-*d*₈ were recorded prior to inversion of the NMR tube: **5**, δ 6.76 (s, 4 H), 6.34 (s, 2 H), 0.31 (s, 36 H); **3**, δ 6.60 (AA' m, 4 H), 6.40 (BB' m, 4 H), 6.29 (s, 2 H). After metal contact, the initially red solution turned to emerald green and the NMR spectra disappeared, presumably

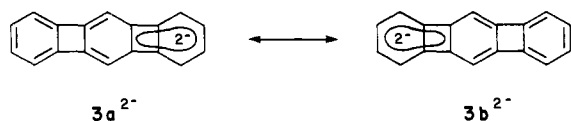
a consequence of radical anion formation. After exposure to the metal surface for 45 min, the now deep red-brown solutions afforded sharp, well-resolved ¹H NMR spectra consisting of, in the case of **5**, three singlets at 6.52, 6.23, and 0.16 ppm and, in the case of **3**, a singlet at δ 6.49 and an AA'BB' multiplet at 5.79 and 5.41 ppm. Integration of the ¹H NMR spectrum of **5**²⁻ allowed the signal at 6.52 ppm to be assigned to the central ring protons and the signal at 6.23 ppm to those on the periphery, while for **3**²⁻, the signal at δ 6.49 was assigned to the central ring protons and those at δ 5.79 and 5.41 to H-1 and H-2, respectively, of the peripheral rings.

In order to corroborate the structures of the dianions, the more readily accessible NMR solution of **5**²⁻ was quenched with aqueous methanol. An extremely air sensitive colorless solid was obtained which turned red on exposure to even traces of air to regenerate **5** quantitatively. Similarly (and more simply) the solution of **3**²⁻ when aerated gave **3**, confirming that in neither case had the overall topology of the system been disrupted. We believe that quenching of [3]phenylene dianion results in the corresponding dihydro compound with a structure related to those of the diadducts **26**–**28**. This product appears to be unusually prone to aromatization, perhaps indicating some conjugative stability in [3]phenylene. In support of the proposed course of its protonation, **5**²⁻ reacted with 1-iodobutane to give **28** as the only isolated product.

The chemical shift changes occurring on reduction of **3** and **5** are puzzling. In contrast to expectation, the central hydrogens H-5 move *downfield* and the remaining hydrogens less upfield

(62) For a recent discussion, see: Müllen, K.; Huber, W. Meul, T.; Nakagawa, M.; Iyoda, M. *J. Am. Chem. Soc.* **1982**, *104*, 5403.

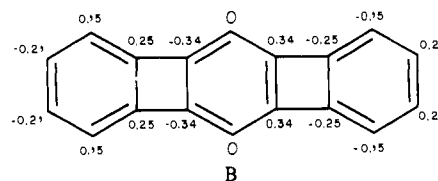
than anticipated, even assuming the *exclusive* operation of charge effects. Inspection of the LUMO of **3** (see A), which is the MO populated by the extra electrons, reveals a node at H-5 providing a partial explanation for the observed trends. Picture A also shows that more charge should enter at C-2 when compared to C-1 based on the relative size of the coefficients, and indeed H-2 is shielded more ($\Delta\delta = 1.19$ ppm) than H-1 ($\Delta\delta = 0.61$ ppm) on going from the neutral to the dianion. However, regardless of the charge distribution, in order to explain the proton chemical shifts one has to invoke increased diatropism and/or decreased paratropism in the molecule when the 18π system is converted to the 20π -electron structure of the dianion. Unfortunately, not much is known about the ring current properties of charged polycyclic systems of this type. Biphenylene dianion⁶³ has never been observed by NMR,⁶⁴ possibly a reflection of equilibration of its ground state with its triplet states.⁶⁵ According to Rabinovitz,⁶⁶ neutral and charged pericondensed polycyclic systems exhibit a tendency to avoid antiaromatic circuits. This desire is fulfilled by sustaining modes of electron delocalization and charge distribution which result in aromatic character and/or reduce antiaromatic contributions. In **3**²⁻, such circuits would involve resonance structures of the type **3a**²⁻ and **3b**²⁻ incorporating benzocyclobutadiene dianion fragments. This picture nicely accounts for the observed NMR trends but may be naive.



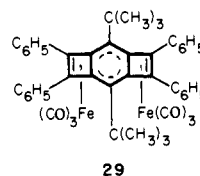
The dication **3**²⁺ was obtained cleanly in an NMR tube by addition of antimony pentafluoride to a suspension of **3** in sulfuric chloride fluoride, cooled to -78 °C.^{67,68} The ¹H NMR spectrum of the purple solution resulting from the oxidation of **3** consisted of an AA'BB' multiplet at 7.10 and 6.87 ppm for the outer-ring protons and a singlet at 6.60 ppm for the nuclei on the central ring (using acetone as an external standard). No change in the spectrum was observed between -60 and -10 °C. The chemical shift changes on oxidizing **3** to its dication are positive for all hydrogens: $\Delta\delta = +0.38$ ppm for H-5 and an average of $\Delta\delta = +0.48$ ppm for H-1 through H-4. This downfield shift is considerably smaller than in the case of the oxidation of biphenylene **2** to its dication, where for both types of protons the $\Delta\delta$ was approximately +3 ppm.⁶⁸ The difference in behavior is in qualitative agreement with our expectation that charge and ring-current effects would counteract each other in **3**²⁺, whereas for **2**²⁺ they work in the same direction.

The ¹³C NMR spectrum of the dication exhibits five lines as expected [62.5 MHz, SO₂ClF-SbF₅, external acetone-*d*₆, δ 185.1, 161.6, 153.2 ($J_{\text{CH}} = 153$ Hz), 130.3 ($J_{\text{CH}} = 161$ Hz), 114.8 ($J_{\text{CH}} = 164$ Hz)], the chemical shift differences between the dication and the neutral having the following values: $\Delta\delta = +21.6$ ppm for the average of the two types of quaternary carbons, $\Delta\delta = +19.5$ ppm for the average of the peripheral tertiary nuclei, and $\Delta\delta = +3.6$ ppm for the central tertiary carbons. The difference between the sum of the chemical shifts of all the carbons and the corresponding sum in **3** amounts to 336.0 ppm. This cumulative change is good evidence for the dicationic nature of the compound, since a total downfield shift of approximately 160 ppm per positive

charge is usually predicted⁶⁹ (170 ppm per charge was found for **2**²⁺).⁶⁸ The noticeably small value of $\Delta\delta$ for C-5 indicates that in the dication the charge density on these carbons is particularly low. This observation may be accounted for by noting that, like the LUMO, the HOMO of **3**, as shown in B, from which the electrons are removed on oxidation, has a node at these positions. Therefore, C-5 appears only slightly perturbed by two-electron oxidation or reduction of the molecule.

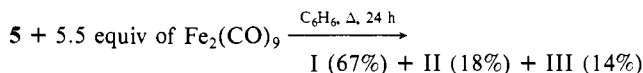


Transition-Metal Complexes of [3]Phenylene. The complexing ability of [3]phenylene to transition metals was considered worth studying, since it raised some interesting questions: Would the four-membered rings behave like cyclobutadienes? Would the central six-membered ring display any unusual features? How would its complexation chemistry compare to that of biphenylene,^{70,71} benzocyclobutadiene (**1**),⁷² and the only known derivative of benzocyclobutadiene **6**?⁷³ The latter case is particularly interesting not only because of its relationship to **3** but also because, in addition to the mono(tricarbonyliron) adduct,

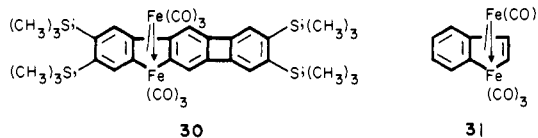


an unusual bis(tricarbonyliron) complex **29** was obtained. In view of these facts, it seemed particularly interesting to investigate how iron would complex to the [3]phenylene nucleus.

