"Super" Phanes

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When defining their synthetic goals, chemists are often inspired by beauty and symmetry, and at first glance it may seem as if their target is only of esthetic value and of no apparent use. Superphanes are indeed such beautiful and highly symmetric targets, and the reader will rightly ask, why synthesize superphanes or "super" phanes? The title of this account reflects our aim not only to define the term *superphane* and to present structures which belong to this class of compound but also to elaborate the salient features of these molecules. We wish to show that designed synthesis of strained structures often leads to the discovery of new preparative procedures, helps us in our understanding of the chemical bond, and reveals unexpected reaction pathways to otherwise unobtainable compounds. In other words, we will try to answer the question, *What makes a phane super?*
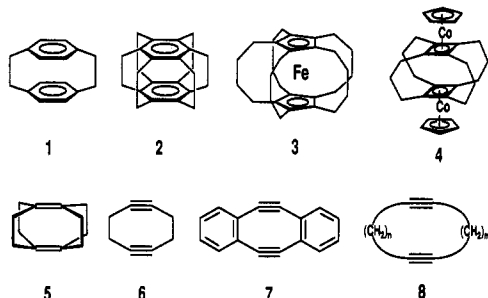
Terminology

Although the word "cyclophane" (from *cyclo, phenyl,* and *alkane*) was originally proposed by Cram and Steinberg[1] in 1951 for tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,-10,12(1),13,15-hexaene (1), it has evolved over the years[2a,3a,4,5] and has led to a systematic set of rules elaborated by Vögtle and Neumann.[6] The suffix "phane" thereby defines a compound containing at least one aromatic moiety (also heteroaromatic and aromatic type rings are included) and at least one bridge. The attribute *super* was suggested by Hopf[4a] for the first

6-fold-bridged cyclophane, [2$_6$](1,2,3,4,5,6)cyclophane (2), the ultimate member of cyclophanes, whose first synthesis was accomplished by Boekelheide in 1979. The superphane terminology is easily adapted for compounds such as 3[7a] and 4,[8] and consequently they have been termed [4$_5$](1,2,3,4,5)ferrocenophane ([4$_5$]-*super*ferrocenophane) and bis(η^5-cyclopentadienyl)-cobalt η^4:η^4-[3$_4$]cyclobutadienophane, a stabilized [3$_4$]-cyclobutadieno*super*phane, respectively. The nomenclature can be further extended to simpler π-systems such as 5[9a] and 6,[10a] and consequently both can be viewed as superphanes with an ethylenic and an acetylenic moiety, respectively.[11a]

This would make it a matter of choice whether diyne 7[12a] is considered an *ortho*cyclophane of benzene with C≡C bridges or viewed as a *super*phane of acetylene connected by benzenoid bridges. However, if the extension of the term phane to cover π-systems is accepted, the simplest superphanes would actually be represented by the general formula of a cyclic diacetylene (8). The logical consequence of this *Gedankenspiel* is that even cyclohexane-1,4-dione and 1,4-diazabicyclo[2.2.2]octane (DABCO) may in fact be classified as superphanes of C=O and N, respectively! Evidently the terminology should not be taken to its limits, and chemical intuition should guide the chemist's concept of a π-system in relation to the word *superphane.*

Rolf Gleiter received his Dr. rer. nat. in the field of synthetic organic chemistry from the University of Stuttgart in 1964 with F. Effenberger. After postdoctoral work at Princeton University with P. v. R. Schleyer and at Cornell University with Roald Hoffmann, he went to the University of Basel in 1969, where he worked on his habilitation in the laboratory of E. Heilbronner. In 1973 he joined the faculty of the Technische Hochschule in Darmstadt as Professor of Chemistry, and in 1979 he moved to the University of Heidelberg. His research interests are the synthesis of theoretically interesting molecules and their investigation by spectroscopy and theoretical means.
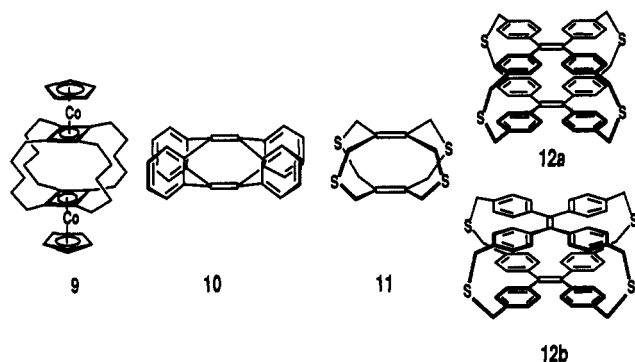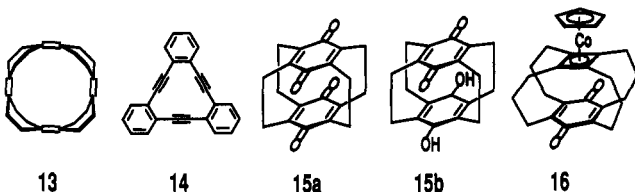
Detlef Kratz studied chemistry at the University of Heidelberg supported by a scholarship of the Studienstiftung des Deutschen Volkes. In the group of Rolf Gleiter he carried out his doctoral thesis (1990) dealing with the organization and reorganization of π-systems with metals, especially the reactions of carbocyclic diacetylenes leading to cyclobutadiene complexes and superphanes. With a Feodor Lynen Fellowship of the Alexander von Humboldt Foundation he spent a postdoctoral year at the California Institute of Technology in the group of R. H. Grubbs, where he worked on the synthesis of conjugated structures via metathesis reactions of cyclic and acyclic acetylenes and olefins. Since 1992 he has been working in the research department of the BASF.