When **5** was heated with an excess of diiron monocarbonyl, a deep red solution formed, from which three major components could be isolated by chromatography. The major complex I, a deep-red solid, was shown by mass spectrometry to contain two



Fe(CO)₃ groups in addition to the elements of **5**. ¹H and ¹³C NMR spectroscopy revealed the loss of the symmetry of the original structure. None of the protons or carbons were shifted upfield, suggesting that none of the expected dieneiron tricarbonyl type complexes had formed, but rather the dibenzoferrule **30**. Benzoferrole **31** and its derivatives are well-known,^{74,75} but a



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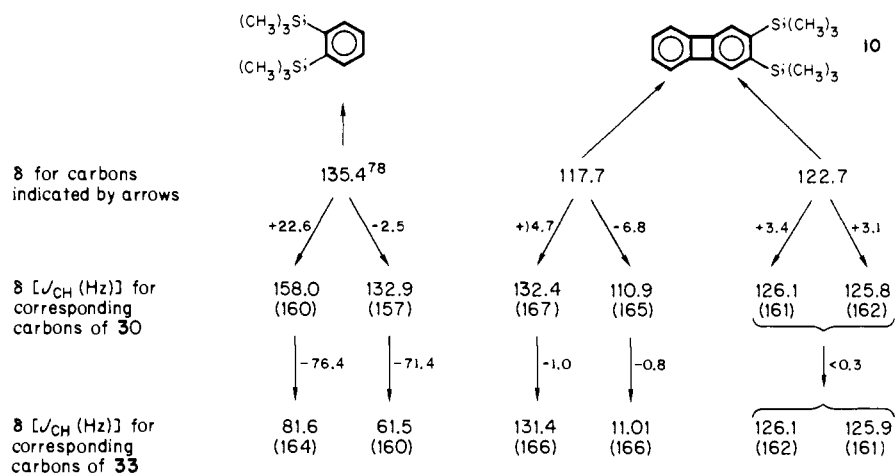
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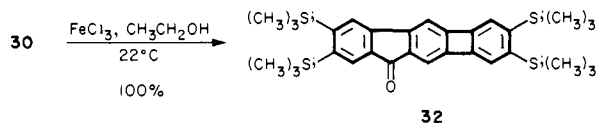
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Scheme IV

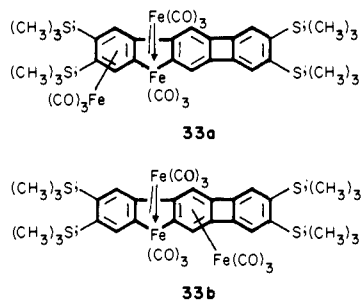


dibenzoferrole structure such as **30** has so far not been described. The reaction affording **30** is presumably very similar to that involving the formation of **31** from benzocyclobutadieneiron tricarbonyl and iron carbonyls.⁷⁵ Good evidence for the structure of **30** is found in the CO region of its ¹³C NMR spectrum, which displays a large peak at 216.9 ppm and three smaller absorptions at 209.7, 207.5, and 207.1 ppm, best observed at -20 °C, because line broadening begins to occur at room temperature. This pattern, in perfect agreement with the known ¹³C data on binuclear ferroles,⁷⁶ reflects the inequivalence of the three carbonyls born by the ferrole ring iron, whereas the carbonyl groups on the second iron are rapidly exchanging their positions.

Oxidative demetalation of **30**, carried out by using iron trichloride in ethanol, occurred with CO insertion to give **32**. Structure **32** is supported by all spectral data. One example of a similar reaction has been reported, involving bromine oxidation of a ferrole complex to give tetraphenylcyclopentadienone.⁷⁷

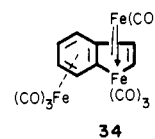


Complex II, a red solid, was obtained only when a large excess of iron was used in the reaction. Although its mass spectrum could unfortunately not be obtained, it was clear from IR and analytical data that it contained one more Fe(CO)₃ group than **30**. ¹H and ¹³C NMR spectra indicated a highly unsymmetrical compound, with two protons appearing at high field (δ 3.71 and 4.24). These data, as well as the pattern of the carbonyl region of the ¹³C NMR spectrum (showing two intense peaks, assigned to diene complexed Fe(CO)₃ groups, and three low-intensity signals, associated with ferrole ring carbonyls), suggested either structure **33a** or **33b**. The



formation of such a complex under our reaction conditions is not

surprising, since complex **34** is known to be obtained from **31** in the presence of an excess of iron carbonyl.^{74b} A careful com-



parison of ¹³C NMR spectra of II and **30** allowed a distinction between the two alternatives **33a** and **33b** to be made with a fair degree of confidence. On going from **30** to II, four of the six peaks corresponding to the six hydrogen-bearing carbons undergo a chemical shift change smaller than 1 ppm, whereas the two others, appearing in **30** at 158 and 132 ppm, are shielded by an average of 74 ppm (Scheme IV). We can therefore conclude that these two carbons belong to the diene moiety complexed to the third iron unit in II. In order to establish the location of the latter, the hydrogen-bearing carbons of **30** had to be assigned. This task was accomplished by using comparative data (Scheme IV) with the literature.

It appears that the influence of the ferrole ring on each of the two adjacent aromatic rings is reasonably similar: a strong downfield shift (+23 and +15 ppm) for one type of carbon, a slight upfield shift (-3 and -7 ppm) for the other one. There are not many ¹³C NMR data on benzoferroles, but those obtained on methyl-substituted ferroles⁷⁶ suggest that the carbons bonded to the 3 and 4 positions of the metallacycle are much more deshielded than those at C-2 and C-5. Any assignment other than the one shown in Scheme IV would have led to very unlikely assumptions. For instance, had we assigned the carbons giving rise to the peaks at 158 and 132 ppm to the biphenylene moiety in **33**, the influence of the ferrole ring on fusion would have been a strong downfield shift of +40 and +15 ppm of both adjacent biphenylene carbons but an upfield shift for both adjacent carbons on the fused benzene nucleus, which appears unreasonable. Therefore, we assign structure **33a** to complex II. A similar analysis of the chemical shifts of the 12 quaternary carbons, although not completely conclusive, also supports this assignment. The two diene-complexed Fe(CO)₃ groups of **33a** are presumed to be on opposite sides of the ligand in analogy with **34**, whose anti structure has been established by X-ray analysis,⁷⁹ and whose syn isomer is not known.

The regioselectivity of the iron complexation of **30** to give exclusively **33a** might be rationalized by simple electronic arguments. Because complexation increases overlap between C-2 and C-3 of a 1,3-diene, it would have introduced unfavorable benzocyclobutadienoid character in **33b**. On the other hand, the alternative benzene ring is already bond-fixed in **30** and does not

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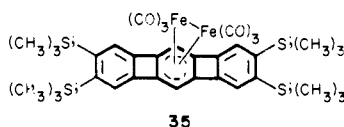
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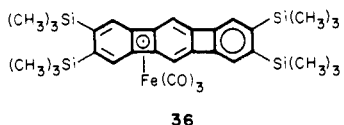
undergo an electronically unfavorable change on additional complexation.

Complex III, an orange solid, was shown by mass spectrometry to be an isomer of **30**. In contrast to **30**, its mass spectrum exhibited a strong fragment peak at m/e 514 (molecular ion corresponding to **5**) and additional signals corresponding to the fragmentation pattern of **5**, indicating that the [3]phenylene structure had been retained. The ^1H NMR spectrum revealed only three singlets, suggesting a highly symmetrical structure: δ 7.50 (4 H, assigned to the outer ring protons), 5.53 (2 H, central ring), and 0.36 (36 H, trimethylsilyl groups). The ^{13}C NMR spectrum exhibited one peak in the CO region at 212.8 ppm, one hydrogen-bearing and three quaternary aromatic carbons between 125 and 150 ppm, and two signals shifted upfield by apparent complexation: a quaternary carbon at 68.8 ppm and a hydrogen-bearing carbon at 58.2 ppm, assigned to the central ring. This result was very surprising, since it ruled out a structure similar to **29** obtained by Toda et al.⁷³ In such a molecule two different types of quaternary carbons corresponding to the cyclobutadiene units would have been expected to absorb in a relatively shielded region. Our data indicate that only the central six-membered ring was involved in complexation. Cooling to -90°C did not result in a change in the ^1H NMR spectrum. This observation and the chemical shift data make a fluxional structure unlikely and lead us to propose the novel structure **35** for III. Although a variety



of bisallyl diiron hexacarbonyl complexes have been reported, for instance those of naphthalene⁸⁰ and cycloheptatriene,⁸¹ there have been no examples in which the two allyl units involved originated from a single aromatic ring. Recently Jonas et al. prepared the derivatives $(\text{CpFe})_2\text{C}_6\text{R}_6$, where the two iron atoms are located on the same side of a bent benzene ring⁸² and different types of cobalt⁸² and vanadium⁸³ binuclear arene complexes in which the metals may also be located on opposite sides of the arene ligand. Although for complex III we cannot completely rule out such structures on the basis of spectral data, we favor the bisallyl structure **35** because it provides a straightforward way of providing 18 electrons around each iron atom.

In addition to the three described complexes, a minor compound (1%) was isolated from the reaction mixture. Although it was not fully characterized, mass spectroscopy (molecular ion at m/e 634, and a fragmentation pattern similar to that of **5**), IR (two bands in the CO absorption region), and ^1H NMR (three equally sized singlets at 7.63, 7.43, and 6.36 ppm, and two trimethylsilyl peaks at 0.29 and 0.27 ppm) strongly suggest structure **36**. Similar complexes can be observed spectroscopically with CpCo and η^6 -tolueneiron.⁸⁴



When only 2 equiv of $\text{Fe}_2(\text{CO})_9$ were used in the complexation of **5**, after 18 h in boiling benzene the following approximate yields of products were obtained: starting material **5** (20%), **30** (40%),

33a (not detected), **35** (20%), and **36** (5%).

As expected, [3]phenylene appears to offer several interesting possibilities of complexation to iron, all of them showing the tendency of the system to localize bonds in a way that avoids antiaromatic contributions.