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Superphanes may show a number of variations. Apart from the requirement that at least two π-systems be connected at all of their corners, a first modification is achieved by simple variation of the bridging units, as is evident from the comparison of compounds **4** and **9**[13] or **5** and **10**[14] or **11**[15] (in fact, **10** is the first reported ethyleno*superphane*). The thiasuperphanes **12a,b**[16] demonstrate nicely one of the attributes of *super-connectivity*, in that the orientation is fixed with respect to the two π-moieties.

Synthesis

The synthetic methods that lead to superphanes fall into different categories. Not only does each π-system require special methods, but the optimum reaction conditions will depend on the type of bridge that is desired. In principle, three synthetic routes may be distinguished:

(I) The first approach sets out from two π-systems, joins them at one or two corners, and continues to build up the remaining chains one after the other. Good examples for this procedure are the syntheses of **2** and

Just as in cyclophanes that contain more than two aromatic moieties, *extended superphanes* may be constructed by adding the corresponding unit to the simplest forms **5** or **7**, thus obtaining higher congeners such as **13**[17a,b] or **14**.[18] Finally, mixed superphanes may be generated by incorporating different π-systems into the molecular framework, leading to systems such as **15b**[19] and **16**.[20]

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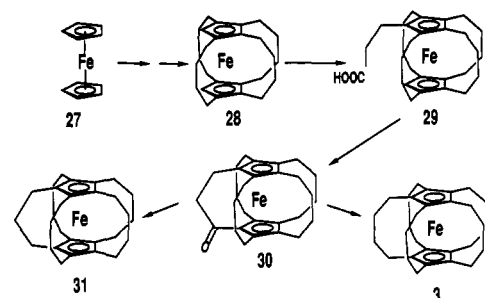
(19) (a) Staab, H. A.; Schwendemann, V. M. *Liebigs Ann. Chem.* **1979**, 1258. (b) Staab, H. A.; Schwendemann, V. M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 756.

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Scheme I
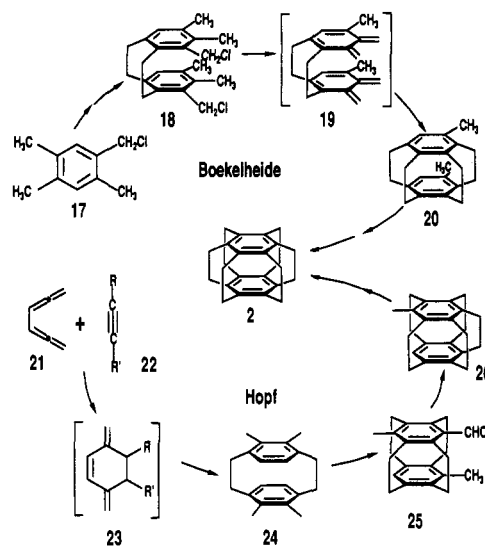
Scheme II

3, which have been described in detail elsewhere, so only the decisive chain-forming step will be presented here. While Boekelheide[21] uses the *in situ* generation and dimerization of an *o*-xylene derivative to obtain two ethano bridges in one step (**18** → **19** → **20**) (Scheme I), Hopf[22] opted for a route that introduces one dimethylene chain after the other by Rieche formylation and subsequent carbene insertion (**25** → **26**). Both routes entail a small number of steps (six to eight), and **2** can easily be prepared on a multigram scale.
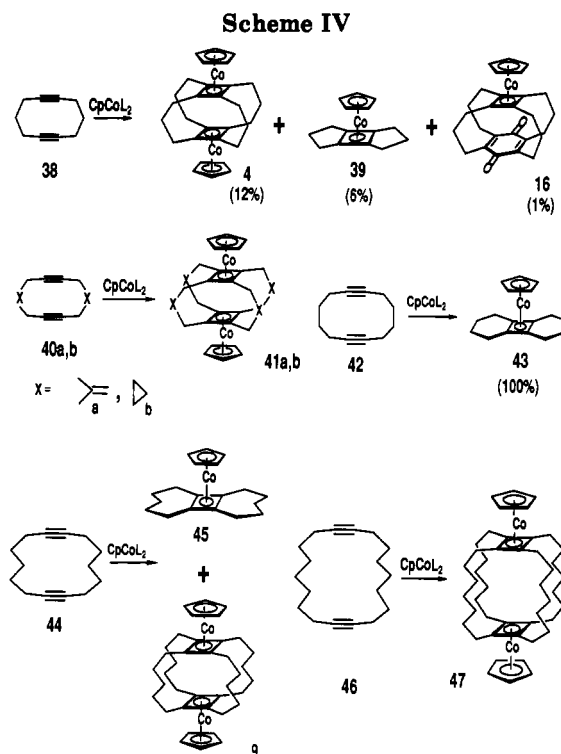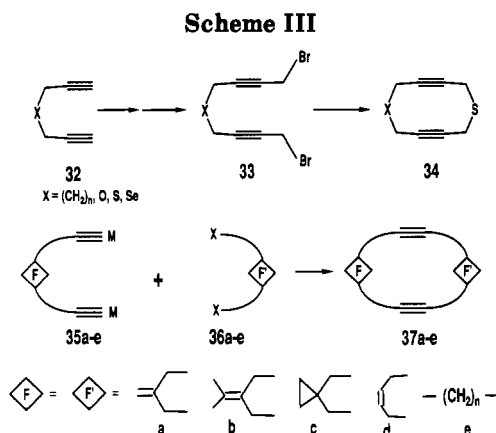
For the synthesis of **3**[7b] the introduction of the final tetramethylene chain is shown in Scheme II, in which the decisive step is bridge enlargement of **30** via Wolff rearrangement, while reduction of the keto group yields **31**, which is the first reported *super*ferrocenophane.[7c] Each butano bridge requires seven steps, so the total number of steps to [4₅]*super*ferrocenophane starting from ferrocene amounts to 35.

A good example in which thiacyclization[23] was employed to form a bridge is Shriver's simple one-step synthesis of **11**.[15] Ring closure of the smaller acetylenic precursors **33** with sulfur to the heterocycles **34** is

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Scheme III

32   33   34

X = (CH₂)ₙ, O, S, Se

35a-e   +   36a-e   →   37a-e

Scheme IV

38   →   4   +   39   +   16
           (12%)   (6%)   (1%)

40a,b   →   41a,b   42   →   43
                                   (100%)

X =

44   →   45   +   46   →   47
                      9

achieved without a problem,[24] and cyclization of **35** with a second bridge (**36**) affords the diacetylenes of general formula **37** in acceptable yields (Scheme III). Thus diacetylenic superphanes can be prepared efficiently with a large variety of bridging units.[25]

(II) Instead of synthesizing the individual connecting moieties, the second route uses functionalized cyclic substrates (chain type and chain length are determined) to build up the respective π-systems. In principle, the formation of intermolecularly bridged compounds represents the conversion of the simplest type of *super*phane (e.g. **8**) to higher *super*phanes. This direct approach was first attempted in 1965 by Hubert and Dale[26] with a number of macrocyclic nonconjugated diacetylenes, yet on reaction with Ziegler catalysts only formation of insoluble polymers was observed. Later Stephens[27] published a report of the one-step double cyclization of 1,7-cyclododecadiyne (**42**) to a compound he named "percyclophane-4", an analogue of **2** with bridging butano units, but this was refuted in a later paper.[28]

In 1987 trimerization of 1,6-cyclodecadiyne (**38**)[29] with (η⁵-cyclopentadienyl)cobalt dicarbonyl (CpCo(CO)₂) was attempted.[8] Not only could the expected tricyclic complex **39** be characterized but as the major component superphane **4** was isolated. No formation of trimeric products was observed. Some features of this direct (one-pot) synthesis of stabilized η⁴-cyclobutadiene superphanes are worth noting (Scheme IV).[30] The successful outcome of this reaction depends markedly on the ring size of the starting diacetylene. While nearly all derivatized 10-membered diacetylenes lead to superphanes in yields of 2–40% depending on the cobalt catalyst used (e.g. **40a,b** → **41a,b**), 1,7-cyclododecadiyne (**42**) all too readily forms the tricyclic cyclization product **43**.[31] When larger cyclic diacetylenes such as 1,8-cyclotetradecadiyne (**44**) or 1,10-cyclooctadecadiyne