Experimental Section

General. ^1H NMR spectra were recorded on a Varian EM-390 (90 MHz) or on home-built 200-, 250-, and 300-MHz instruments, consisting of Cryomagnets Inc. magnets, Nicolet Model 1180 computers, and software, assembled by Mr. R. Nunlist (U.C. Berkeley). Spectra are reported in δ referenced to Me_4Si when CCl_4 was the solvent. When other solvents were used, peaks were measured relative to the residual solvent proton absorptions. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, b = broad), coupling constant (Hz), and integration. THF-d_4 was dried over K prior to use. IR spectra were observed on a Perkin-Elmer 337 or 681 spectrometers. Electronic spectra were obtained on a Cary 219 or Perkin-Elmer 552A instruments and are reported in nm ($\log \epsilon$) (sh = shoulder). Mass spectral analyses (MS) and elemental analyses were performed by the Mass Spectral Service and Microanalytical Laboratory of the University of California, Berkeley. Only the more intense or structurally diagnostic mass spectral fragment ion peaks are reported. Melting points were determined in open capillary tubes on a Thomas Hoover Unimelt apparatus, or on a Fischer-Johns hotstage, and are uncorrected. Gas chromatography utilized an HP 5880A chromatograph. Column chromatography was carried out with use of Alfa alumina, activated, neutral, CAMAG, 95+%, -60 mesh, to which 5% of its weight of water was added (activity III). Alternatively, EM Reagents silica gel 60, 70–230 mesh ASTM, or neutral alumina (NOAH chemicals) was used for column chromatography. Preparative TLC was performed by using plates (1 or 2 mm) prepared from EM Reagents silica gel PF-254 and $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ or alumina CF-254. A spinning plate, continuous elution system (Chromatotron, Harrison Research) was used. Analytical TLC was performed on Analabs silica gel plates.

High-pressure liquid chromatography (HPLC) was carried out with an Altex system consisting of a Model 110A pump, a Model 153 UV detector at 254 nm, and an Ultrasphere ODS 1 cm \times 25 cm column. All solvents were dried by conventional procedures. Reactions involving air- or moisture-sensitive organometallic reagents were carried out under dry nitrogen. Solvents were degassed by freeze-thaw under high vacuum. Unless otherwise noted, all starting materials were obtained from commercial suppliers without further purification. X-ray crystallographic data were collected on an Enraf-Nonius CAD-4 apparatus and the structures solved by Dr. F. J. Hollander, U.C. Berkeley X-ray Crystallographic Facility. The syntheses of new compounds are described in the order of appearance in the Discussion section.

General Procedure for the Preparation of Biphenylenes (Not Using Btmse as Solvent). A solution of diyne (1 mmol), alkyne (1.05 mmol), and $\text{CpCo}(\text{CO})_2$ (5 μL) in *o*-xylene (5 mL, degassed) was added via syringe pump over a period of 4–5 h to boiling *o*-xylene (10 mL, degassed) while the reaction mixture was irradiated with a slide projector lamp (GE ELH, 300 W) at a distance of ca. 8 cm. Heating to reflux and irradiation was continued for 2 h after the addition was complete. The reaction mixture was then cooled and the volatile materials were removed by vacuum transfer. The dark residue was dissolved in benzene and chromatographed on Al_2O_3 (neutral, act 1, 50 g) with hexane as eluent to give the products.

12: colorless oil; IR (thin film) 2950, 1442, 1245, 1110, 835, 730 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.73 (s, 1 H), 6.70 (m, 2 H), 6.60 (m, 2 H), 6.55 (s, 1 H), 2.51 (m, 2 H), 1.54 (m, 2 H), 1.36 (m, 4 H), 0.92 (t, J = 7.0 Hz, 3 H); UV λ_{max} (isooctane) 363 ($\log \epsilon$ 4.02), 347 (3.66), 343 (3.84), 335 (3.56), 330 (3.53), 255 (5.09), 248 (sh, 4.82), 246 (4.83), 203 (4.27) nm; MS, m/e (rel intensity) 294 (M^+ , 100), 279 (15), 238 (42), 237 (30), 235 (19), 223 (19), 221 (25), 73 (41); HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{Si}$ 294.1805, found 294.1799.

13: light yellow crystals (from MeOH), mp 34°C ; IR (thin film) 2920, 1570, 1460, 1435, 1255, 1105, 730 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.70 (m, 2 H), 6.59 (m, 2 H), 6.52 (m, 3 H), 2.39 (t, J = 7.4 Hz, 2 H), 1.54 (quint, J = 7.2 Hz, 2 H), 1.32 (m, 4 H), 0.90 (t, J = 6.3 Hz, 3 H); UV λ_{max} (isooctane) 362 ($\log \epsilon$ 4.02), 352 (3.66), 347 (3.80), 343 (3.84), 334 (3.55), 329 (3.51), 326 (sh, 3.45), 250 (5.03), 241 (4.79), 235 (sh, 4.46) nm; MS, m/e (rel intensity) 222 (M^+ , 51), 166 (19), 165 (100), 164 (11); HRMS calcd for $\text{C}_{17}\text{H}_{18}$ 222.1409, found 222.1416.

14: colorless oil; IR (thin film) 2955, 1460, 1440, 1265, 1148, 1098, 730 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 6.70–6.57 (m, AA'BB', 4 H), 6.48 (s, 2 H), 2.43 (t, J = 7.6 Hz, 4 H), 1.46 (m, 8 H), 0.96 (t, J = 7.1 Hz, 6 H); UV λ_{max} (isooctane) 364 ($\log \epsilon$ 4.13), 354 (3.78), 348 (sh, 3.90), 344 (3.94), 336 (3.63), 330 (3.59), 252 (5.09), 243 (4.85), 200 (4.36); MS, m/e (rel intensity) 264 (M^+ , 100), 179 (43); HRMS calcd

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for $C_{20}H_{24}$ 264.1879, found 264.1873.

15: yellow crystals (from MeOH), mp 127–128 °C; IR (KBr) 3020, 1448, 1440, 843, 829, 730 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 7.4 (m, 5 H), 6.9 (m, 3 H), 6.7 (m, 4 H); UV λ_{max} (isooctane) 366 (log ϵ 4.00), 347 (3.96), 335 (sh, 3.77), 262 (4.74), 238 (4.43), 231 (sh, 4.35) nm; MS, m/e (rel intensity) 228 (M^+ , 100), 226 (29). Anal. Calcd for $C_{18}H_{12}$: C, 94.75; H, 5.30. Found: C, 94.48; H, 5.49.

16: yellow crystals (from MeOH), mp 120–121 °C; IR (KBr) 3055, 1422, 870, 760, 730, 696 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 7.14 (m, 6 H), 7.05 (m, 4 H), 6.78–6.68 (m, AA'BB', 4 H), 6.71 (s, 2 H); UV λ_{max} (isooctane) 368 (log ϵ 4.03), 348 (3.91), 336 (sh, 3.61), 295 (3.65), 263 (4.86) nm; MS, m/e (rel intensity) 304 (M^+ , 100), 303 (21), 302 (39), 300 (14). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.46; H, 5.35.

17: yellow crystals (from cyclohexane), mp 80–81 °C; IR (KBr) 2950, 1720, 1605, 1450, 1422, 1285, 1235, 1092, 1080, 735 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 6.87 (s, 2 H), 6.84–6.72 (m, AA'BB', 4 H), 3.84 (s, 6 H); UV λ_{max} (isooctane) 361 (log ϵ 3.79), 345 (3.63), 341 (sh, 3.60), 332 (3.35), 328 (sh, 3.33), 260 (4.85), 253 (sh, 4.76), 206 (4.21) nm; MS, m/e (rel intensity) 268 (M^+ , 33), 237 (31), 151 (13), 150 (14), 84 (69), 69 (24), 56 (100), 55 (33). Anal. Calcd for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.96; H, 4.68.

18: yellow crystals (from MeOH–ether, 1:1), mp 176–177 °C; IR (KBr) 2950, 1365, 1245, 1085, 855, 830, 755 cm^{-1} ; 1H NMR (250 MHz, C_6D_6) δ 7.06 (s, 2 H), 6.40 (s, 2 H), 0.38 (s, 18 H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 151.4, 149.3, 148.1, 130.9, 123.6, 119.9, 2.1; UV λ_{max} (isooctane) 374 (log ϵ 4.01), 357 (3.77), 353 (3.77), 263 (4.76), 230 (4.08), 224 (4.07), 211 (4.19) nm; MS, m/e (rel intensity) 366 (M^+ , 9.5), 365 (M^+ , 3.8), 364 (M^+ , 12.7), 335 (3.5), 333 (4.4), 163 (2.8), 73 (100), 45 (52), 44 (7.6), 43 (25). Anal. Calcd for $C_{18}H_{22}Cl_2Si_2$: C, 59.18; H, 6.03. Found: C, 59.05; H, 6.00.