(**46**) are reacted with CpCo(CO)₂, again superphanes (**9** and **47**, respectively) may be isolated.[13,32]

(III) A third route utilizes the fact that a difunctional (possibly monoprotected) cyclic precursor may be transformed to a new π-system at only one of its π-functionalities to yield an intermediate that, after derivatization, can undergo a second cyclization. This approach was adopted for the synthesis of the extended ethylenophane **13**[17] and its next lower congener by McMurry et al., who used the well-known TiCl₃/Zn/Cu-induced formation of olefins from ketones[33] in the final cyclization step.

The step-by-step route was also attempted for the synthesis of benzenoid superphanes from 1,8-cyclotetradecadiyne (**44**).[34] Formation of one benzene ring with three pendant triple bonds was accomplished, but all attempts at further trimerization failed to yield [5₆]-superphane. Starting from cyclic diacetylenes and dinitriles, efforts to prepare pyridinosuperphanes in which only five trimethylene chains need to span the two six-membered heteroaromatic rings did not lead to the desired compounds.[35-37]

The above unsuccessful experiments led to the conclusion that trimerization of three triple bonds to form a caged structure is hindered through crowding of the bridging groups. Simply by allowing for the formation of other, smaller cyclization products (i.e. four-membered rings), steric inhibition might be overcome, and with this in mind a strategy can be devised for the synthesis of cyclobutadienosuperphanes.[38] The beauty of this synthesis lies in the versatility of the

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(38) Gleiter, R.; Schehlmann, V. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1426. Gleiter, R.; Karcher, M.; Kratz, D.; Rittinger, S.; Schehlmann, V. In *Organometallics in Organic Synthesis 2*; Werner, H., Erker, G., Ed.; Springer Verlag: Berlin, Heidelberg, 1989.
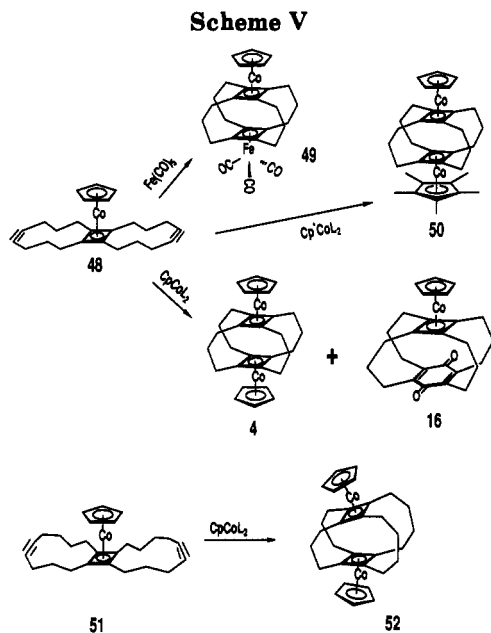
Scheme V

CpCo-complexed tricyclic diacetylene **48**, which on reaction with metal complexes yields the symmetric or mixed superphanes **4, 16, 49**, and **50**, respectively (Scheme V). Similarly, a superphane with two different sets of bridges was obtained from the second dimerization of **51** to **52**.[39]

Structural Characteristics

How is stacking of π-systems in close proximity reflected in the structures of superphanes? Fortunately, most of the superphanes that have been introduced in this Account have been subjected to X-ray crystallographic analysis (Tables I and II) so that we can attempt to answer this question. For the sake of brevity, we will limit our discussion to those superphanes that contain only two π-systems and are connected by units of equal length. A first important point that is characteristic of superphanes (compared to the less highly bridged cyclophanes) is that *super-connectivity* has the effect of sandwiching two moieties without allowing the π-systems to relieve strain by deformation from planarity. In the case of short bridges, say ethano or propano moieties, the rigidity of the connecting framework allows no rotation and the π-systems are always perfectly coplanar. In the butano-bridged compound 1,7-cyclododecadiyne **42**, on the other hand, the two triple bonds are at an angle of 24°,[29] and for longer chains even more freedom for the π-units is anticipated. Nevertheless, significant bending of the attached groups is observed, and this may serve as a measure of strain imposed on the structure, which simultaneously leads to tilting of the p-orbitals of the respective π-system. Our survey includes the most important bonding and nonbonding distances as well as the angle ω by which the p-orbitals are tilted out of the π-plane. By far the smallest transannular stacking distance ($\pi\cdots\pi$) is observed in the olefinic systems **5** and **10** ($\approx$2.4 Å)[9c,14] and increases to about 2.6 Å for the superphanes containing two triple bonds[10b] or benzene rings.[21a] Deviations from normal values are also reflected in the other parameters listed in Table I.