2,3-Bis(trimethylsilyl)biphenylene (10). Run No. 1. A solution of 1,2-diethynylbenzene (**11**) (132 mg, 1.05 mmol) and $CpCo(CO)_2$ (10 μL , 0.079 mmol) in *btmse* (5 mL) was added via syringe to boiling *btmse* (25 mL) (bath temperature 155 °C) over a period of 8 h with magnetic stirring. During the reaction, the flask was irradiated with a slide projector lamp (GE ELH, 300 W) at a distance of ca. 4 cm from the center of the flask. The power source for the lamp was regulated with a variable transformer to 50 V. Heating to reflux and irradiation was continued for 2 h after the addition was complete. The reaction mixture was then cooled and the volatile material removed by vacuum transfer. The dark residue was filtered through alumina to give **10** (284 mg, 96%): yellow-orange, viscous oil; GC (fused silica column, 30 m \times 0.25 mm, liquid phase DB-30, flow rate 2 mL min^{-1} of He, flame-ionization detector, column temperature 110 °C for 3 min, the 110–200 °C rising by 10 °C min^{-1}) single peak, retention time 19.41 min; colorless crystals (from ether–MeOH), mp 64.5–65 °C; IR (neat) 3070, 2955, 2900, 1930, 1885, 1835, 1775, 1450, 1438, 1412, 1250, 1160, 1110, 1070, 1060, 1020, 975, 960, 918, 840, 800, 752, 738, 692, 680, 650, 640, 618 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 6.94 (s, 2 H), 6.71 (AA' m, 2 H), 6.64 (BB' m, 2 H), 0.31 (s, 18 H); ^{13}C NMR (62.5 MHz, $CDCl_3$, using central $CDCl_3$ peak = 77 ppm as a reference) δ 152.5, 150.5, 147.7, 128.1, 122.7, 117.6, 2.14; UV λ_{max} (isooctane) 363 (log ϵ 3.84), 347 (3.74), 343 (3.70), 334 (3.42), 257 (4.97), 248 (4.75), 205 (4.31) nm; MS m/e (relative intensity) 296 (M^+ , 59), 281 (17), 265 (31), 209 (13), 208 (10), 169 (15), 155 (17), 73 (100); HRMS calcd for $C_{18}H_{24}Si_2$ 296.1416, found 296.1422. Anal. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.66; H, 8.30.

Run No. 2. On a larger scale, **11** (4.0 g, 32 mmol) and $CpCo(CO)_2$ (0.38 mL, 3.0 mmol) in *btmse* (30 mL) were added to boiling *btmse* (125 mL) over a period of 9 h, with irradiation as described above. After heating and irradiation for an additional 4 h, the volatiles were removed. The residue was chromatographed on silica gel (3 \times 50 cm, pentane) collecting 8-mL fractions. Fractions 38–148 contained **10**. After standing overnight in air, a green precipitate appeared, which was filtered from the combined fractions. Removal of the solvent yielded a yellow orange oil (9.07 g). Crystallization gave **10** (6.49 g, 69%).

Run No. 3. This run was accidentally performed in the absence of high-dilution conditions with **11** (0.788 g, 6.25 mmol), $CpCo(CO)_2$ (0.07 mL, 0.55 mmol), and *btmse* (130 mL). Chromatography on alumina (1.5 \times 25 cm, pentane) gave two yellow bands. Fraction 1 furnished a yellow-orange oil (1.87 g) consisting of **10**. Fraction 2 gave a yellow oil of **19** (0.13 g, 44%): 1H NMR (90 MHz, $CDCl_3$) δ 7.35 (m, 4 H), 6.65 (m, 7 H), 4.83 (s, 5 H), 3.96 (s, 1 H), 0.10 (s, 9 H), 0.00 (s, 9 H); MS, m/e (rel intensity) 546 (M^+ , 41), 526 (12), 420 (16), 295 (18), 294 (69), 252 (16), 232 (13), 196 (11), 165 (36), 73 (100); HRMS calcd for $C_{33}H_{35}CoSi_2$ 546.1609, found 546.1602.

1,2-Dichloro-4,5-diiodobenzene. To a solution of sodium nitrite (1.59 g, 23 mmol) in sulfuric acid (11 mL) was carefully and slowly added 4,5-dichlorobenzene-1,2-diamine (1.77 g, 10 mmol) in acetic acid (15

mL) with cooling to 0 °C. After the addition was complete, the resulting slurry was stirred for 20 min at 2 °C and then mixed slowly into a solution of potassium iodide (15.43 g, 93 mmol) in water (60 mL) at 60 °C. After 15 min at this temperature a solid precipitated. Neutralization (26 g of NaOH in 50 mL of H_2O), filtration of the solid, and redissolution in CH_2Cl_2 (100 mL) were followed by aqueous wash, extraction with saturated $NaHSO_3$ (3 \times 50 mL), and drying ($MgSO_4$). Chromatography through silica (100 g) eluting with hexane gave the diiodide (1.70 g, 42.5%): colorless crystals, mp 106–107 °C; IR (CCl_4) 3085, 1450, 1425, 1305, 1145, 1035, 880 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.00 (s); MS, m/e (rel intensity) 402 (M^+ , 10), 400 (M^+ , 59), 398 (M^+ , 95), 74 (100), 73 (61), 57 (71), 55 (64). Anal. Calcd for $C_6H_2Cl_2I_2$: C, 18.07; H, 0.51; Cl, 17.78; I, 63.64. Found: C, 18.32; H, 0.49; Cl, 17.58; I, 63.42.

1,2-Bis(trimethylsilyl)ethynyl-4,5-dichlorobenzene. Bis(benzonitrile)palladium dichloride (145 mg, 10 mol%), triphenylphosphine (100 mg), cuprous iodide (42 mg), and 1,2-dichloro-4,5-diiodobenzene (1.51 g, 3.78 mmol) were treated with triethylamine (50 mL), followed by (trimethylsilyl)ethyne (*tmse*, 0.93 mL, 9.46 mmol). Within 5 min a white solid precipitated. After being stirred for 10 h, the now black mixture was heated for 1 h to 85 °C and then subjected to aqueous workup. Chromatography (silica) eluting with hexane gave as a first fraction bis(trimethylsilyl)butadiyne (150 mg), followed by the desired diyne (1.12 g, 87%): colorless crystals (from EtOH), mp 49 °C; IR (thin film) 3080, 2960, 2900, 2160, 1470, 1347, 1253, 1237, 1168, 1132, 840, 760, 700 cm^{-1} ; 1H NMR (250 MHz, C_6D_6) δ 7.18 (s, 2 H), 0.29 (s, 18 H); MS, m/e (rel intensity) 342 (M^+ , 3), 340 (M^+ , 12), 338 (M^+ , 17), 325 (15), 323 (21), 149 (13), 73 (100).

1,2-Diethynyl-4,5-dichlorobenzene. The (silyl)ethynylbenzene from above (0.55 g, 1.62 mmol) was dissolved in ether (20 mL) and a solution of KOH (0.45 g, 8.11 mmol) in methanol added at once. After 30 min, aqueous workup gave the desilylated diyne (0.235 g, 75%): colorless crystals, mp 135 °C dec (oil bath preheated to 130 °C); IR (CCl_4) 3320, 2120, 1460, 1350, 1220, 1150, 1135, 940, 895, 660, 630 cm^{-1} ; 1H NMR (250 MHz, C_6D_6) δ 7.22 (s, 2 H), 3.03 (s, 2 H); MS, m/e (rel intensity) 198 (M^+ , 10), 196 (M^+ , 64), 194 (M^+ , 100), 123 (19), 98 (16). Anal. Calcd for $C_{10}H_4Cl_2$: C, 61.58; H, 2.07; Cl, 36.35. Found: C, 61.37; H, 2.03; Cl, 36.14.

Biphenylene (2). A solution of **10** (27 mg, 0.091 mmol) in CH_2Cl_2 (4 mL) was treated with trifluoroacetic acid (100 mg) and this mixture was stirred for 20 min. An additional portion of acid (1 mL) was then added. After 1 h, the reaction mixture was subjected to aqueous workup and the resulting brown solid (24 mg) filtered through an alumina column (5% ether in pentane) to give **2** (10 mg, 73%): pale yellow crystals, mp 106–108 °C (lit.²⁷ mp 109–112 °C); 1H NMR (250 MHz, $CDCl_3$) δ 6.71 (AA' m, 4 H), 6.60 (BB' m, 4 H) (lit.⁹ δ 6.70, 6.60); MS, m/e (rel intensity) 152 (M^+ , 100), 151 (31), 150 (14), 126 (6); HRMS calcd for $C_{12}H_8$ 152.0625, found 152.0621.

2,3-Diiodobiphenylene (9). A solution of **10** (2.96 g, 10.0 mmol) in CCl_4 (50 mL) was stirred in an ice bath while ICl_3 (3.25 g, 20.0 mmol) in CCl_4 (10 mL) was added over a period of 10 min. After the mixture was stirred an additional 5 min, the ice bath was removed. The mixture was then stirred 45 min at room temperature and poured into saturated aqueous sodium bisulfite. Normal aqueous workup gave the diiodide **9** (2.54 g, 63%): yellow crystals (from hexane, –80 °C), mp 117–119 °C; IR ($CHCl_3$) 2420, 1420, 1380, 1318, 1160, 670 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 7.13 (s, 2 H), 6.78 (AA' m, 2 H), 6.67 (BB' m, 2 H); MS (70 eV) 404 (M^+ , 7) 350 (27), 335 (16), 333 (30), 241 (24), 209 (13), 208 (34), 207 (12), 206 (10), 205 (11), 179 (38), 165 (30), 149 (43), 73 (100); HRMS calcd for $C_{12}H_6I_2$ 403.8562, found 403.8563. The analytical sample was recrystallized from ether–MeOH. Anal. Calcd for $C_{12}H_6I_2$: C, 35.68; H, 1.50; I, 62.38. Found: C, 35.86; H, 1.36; I, 62.46.