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Table I. Structural Data of Superphanes with C_2 Bridges

	6	7	5	10	2	15a
symmetry	D_{2h}	D_{2h}	D_{2h}	D_{2h}	D_{6h}	D_{2h}
distances (Å)						
$\pi\cdots\pi$	2.57	2.61	2.394	2.42	2.624	2.67
a^a	1.46	1.44	1.517	1.508	1.518	
b^a	1.57	1.42	1.595	1.42	1.580	1.556
angles (deg)						
ω (p-orbital)	10.5	12.1	13.5	10	10	

^{a} a = bond length between the C atom of the π-system and the adjacent C atom; b and c = bond lengths of the C–C bonds once or twice removed from the π-system, respectively.

Table II. Structural Data of Superphanes with C_3 and Higher Bridges

	38	37a	4	42	37d	3
symmetry	C_{2h}	C_{2h}	$C_{4h}{}^b$	D_2	D_2	D_{5h}
distances (Å)						
$\pi\cdots\pi$	2.99	3.003	2.944	4.06	3.363	3.244
a^a	1.466	1.475	1.499	1.466	1.469	1.52
b^a	1.516	1.512	1.518	1.527	1.505	1.43
c^a				1.523	1.323	1.33
angles (deg)						
ω (p-orbital)	4.4	4.0	0.27	3.1	2.95	–6

^{a} a = bond length between the C atom of the π-system and the adjacent C atom; b and c = bond lengths of the C–C bonds once or twice removed from the π-system, respectively. ^{b} Symmetry assignment refers to the cage structure without the CpCo fragment.

Stretching of the central C–C bond (b) as well as tilting of the p-orbitals (ω) is most pronounced in ethylenophane **5** and diyne **7** (the connecting bond b in **7** and **10** is stretched by 0.3–1.42 Å compared to the remaining bonds (1.39 Å) of the benzenoid bridge[12b]). The central bond in **2** is also appreciably elongated, whereas the quinoid superphane **15a** is able to relieve a substantial amount of strain by twisting of the C=O groups (16°) outward while the α-atoms are bent in the opposite direction;[19b] similar distortions are observed for the mixed superphane **16** where the C=O groups are tilted outward by as much as 26°.[20]

Superphanes containing a C_3 bridge (Table II) also tend to distribute the imposed strain over the whole molecular framework. With a mean transannular distance of $\approx$3 Å, all compounds stack two π-systems closer than the amount expected for twice the van der Waals radius of p-orbitals (approximately 3.4 Å). The p-orbitals are also tilted in **38, 37a, 37d**, and **42**,[29b] yet to a much lesser extent than in **6**, and most of the transannular repulsion of the π-systems is evident in larger than average angles in the tri- and tetramethylene chains. No significant bending of the C atoms adjacent to the η^4-complexed cyclobutadiene moiety in **4** is observed, as this would decrease overlap with the d-orbitals of the CpCo fragment. The opposite is true for the butano-bridged superphane **3**.[7b] The C_4 chain requires that the α-carbons lie 0.13–0.16 Å above the plane of the Cp ring, and in this structure the p-orbitals of the two Cp rings will be tilted inward ($\omega = -6°$), severely diminishing overlap with the Fe d MOs.[40]

A final point deserves comment with respect to the structure of superphanes. While an ethano-type chain can take only one conformation (*super*-connectivity

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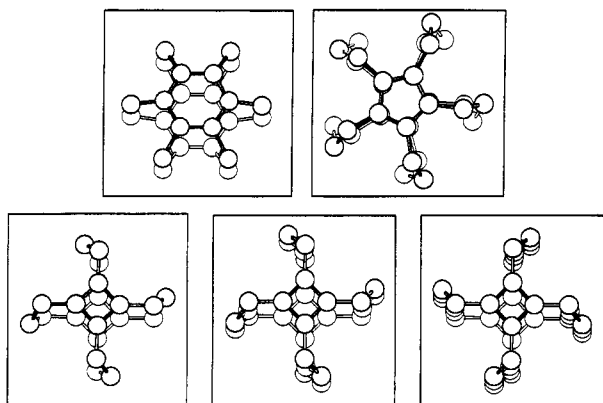
Figure 1. Perspective views of superphanes bridged by ethano (2), propano (4), butano (3), pentano (9) and heptano (47) moieties, demonstrating a rigid conformation for even-numbered and a pinwheel arrangement for odd-numbered bridges.

forces an eclipsed geometry of the H atoms), the trimethylene chains will be able to form a chair or boat conformation. Chair-type conformation is observed in all 10-membered diacetylenes and also in the C_3-connected bis-cyclobutadienosuperphanes (Figure 1) if the diagonal through the four-membered ring is used as reference. As a result a pinwheel conformation is observed for the four bridges in **4** as well as for the five- and seven-membered methylene chains in **9** and **47**. As viewed from the perspective chosen in Figure 1, uneven bridges longer than three atoms will preferentially adopt a strain free zigzag arrangement.[41] Once the chains become longer, more flexibility is possible and other features are observed. The 4-fold heptamethylene bridged superphane **47**, for instance, reveals a slightly lopsided structure that somewhat resembles a partially squeezed accordion.[32]

Spectroscopy

The spectroscopic implications of sterically fixing two π-systems into close proximity are numerous. Transannular interaction (through space) will split the π-MOs into bonding and antibonding sets, which, depending on symmetry, will further be perturbed by the σ-orbitals of the connecting bridges (through-bond interaction).[42] The normal MO pattern for the respective π-system will therefore be modified and result in stabilization or destabilization of HOMO and LUMO energies. Twisting of the p-orbitals may enhance or diminish overlap and further contribute to changes in MO energies. Furthermore, the π-systems can be classified as either electron rich or electron deficient and the dependence of donor–donor, donor–acceptor, and acceptor–acceptor interactions can be correlated to transannular distance. Ideal spectroscopic tools to probe these effects are methods related to uptake or release of electrons. Photoelectron (PE), UV/vis, and ESR-spectroscopy as well as cyclovoltammetry have been employed extensively to determine such influences in phanes.[3b,11,43]

PE spectroscopy, allows an estimation of MO energies of occupied states; in combination with semiempirical and *ab initio* MO calculations, the influence of bridges

on the π-systems of superphanes may be unraveled. For simpler systems such as **5**, **6**, and **38**, this has been discussed extensively.[42] Interplay of through-space and through-bond effects leads to reversal of the normal orbital sequence in **6**,[10b] to an accidental degeneracy of both π-bands in **5**,[44] and to a large splitting in **38**.[45] Another good example to demonstrate this effect is seen on comparison of the PE bands of hexamethylbenzene and the ethano-bridged superphane **2**. An analysis shows that both through-bond and through-space interactions are important to explain the splitting of the benzene MOs.

Due to the propano bridges in superphanes with a trimethylene bridge, variations in the ordering of orbitals are much easier to observe. Why is this the case? Analysis of a series of compounds is especially informative: The tricyclic cyclobutadiene complex **43** gives a typical picture for this type of complex in that three d MOs and two e MOs located at the cyclobutadiene ring give rise to a broad feature at low energy (−6.8 to −7.2 eV). This picture remains more or less unchanged for the $(CH_2)_5$-bridged cyclobutadienosuperphane **9**, although all intensities are doubled. On reducing the bridge length to propano units as in **4**, the perturbations described above become effective. Not only are ionization energies registered at slightly lower values, but a new band is found at $\epsilon_j = -7.5$ eV, which can only be attributed to the bonding combination of the e MOs of the two cyclobutadiene moieties.

How is the strong destabilization of the HOMO (leading to a reduced HOMO/LUMO gap) reflected in the electronic spectra? Compared to the UV/vis absorptions of the unbridged reference systems (hexamethylbenzene, tetramethylethylene, and 2-butyne), not only do the corresponding superphanes show shifts of the normally occurring bands but new transitions are registered in the region of longer wavelengths. The latter absorptions are relatively weak but are characteristic for cyclophanes and have been termed "cyclophane" band in benzenoid compounds such as **1** and **2**.[3b]

The reduced HOMO/LUMO energy can again be traced nicely on comparison of the UV spectra of the series of cyclobutadienosuperphanes **4** and **9** (Figure 2). With reference to the spectrum of a simple alkylated derivative **43**, the ε-values are expected to be doubled in all superphanes, but only in the transitions of the C_3-bridged compounds **4** should a red shift be evident. This proves to be the case.