2,3-Bis(trimethylsilyl)ethynylbiphenylene. A solution of diiodide **9** (0.566 g, 1.40 mmol) and *tmse* (0.50 g, 5.1 mmol) in piperidine (10 mL) was treated with $PdCl_2(PhCN)_2$ (10 mg, 0.03 mmol) and CuI (4 mg, 0.02 mmol) as in the preparation of 1,2-bis(trimethylsilyl)ethynyl-4,5-dichlorobenzene to give the product (0.36 g, 75%): green-yellow needles (from ether– CH_3OH), mp 109.8–110.5 °C; IR ($CHCl_3$) 3075, 2965, 2900, 2400, 2145, 1450, 1420, 1400, 1265, 1248, 1175, 1155, 1105, 1050, 975, 910, 850, 700, 665, 635 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$) δ 6.80 (AA' m, 2 H), 6.67 (BB' m, 2 H), 6.67 (s, 2 H), 0.23 (s, 18 H); UV λ_{max} (isooctane) 415 (log ϵ 3.07), 382 (4.12), 371 (3.76), 365 (3.88), 360 (3.86), 345 (3.56), 277 (4.95), 269 (4.91) nm; MS, m/e (rel intensity) 344 (M^+ , 66), 329 (17), 248 (11), 241 (15), 233 (15), 149 (22), 111 (12), 109 (11), 97 (22), 95 (17), 85 (16), 83 (25), 81 (19), 73 (100); HRMS calcd for $C_{22}H_{24}Si_2$ 344.1417, found 344.1423. Anal. Calcd for $C_{22}H_{24}Si_2$: C, 76.68; H, 7.02. Found: C, 76.82; H, 7.08.

2,3-Diethynylbiphenylene (8). A solution of the bisilylated diyne (1.03 g, 2.99 mmol) in ether (2 mL) was treated with a solution of KOH

(1 g, 18 mmol) in methanol (60 mL). After several minutes, crystals separated from the solution. A sufficient quantity of ether was added to make the mixture homogeneous. Aqueous workup gave **8** (0.60 g, 100%): yellow crystals, darkening with decomposition at 120 °C; IR (KBr) 3275, 3262, 2920, 2100, 1938, 1890, 1730, 1440, 1435, 1260, 1210, 1135, 1095, 1040, 972, 920, 815, 800, 740, 672, 658, 630 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 6.82 (AA' m, 2 H), 6.70 (BB' m, 2 H), 6.69 (s, 2 H), 3.33 (s, 2 H); MS, *m/e* (rel intensity) 200 (M⁺, 100), 199 (17), 198 (17), 100 (13), 57 (11); HRMS calcd for C₁₆H₈ 200.0626, found 200.0625.

2,3-Bis(trimethylsilyl)benzo[3,4]cyclobuta[1,2-*b*]biphenylene (4). This cycylation was not run under high dilution (slow addition) conditions because the diyne **8** is soluble in btms only at elevated temperatures. A mixture of **8** (158 mg, 0.79 mmol), btms (28 mL), and CpCo(CO)₂ (22 μL, 0.17 mmol) was stirred and heated to reflux for 4 h, while irradiating as described in the preparation of **10**. Chromatography gave **4** (105 mg, 36%): deep red crystals (from ether–MeOH, –80 °C), mp 171–174 °C; IR (KBr) 3063, 2955, 1917, 1866, 1768, 1441, 1422, 1414, 1347, 1278, 1252, 1195, 1154, 1110, 1091, 1051, 1012, 975, 960, 910, 846, 758, 736, 691, 684, 651, 630, 622 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 6.84 (s, 2 H), 6.45 (AA' m, 2 H), 6.19 (BB' m, *J*_{6,7} = 6.7, *J*_{7,8} = 8.4, 2 H), 6.07 (s, 2 H), 0.29 (s, 18 H); UV λ_{max} (isooctane) 436 (log ε 4.46), 422 (4.18 sh), 410 (4.24), 320 (3.80 sh), 290 (5.06), 279 (4.85), 203 (4.14) nm; MS, *m/e* (rel intensity) 370 (M⁺, 19), 203 (42), 202 (94), 201 (29), 200 (54), 199 (11), 177 (22), 176 (83), 175 (25), 174 (24), 167 (16), 155 (13), 151 (10), 150 (39), 149 (86), 73 (36), 57 (100); HRMS calcd for C₂₄H₂₆Si₂ 370.1573, found 370.1569.

1,2,4,5-Tetrakis(trimethylsilyl)ethynylbenzene (21). A solution of 1,2,4,5-tetraiodobenzene (**20**) (4.90 g, 8.42 mmol) and tmse (4.54 g, 46.3 mmol) in a mixture of triethylamine (150 mL) and piperidine (30 mL) was treated with PdCl₂(PhCN)₂ (322 mg, 0.84 mmol), triphenylphosphine (220 mg, 0.84 mmol), and CuI (65 mg). The originally yellow solution turned to green and then brown. After 3 h at room temperature it was heated at 80 °C for 2 h. Acidic aqueous workup and chromatography (silica) eluting with hexane gave tetrayne **21** (3.42 g, 88%): white crystals (from ether–MeOH, 1:9, –20 °C), mp 163.5–164 °C; IR (KBr) 2960, 2895, 2160, 1485, 1375, 1255, 1245, 1185, 915, 850, 760, 700, 630 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 7.67 (s, 2 H), 0.33 (s, 36 H); ¹³C NMR (62.5 MHz, CDCl₃) 136.0, 125.3, 102.0, 100.8, –0.09; UV λ_{max} (isooctane) 347 (log ε 2.81), 341 (2.86), 333 (2.98), 318 (4.24), 312 (4.02), 305 (4.16), 298 (4.08), 293 (3.99), 287 (3.90), 282 (3.83), 269 (4.71), 262 (4.40), 255 (4.36), 247 (3.90), 243 (3.72) nm; MS, *m/e* (rel intensity) 462 (M⁺, 69), 447 (32), 359 (21), 97 (12), 73 (100). Anal. Calcd for C₂₆H₃₈Si₄: C, 67.53; H, 8.22. Found: C, 67.37; H, 8.22.

1,2,4,5-Tetraethynylbenzene (22). CAUTION: This compound is unstable and will detonate with inflammation if heated in air and even on attempted vacuum sublimation. A solution of **21** (1.10 g, 2.38 mmol) in ether (20 mL) was treated with a solution of KOH (1.20 g, 21.6 mmol) in methanol (40 mL). Ether–water workup and concentration of the ether solution under reduced pressure to a volume of ca. 10 mL gave **22** (0.335 g, 82%): tan crystals which darkened on standing (under N₂); mp detonates at 80 °C, decomposes at 50 °C; IR (KBr) 3270, 3090, 3020, 2105, 1805, 1480, 1365, 1275, 1265, 905, 680, 650, 630 cm⁻¹; ¹H NMR (90 MHz, Me₂SO-*d*₆) δ 7.65 (s, 2 H), 4.60 (s, 4 H).

2,3,7,8-Tetrakis(trimethylsilyl)benzo[3,4]cyclobuta[1,2-*b*]biphenylene (5). Two solutions, one consisting of tetrayne **22** (110 mg, 0.63 mmol) in btms (12 mL), toluene (12 mL), and DMF (2 mL) and the other of CpCo(CO)₂ (17 μL, 0.14 mmol) in a 1:1 mixture of btms and toluene (5 mL), were added simultaneously by syringe pumps to boiling btms (20 mL) over a period of 4 h while irradiating as described in the preparation of **4**. After the addition was complete, the dark red-brown solution was irradiated and heated to reflux for an additional 2 h. The crude product was filtered through a short alumina (activity III) column (hexane) and then chromatographed on silica (hexane) to give first **5** (220 mg, 71%): deep red crystals, mp 230–239 °C dec; IR (KBr) 3060, 2950, 2900, 1630, 1440, 1400, 1340, 1250, 1170, 1090, 1030, 990, 840, 750, 640 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 6.85 (s, 4 H), 6.23 (s, 2 H), 0.29 (s, 36 H); ¹³C NMR (62.5 MHz, C₆D₆) 153.8, 149.9, 147.7, 121.1 (*J*_{CH} = 158 Hz), 111.2 (*J*_{CH} = 165 Hz), 2.3 ppm; UV λ_{max} (isooctane) 438 (log ε 4.81), 412 (4.56), 297 (5.32), 287 (5.11), 276 (sh, 4.89) nm; MS, *m/e* (rel intensity) 514 (M⁺, 100), 499 (6), 411 (5), 387 (8), 149 (4), 97 (5), 83 (4), 73 (61), 57 (8). Anal. Calcd for C₃₀H₄₂Si₄: C, 70.04; H, 8.17. Found: C, 69.85; H, 8.33.

The next compound to be eluted was **23** (65 mg, 94%): mp 311–315 °C; IR (KBr) 2950, 2900, 1350, 1315, 1245, 1060, 1020, 840, 805, 750 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 7.41 (s, 2 H), 7.19 (s, 2 H), 4.84 (s, 10 H), 4.60 (s, 2 H), 0.36 (s, 36 H), 0.32 (s, 18 H); ¹³C NMR (62.5 MHz, C₆D₆) 150.0, 147.6, 135.7, 122.7, 120.6, 89.8, 79.6, 71.7, 70.1, 65.0, 2.2, 1.3, 0.16 ppm; UV λ_{max} (isooctane) 404 (log ε 3.60), 262 (4.41), 210 (4.22); MS, *m/e* (rel intensity) 932 (M⁺, 23), 859 (7), 762 (6), 638

(2), 294 (15), 196 (9), 189 (10), 73 (8).

[3]Phenylene (3). To a solution of **5** (75 mg, 0.15 mmol) in THF (25 mL) and Me₂SO (8 mL) was added 2.5 g of a solution prepared by dissolving potassium *tert*-butoxide (0.35 g, 3.13 mmol) in *tert*-butyl alcohol (8 mL). The mixture was stirred and heated under N₂ to 85 °C for 6 h, followed by aqueous workup to give **3** (28 mg, 85%). Recrystallization from boiling toluene gave **3** (23 mg, 71%): red-orange crystals (plates), mp 275–280 °C dec; IR (KBr) 3050, 3025, 1435, 1408, 1403, 1270, 1240, 1198, 1142, 1130, 1112, 1070, 1055, 1022, 1008, 960, 915, 878, 850, 838, 820, 723 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 6.44 (AA' m, 4 H), 6.19 (BB' m, *J*_{1,2} = 6.6, *J*_{2,3} = 8.6, 4 H), 5.91 (s, 2 H); ¹³C NMR (62.5 MHz, CS₂, acetone-*d*₆) 152.6, 150.7, 128.4, 116.0, 111.2 ppm; λ_{max} (THF) 432 (log ε 4.31), 406 (4.10), 285 (4.90), 274 (4.75) nm; MS, *m/e* (rel intensity) 226 (M⁺, 100), 224 (30), 113 (16); HRMS calcd for C₁₈H₁₀ 226.0782, found 226.0783. Anal. Calcd for C₁₈H₁₀: C, 95.54; H, 4.45. Found: C, 94.93; H, 4.74.

cis,cis-syn-4b,5,5a,9b,10,10a-Hexahydro[3]phenylene (24). A mixture of **3** (13 mg, 0.058 mmol) in THF (2 mL) and 5% Pd/C (4 mg) was placed under H₂ (1 atm) and stirred for 3 h. The decolorized solution was filtered and evaporated to give a colorless solid of **24** (10 mg, 74%): colorless crystals (from ether–MeOH), mp 158–160.5 °C; IR (KBr) 3060, 3005, 2850, 2800, 2750, 1450, 1350, 1275, 1215, 990, 750, 738 cm⁻¹; ¹H NMR (200 MHz, C₆D₆) δ 7.10 (AA' m, 4 H), 6.97 (BB' m, 4 H), 3.28 (m, 4 H), 2.22 (dt, *J* = 6, 12, 2 H, H-3), 1.42 (dt, *J* = 12, 13 Hz, 2 H, H-2); UV λ_{max} (isooctane) 271 (log ε 3.61), 266 (3.62), 259 (3.53) nm; MS, *m/e* (rel intensity) 232 (M⁺, 66), 231 (32), 218 (15), 217 (84), 216 (34), 215 (51), 204 (22), 203 (29), 202 (44), 191 (23), 179 (10), 178 (55), 149 (42), 128 (53), 117 (58), 115 (65), 102 (100); HRMS calcd for C₁₈H₁₆ 232.1252, found 232.1251.

2,3,7,8-Tetrakis(trimethylsilyl)-cis,cis-syn-4b,5,5a,9b,10,10a-hexahydro[3]phenylene (25). A mixture of **5** (25 mg, 0.05 mmol) in ether (10 mL) and 5% Pd/C (20 mg) was stirred in a H₂ atmosphere for 8 h. The colorless solution was filtered and the solvent removed to give a colorless oil. Chromatography on silica eluting with hexane gave **25** (20 mg, 79%): colorless crystals (from ether–MeOH, 1:9), mp 202–203 °C; IR (KBr) 2950, 2900, 1255, 1245, 1085, 845, 755, 645 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 7.64 (s, 4 H), 3.40 (m, 4 H), 2.40 (dt, *J* = 13.2, 5.9 Hz, 2 H), 1.51 (dt, *J* = 13.0, 12.0 Hz, 2 H), 0.49 (s, 36 H); UV λ_{max} (isooctane) 275 (log ε 3.92), 270 (3.85), 264 (3.71) nm; MS, *m/e* (rel intensity) 520 (M⁺, 8.4), 505 (16), 489 (7), 466 (35), 451 (12), 245 (8), 229 (10), 131 (8), 73 (100), 57 (13); HRMS calcd for C₃₀H₄₀Si₄ 520.2834, found 520.2816.

Reaction of 5 with *n*-Butyllithium Followed by Trimethylsilylation. To a solution of **5** (52 mg, 0.10 mmol) in THF (10 mL) at –78 °C was added *n*-butyllithium (0.08 mL, 1.35 M in hexane). The mixture turned instantly to emerald green and then to dark blue. After the mixture was stirred at –78 °C for 30 min (chlorotrimethyl)silane (22 mg, 0.20 mmol) was added dropwise. The solution was stirred at –78 °C for 15 min and subsequently allowed to warm up to room temperature. Aqueous workup gave adduct **26** or **27** (54 mg, 84%): colorless crystals (from ether–MeOH), mp 248–250 °C; IR (KBr) 3050, 2940, 1240, 1080, 830, 750, 645 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 7.90 (d, *J* = 0.9 Hz, 1 H), 7.81 (d, *J* = 0.9 Hz, 1 H), 7.74 (d, *J* = 0.9 Hz, 1 H), 7.70 (d, *J* = 0.9 Hz, 1 H), 6.27 (d, *J* = 0.6 Hz, 1 H), 6.14 (d, *J* = 0.6 Hz, 1 H), 2.37 (m, 1 H), 2.16 (m, 1 H), 1.78 (m, 2 H), 1.40 (m, 2 H), 0.94 (t, *J* = 7.5 Hz, 3 H), 0.54 (s, 9 H), 0.52 (s, 9 H), 0.49 (s, 9 H), 0.48 (s, 9 H), 0.29 (s, 9 H); ¹³C NMR (62.5 MHz, C₆D₆) 152.4, 149.2, 148.4, 148.0, 146.1, 145.8, 145.5, 144.7, 127.3, 127.2, 126.8, 126.4, 125.9, 125.1, 121.0, 119.3, 64.4, 60.2, 42.8, 29.3, 23.5, 14.3, 2.5, 2.4, –1.7 ppm; ¹³C NMR (CDCl₃) 151.6, 148.3, 148.1, 147.6, 146.5, 145.2, 144.1, 143.5, 127.6, 127.2, 125.2, 124.3, 120.3, 120.1, 118.9, 63.8, 60.2, 42.4, 28.8, 23.2, 14.2, 2.34, 2.30, –1.8 ppm; UV λ_{max} (isooctane) 311 (log ε 3.87), 300 (3.94), 263 (4.28), 233 (4.34), 216 (4.32), 199 (4.32) nm; MS, *m/e* (rel intensity) 644 (M⁺, 24), 546 (35), 464 (5), 73 (100).

Reaction of 5 with *n*-Butyllithium Followed by Butylation. Formation of 28. To a solution of **5** (52 mg, 0.10 mmol) in THF (8 mL) at –78 °C was added *n*-butyllithium (0.08 mL, 1.35 M in hexane). The blue solution was stirred at –78 °C for 20 min, 1-iodobutane (37 mg, 0.20 mmol) added, the mixture stirred at –78 °C for 15 min and then allowed to warm up to room temperature upon which the deep blue color turned into pale orange. Workup with saturated Na₂S₂O₃ (5 mL) and ether–water (15 mL) gave **28** (50 mg, 81%): colorless crystals (from ether–EtOH), mp 165.5–166 °C; IR (KBr) 2950, 2920, 2850, 1250, 1080, 830, 750, 645 cm⁻¹; ¹H NMR (250 MHz, C₆D₆) δ 7.95 (d, *J* = 0.9 Hz, 2 H), 7.78 (d, *J* = 0.9 Hz, 2 H), 6.34 (s, 2 H), 2.48 (m, 2 H), 2.25 (m, 2 H), 1.78 (m, 4 H), 1.40 (m, 4 H), 0.94 (t, *J* = 7.3 Hz, 6 H), 0.52 (s, 18 H), 0.48 (s, 18 H); ¹³C NMR (62.5 MHz, C₆D₆) 151.1, 150.7, 146.2, 145.8, 144.0, 127.8, 125.6, 120.2, 63.4, 41.9, 29.3, 23.1, 14.2, 2.30 ppm; UV λ_{max} (isooctane) 307 (log ε 3.99), 296 (4.12), 278 (sh, 4.39), 259 (4.48), 231 (4.59), 214 (4.52) nm; MS, *m/e* (rel intensity) 628 (M⁺, 51), 613 (21),