Cyclovoltammetry further helps to establish these observations (Figure 3). Compared to the tricyclic cyclophane **43** (E_{ox1} = +0.46 V), the stretched superphanes **9** and **47** behave as two independent complexed cyclobutadiene moieties in their neutral form but as superphanes when ionic. Two close-lying reversible oxidations ($E_{ox1a,b}$ = +0.47/+0.62 V (**9**); $E_{ox1a,b}$ = +0.45/+0.53 V (**47**)) are registered, the first at values similar to those in **43**, the second at higher potential. The dependence of the second oxidation step on chain length demonstrates that even **9** and **47** behave as typical superphanes. The first reversible oxidation of **4**, on the other hand, proceeds more easily at E_{ox1} = +0.31

(41) Dale, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 1000.
(42) (a) Gleiter, R.; Schäfer, W. *Acc. Chem. Res.* **1990**, *23*, 369. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Paddon-Row, M. N. *Acc. Chem. Res.* **1982**, *15*, 245.
(43) Gerson, F. *Top. Curr. Chem.* **1983**, *115*, 57.

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(45) Gleiter, R.; Kratz, D.; Schäfer, W.; Schehlmann, V. *J. Am. Chem. Soc.* **1991**, *113*, 9258.
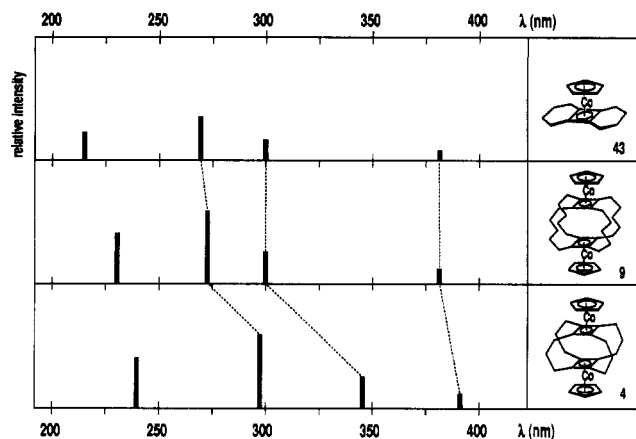
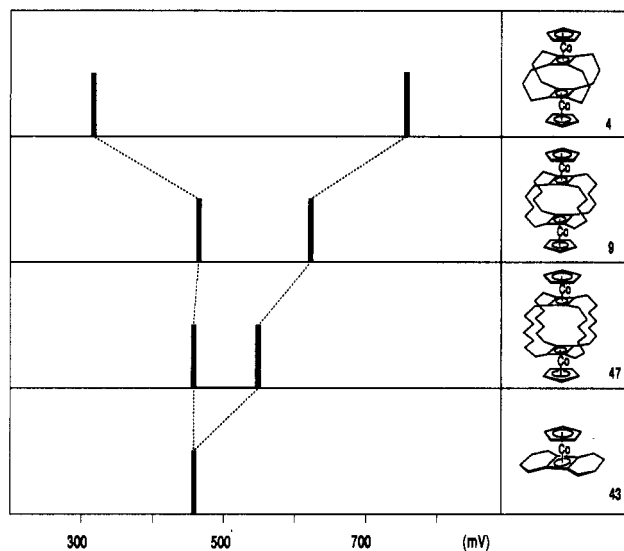**Figure 2.** Correlation of the UV bands of cyclobutadieno compounds 43, 9, and 4.

Figure 3. Correlation of the CV oxidation potentials of cyclobutadieno compounds 4, 9, 47, and 43.

V (Δ = +0.16 V compared to **43**), which may be attributed to the higher energy of the HOMO in the neutral form. In **4** the two cyclobutadiene units are so close that, once oxidized, the charge of the radical cation may be distributed over both cyclobutadiene moieties. On further oxidation (irreversible potential at E_{ox2} = +0.76 V) a dication is formed that may now localize the positive charge at either of the cyclobutadiene units, which after extrusion of the CpCo fragment leads to decomposition.[37,46]

Up to now we have only discussed the properties of symmetric donor–donor and acceptor–acceptor super-phanes, so we will briefly turn our attention to mixed superphanes of the donor–acceptor type. Most characteristic are changes in the long-wavelength region of the absorption spectra. A prominent and fairly intense feature appears between about 300 and 600 nm (e.g. **15b**) in all such compounds, which is the reason for the colored nature of donor–acceptor complexes. A simple MO picture is able to explain the occurrence of this band, as will be exemplified by an analysis of **16**. Due to the electron deficient nature of the duroquinone unit in **16**, the energy of the occupied MOs of this unit alone is relatively low, and no intense long-wavelength