Table IV. Crystal and Data Collection Parameters for 5 and 28

compd	C ₃₀ H ₄₂ Si ₄ (5)	C ₃₈ H ₆₀ Si ₄ (28)
Crystal Parameters at 25 °C ^a		
<i>a</i> , Å	6.6856 (9)	11.6583 (23)
<i>b</i> , Å	9.5412 (9)	18.0934 (28)
<i>c</i> , Å	25.1327 (29)	39.1952 (39)
β , deg	96.446 (10)	92.111 (12)
<i>V</i> , Å ³	1593.0 (6)	8262 (4)
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>M_r</i> , amu	515.01	629.25
<i>Z</i>	2	8
<i>d</i> (calcd), g cm ⁻³	1.074	1.012
μ (calcd), cm ⁻¹	1.96	1.61
size, mm	0.15 × 0.27 × 0.40	0.22 × 0.30 × 0.37
Data Measurement Parameters		
diffractometer	Enraf-Nonius CAD-4	
radiation	Mo K α (λ = 0.71073 Å)	
monochromator	highly oriented graphite (2 θ = 12.2°)	
detector	perpendicular mode, assumed 50% perfect crystal scintillation counter, with pulse-height analyzer	
aperture-crystal dist., mm	173	
vertical aperture, mm	2.0	
horizontal aperture, mm	2 + 1.0 tan (θ) (variable)	1.6 (fixed)
reflections measured	+ <i>h</i> , + <i>k</i> , ± <i>l</i>	
2 θ range, deg	3–55	3–45
scan type	θ –2 θ	moving crystal-stationary
scan speed (θ), deg/min	0.60–6.7	
scan width ($\Delta\theta$)	0.5 + 0.347 tan θ	0.5 (fixed)
bkgd	0.25 ($\Delta\theta$) at each end of the scan	
reflections collected	4169	11834
unique reflections	3650	10794
stand reflections ^b	433, 1·3·15, 16 $\bar{7}$	(5,4,13), (1,10,-10), (2,5,19)
orientation ^c	3 reflections were checked after every 250 measurements	

^a Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo K α components of 24 reflections with 2 θ near 28° for 5 and between 24° and 29° for 28. ^b Measured every 2 h of X-ray exposure time. Over the period of data collection no decay in intensity was observed for 5, and a 7% decrease for 28. ^c Crystal orientation was redetermined if any of the reflections were off-set from their predicted position by more than 0.1°. Reorientation during data collection was carried out once for 5 and eight times for 28.

586 (25), 572 (62), 529 (15), 73 (100). Anal. Calcd for C₃₈H₆₀Si₄: C, 72.61; H, 9.55. Found: C, 72.27; H, 9.31.

Crystal Structure of 5. (For references and footnotes relevant to this discussion, see ref 43–52 in Hersh, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* 1983, 105, 5834.)

Large orange blade-like crystals of the compound were obtained by slow crystallization from ether–MeOH via a combination of vapor diffusion and evaporation. The crystals cleaved well parallel to the long axis but tended to fracture when cut crosswise. Fragments were mounted on glass fibers with use of polycyanoacrylate cement and tested for quality via Laue photographs. Preliminary precession photographs confirmed the crystal quality of the data crystal and yielded preliminary cell dimensions.

The crystal was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing procedures yielded a monoclinic reduced primitive cell. Inspection of the Niggli values revealed no conventional cells of higher symmetry and inspection of the major zones showed systematic absences consistent only with space group *P*2₁/*c*. The final cell parameters and specific data collection parameters are given in Table IV.

The 4169 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz and polarization effects. A correction for crystal decomposition was unnecessary. Inspection of the azimuthal scan data (reflections used for azimuthal scans were located near $k = 90^\circ$ and the intensities were measured at 10° increments of rotation of the crystal about the diffraction vector) showed a variation $I_{\min}/I_{\max} = 0.975$ for the average

curve and approximately $\pm 2\%$ random variation. A correction for absorption was not applied. Removal of systematically absent and redundant data left 3650 unique data.

The structure was solved by MULTAN and refined via standard least-squares and Fourier techniques. A difference Fourier map calculated after all non-hydrogen atoms had been refined with anisotropic thermal parameters clearly showed the positions of the hydrogen atoms. These were included in idealized positions ($d = 0.95$ Å) but not refined. The final residuals for 154 variables refined against the 2564 data for which $F^2 > 3\sigma(F^2)$ were $R = 3.87\%$, $wR = 5.62\%$, and GOF = 2.158. The R value for all 3650 data was 6.79%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.035 in the last cycles of the refinements. The analytical forms of the scattering factor tables for the neutral atoms were used, and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of $\sin \theta/\lambda$, $|F_o|$, and parity and value of the individual indexes did not show unusual features or trends. There was no evidence of secondary extinction in the low-angle, high-intensity data. The largest peak in the final difference Fourier map had an electron density of 0.30 e/Å³ and was located between Si-2 and C-22.

The positional and thermal parameters of the refined atoms and a listing of the values of F_o and F_c are available as supplementary material.

Crystal Structure of 28. Large clear colorless plate-like crystals of the compound were obtained by slow cooling of MeOH–ether solutions. Fragments cleaved from some of these crystals were mounted on glass fibers by using polycyanoacrylate cement. Preliminary precession photographs indicated monoclinic Laue symmetry and yielded preliminary cell dimensions. They also showed a very rapid fall-off of intensity with $\sin \theta/\lambda$. Systematic absences were consistent only with space group *P*2₁/*n*, and the volume was consistent with two molecules in the asymmetric unit.

The crystal used for data collection was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. Automatic peak search and indexing procedures yielded the monoclinic reduced primitive cell. Inspection of the Niggli values revealed the absence of conventional cells of higher symmetry. The final cell parameters and specific data collection parameters are given in Table IV.

The 11 384 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz and polarization effects. Inspection of the intensity standards showed a monotonic isotropic decrease to 93% of the original intensity. The data were corrected for this decay. Inspection of the azimuthal scan data showed a variation $I_{\min}/I_{\max} = 0.96$ for the average curve. No correction for absorption was applied. Removal of systematically absent and redundant data left 10 794 unique data. The structure was solved by using MULTAN 11/82 and refined via standard least-squares and Fourier techniques.

Refinement was stopped after all non-hydrogen atoms had been given anisotropic thermal parameters because no hydrogen positions could be found and because the anisotropic thermal motions of most of the atoms were such that they could not be well-characterized for a prediction model.

The final residuals for 757 variables refined against the 5549 data for which $F^2 > 3\sigma(F^2)$ were $R = 9.4\%$, $wR = 12.7\%$, and GOF = 4.95. The R value for the 6202 data with $I > 0$ was 10.0%, and the R value for all 10 794 data was 18.5%.

The quantity minimized by the least-squared program was $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used, and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.

Inspection of the residuals ordered in ranges of $\sin \theta/\lambda$, $|F_o|$, and parity and value of the individual indexes showed the absence of trends not assignable to the fact that the hydrogen contribution to the scattering was not included in the model. There was no evidence of secondary extinction in the low-angle, high-intensity data. The largest peak in the final difference Fourier map has an electron density of 0.68 e/Å³ and was located near C-232, C-233, and C-234. All other peaks were less than 0.37 e/Å³.

The positional and thermal parameters of the refined atoms and a listing of the values of F_o and F_c are available as supplementary material.

Iron Complexes of 5. A solution of 5 (100 mg, 0.19 mmol) in benzene (4 mL, degassed) was added to Fe₂(CO)₉ (394 mg, 1.08 mmol), and the mixture was heated to reflux for 24 h. After being cooled, the resulting deep-red solution was poured into hexane and subjected to aqueous

workup. After evaporation of the solvent the residue was chromatographed through a silica column, with hexane as eluent. The first compound to be eluted was **30** (93 mg, 60%): deep-red crystals (from ether-MeOH) mp 190–195 °C dec; IR (CCl₄) 2060, 2025, 1990, 1915 cm⁻¹; ¹H NMR (300 MHz, C₆D₆) δ 8.36 (s, 1 H), 8.25 (s, 1 H), 7.48 (d, *J* = 1 Hz, 1 H), 7.34 (d, *J* = 1 Hz, 1 H), 7.28 (d, *J* = 0.7 Hz, 1 H), 6.92 (d, *J* = 0.8 Hz, 1 H), 0.339 (s, 9 H), 0.332 (s, 9 H), 0.328 (s, 9 H), 0.294 (s, 9 H); ¹³C NMR (62.5 MHz, CDCl₃, 25 °C) δ 216.6, 209.2 (b), 207.2 (b), 158.0 (*J*_{CH} = 160 Hz), 152.7, 150.4, 150.0, 149.8, 148.4, 147.9, 147.1, 146.9, 143.1, 142.3, 132.9 (*J*_{CH} = 157 Hz), 132.4 (*J*_{CH} = 167 Hz), 126.9, 126.1 (*J*_{CH} = 161 Hz), 125.8 (*J*_{CH} = 162 Hz), 125.3, 110.9 (*J*_{CH} = 165 Hz), 2.1 (*J*_{CH₃} = *J*_{CH₃} = 119 Hz), 1.7 (*J*_{CH₃} = *J*_{CH₃} = 120 Hz); ¹³C NMR (CDCl₃, -20 °C, CO region) δ 216.9 (intense), 209.7, 207.5, 207.1; MS, *m/e* (rel intensity) 794 (M⁺, 31), 710 (33), 682 (51), 654 (48), 626 (100), 516 (23), 313 (40), 83 (21), 73 (81). Anal. Calcd for C₃₆H₄₂Fe₂O₆Si₄: C, 54.41; H, 5.33; Fe, 14.05. Found: C, 54.00; H, 5.51; Fe, 13.2.

Next to be eluted was a mixture of **30** and **33a** (19 mg, 60:40 from NMR), followed by pure **33a** (24 mg, 13%): red crystals (from hexane), mp 125–140 °C dec; IR (hexane) 2065, 2048, 2025, 1998, 1985, 1975 cm⁻¹; ¹H NMR (300 MHz, C₆D₆) δ 7.45 (d, *J* = 0.8 Hz, 1 H), 7.29 (d, *J* = 0.8 Hz, 1 H), 7.19 (d, *J* = 0.8 Hz, 1 H), 6.48 (d, *J* = 0.8 Hz, 1 H), 4.24 (s, 1 H), 3.71 (s, 1 H), 0.38 (s, 9 H), 0.37 (s, 9 H), 0.35 (s, 9 H), 0.31 (s, 9 H); ¹³C NMR (62.5 MHz, CDCl₃) δ 212.4 (intense), 210.6, 209.8, 208.7, 208.3 (intense), 175.3, 155.5, 151.6, 150.5, 149.8, 149.5, 147.6, 145.7, 131.4 (*J*_{CH} = 166 Hz), 129.0, 126.1 (*J*_{CH} = 162 Hz), 125.9 (*J*_{CH} = 161 Hz), 118.6, 110.1 (*J*_{CH} = 166 Hz), 105.5, 103.1, 81.6 (*J*_{CH} = 164 Hz), 61.5 (*J*_{CH} = 160 Hz), 2.09 (*J*_{CH₃} = *J*_{CH₃} = 119 Hz), 174 (*J*_{CH₃} = 120 Hz), 1.59 (*J*_{CH₃} = 120 Hz). Anal. Calcd for C₃₉H₄₂Fe₃O₉Si₄: C, 50.12; H, 4.53; Fe, 17.92. Found: C, 50.21, H, 4.93; Fe, 18.0.

On further elution an orange solid of impure **35** (35 mg) was obtained, which was subjected to HPLC purification [reverse phase, CH₃CN–C–H₂Cl₂ (80:20) as eluent] to give **35** (22 mg, 14%): orange solid, mp 150–170 °C dec; IR (CCl₄) 2050, 2010, 1990, 1960 cm⁻¹; ¹H NMR (300 MHz, C₆D₆) δ 7.52 (s, 4 H), 4.51 (s, 2 H), 0.29 (s, 36 H); ¹H NMR (300 MHz, acetone-*d*₆) δ (20 °C) 7.50 (s, 4 H), 5.53 (s, 2 H), 0.36 (s, 36 H); δ (-90 °C) 7.53 (s, 4 H), 5.66 (s, 2 H), 0.30 (s, 36 H); ¹³C NMR (62.5 MHz, CDCl₃) δ 212.8, 148.4, 144.6, 125.8 (*J*_{CH} = 161 Hz), 68.8, 58.2 (*J*_{CH} = 179 Hz), 2.2 (*J*_{CH₃} = 120 Hz); MS *m/e* (rel intensity) 794 (M⁺,

0.1), 710 (1), 654 (1), 626 (4), 598 (10), 570 (17), 514 (100), 499 (5), 411 (5), 387 (6), 207 (15), 97 (7), 86 (9), 73 (69), 57 (19). Anal. Calcd for C₃₆H₄₂Fe₂O₆Si₄: C, 54.41; H, 5.33; Fe, 14.05. Found: C, 53.97; H, 5.57; Fe, 13.8.

The next compound to be eluted during the HPLC purification of **35** was **36** (1.5 mg, 1%): brown solid; IR (CCl₄) 2030, 1967 cm⁻¹; ¹H NMR (300 MHz, C₆D₆) δ 7.63 (s, 2 H), 7.43 (s, 2 H), 6.36 (s, 2 H), 0.29 (s, 18 H), 0.27 (s, 18 H); MS, *m/e* (rel intensity) 654 (M⁺, 0.4), 598 (16), 570 (28), 514 (100), 499 (6), 442 (13), 411 (6), 387 (7), 97 (15), 83 (13), 73 (87), 57 (32).

Preparation of Ketone 32 by Oxidation of 30. A solution of FeCl₃·6H₂O (1 g) in EtOH (5 mL) was added to a suspension of **30** (43 mg, 0.08 mmol) in EtOH (20 mL). The mixture was stirred for 3 days at room temperature, and the resulting orange solution was subjected to water–hexane workup. Evaporation of the solvent gave **32** (29 mg, 100%): red needles (from ether–EtOH), mp 204 °C; IR (CCl₄) 2960, 1715, 1600, 1255, 1160, 1100, 1060, 1020, 850 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.80 (s, 1 H), 7.62 (s, 1 H), 7.06 (d, *J* = 0.9 Hz, 1 H), 7.04 (d, *J* = 0.9 Hz, 1 H), 6.99 (d, *J* = 1 Hz, 1 H), 6.93 (d, *J* = 0.9 Hz, 1 H), 0.39 (s, 9 H), 0.36 (s, 9 H), 0.33 (s, 9 H), 0.325 (s, 9 H); ¹³C NMR (62.5 MHz, CDCl₃) δ 194.1, 160.4, 155.0, 153.2, 150.4, 148.6 (b), 148.5, 148.1, 147.6, 142.1, 133.4, 131.9, 129.2 (*J*_{CH} = 160 Hz), 125.4 (*J*_{CH} = 158 Hz), 123.6 (*J*_{CH} = 161 Hz), 123.1 (*J*_{CH} = 161 Hz), 113.0 (*J*_{CH} = 167 Hz), 110.5 (*J*_{CH} = 165 Hz), 2.08 (*J*_{CH₃} = 119 Hz), 2.06 (*J*_{CH₃} = 119 Hz), 1.95 (*J*_{CH₃} = 119 Hz), 1.84 (*J*_{CH₃} = 119 Hz); MS, *m/e* (rel intensity) 542 (M⁺, 57), 527 (7), 511 (5), 73 (100), 57 (6); HRMS calcd for C₃₁H₄₂OSi₄ 542.2313, found 542.2333.

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Supplementary Material Available: For compounds **5** and **28**, tables of positional and thermal parameters and their estimated standard deviations, general temperature factor expressions, *B*'s, and listings of observed and calculated structure factors (51 pages). Ordering information is given on any current masthead page.

Cation–Anion Interaction in the [Na-kryptofix-221][W(CO)₅O₂CH] Derivative and Its Relevance in Carbon Dioxide Reduction Processes

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Abstract: The structure of [Na-kryptofix-221][W(CO)₅O₂CH] has been determined by X-ray crystallography and shown to exhibit a novel strong contact ion pairing between the uncoordinated oxygen of the formate ligand with the cryptand-encapsulated sodium cation. The compound crystallizes in the triclinic space group *P* $\bar{1}$ with cell dimensions *a* = 10.221 (2) Å, *b* = 10.845 (2) Å, *c* = 12.779 (2) Å, α = 87.93 (1)°, β = 89.47 (1)°, and γ = 82.99 (1)°. The most significant structural aspect is that the distance between the formate's distal oxygen atom and sodium (2.388 (9) Å) is the shortest Na–O bond distance in the cation's coordination sphere. Although this ion pairing persists for uncomplexed sodium cations in tetrahydrofuran solution, the cryptand-encapsulated species exists as a solvent-separated or free-ion pair in solution. Similar solution behavior is observed for the acetatotungsten pentacarbonyl anionic derivative. In addition, the CH₃CO₂W(CO)₅⁻ anion, in the presence of 18-crown-6 complexed Na⁺, displays a solution structure approximating that of the anion in the existence of the uncomplexed Na⁺ cation. Consistent with these solution structures, the rate of reaction of carbon dioxide with CH₃W(CO)₅⁻ to provide CH₃CO₂W(CO)₅⁻ is enhanced by a factor of 10 in the presence of Na⁺ or Na(18-crown-6)⁺ over that carried out with the non-interacting PPN⁺ (bis(triphenylphosphine)iminium cation) or Na-kryptofix-221⁺. These rate accelerations are attributed to a cation stabilization of the incipient carboxylate during the carbon dioxide insertion process.

Alkali metal interactions with carbon dioxide are prevalent in chemistry associated with the reactivity of this C₁ molecule at transition-metal centers. For example, in the d⁸ complex, [Co-

(pr-salen)K(CO)₂THF]_n, the CO₂ is bonded to the cobalt atom via the C functionality and simultaneously O bonded to two different K⁺ ions.^{1,2} Maher and Cooper³ have shown that W-