Scheme VI
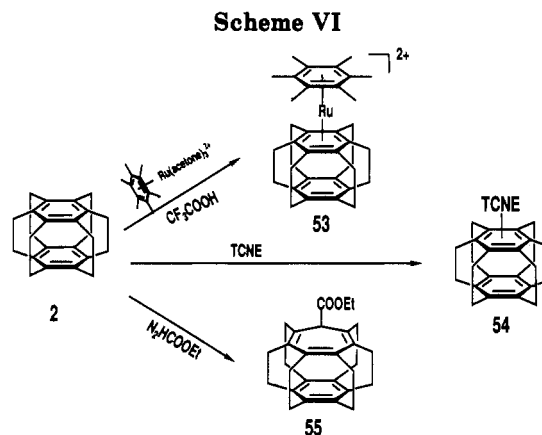
transition is evident. When an electron rich π-system such as a complexed cyclobutadiene fragment is stacked close to the acceptor unit, high-lying orbitals located at the four-membered ring will be located between the large energy gap of the quinone half of the molecule. Now a new transition between the HOMO of the donor and the low-lying LUMO of the acceptor moiety is possible, and charge is transferred from one region of the molecule to the other.[47] This results in the so-called charge-transfer transition of donor–acceptor complexes.

Reactivity

The consequences of *super*-connectivity are most readily seen in the chemistry of the multibridged structures described so far. A convenient way of dividing reactions of superphanes is to distinguish between changes occurring at the bridging units and those pertinent to the π-system. We will concentrate on the latter, yet it is not always possible to separate the influences of the bridge on the reactivity of the π-system, and vice versa. Superphanes are substituted at all of their corners, which will determine the mode of reaction: (1) Substitution reactions at the π-system are excluded if the bridges stay intact; (2) the "inner" half of the molecule is shielded from attack, and only the "outer" half is accessible; (3) steric requirements of the chains will be important, as they may either direct or inhibit a reaction pathway from a kinetic as well as thermodynamic point of view. As discussed above, the connectivity of superphanes usually deforms the π-system from its normal geometry, and enhanced reactivity is to be expected. The choice of examples from the literature serves to illustrate that organization or reorganization of the π-system can ensue on reaction with metal complexes or electrophiles, and changes *with* or *without* rearrangement of the underlying superphane structure are possible.

Complexation of **2** with a Ru–arene fragment (**53**)[48] or TCNE (**54**),[3c] reaction of **38** with Co$_2$(CO)$_8$,[45] or oxidation of **5**[9b] leaves the superphane framework intact, and new superphanes are formed, whereas reaction of superphanes with electrophiles, i.e. **5** with Br$_2$[9b] or **2** with N$_2$CHCOOEt (**55**),[21] may yield transannular addition products and polycyclic cage compounds (Scheme VI). The first type of reaction is of interest with reference to the structural parameters discussed earlier. π-Complexes of carbocyclic ligands prefer

(46) Gleiter, R.; Röckel, H.; Pflästerer, G.; Treptow, B.; Kratz, D. In preparation.

(47) Gleiter, R.; Kratz, D. To be published.

specific hybridization at the complexed carbon atoms (reflected by the deviation of the α-atoms from the π-plane with concomitant tilting of the p-orbitals to maximize overlap with the metal) so that on complexation strain may be either increased or decreased, as is seen on comparison of the angles of the substituents in ferrocene (27) versus superferrocene (3) mentioned above. Complexation of superphanes (i.e. to 53 or 54) can also serve to measure the degree of π-basicity in correlation to the uncomplexed half of the molecule.[48]

The mixed superphane 16 shows no tendency for reduction to 56 on reaction with LiAlH$_4$, as this would create a planar ring within the molecule. Inversion of the CO groups into the superphane cage should be even more difficult as is shown by the reaction of 16 with CpCo(=)$_2$. Compound 57 behaves as a taut spring that soon after formation ejects the CpCo fragment to furnish the starting compound 16.[37]
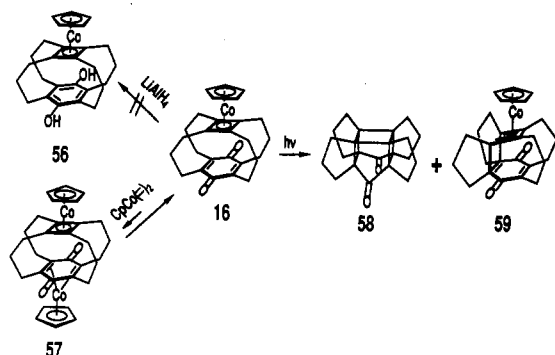

Confining a metal atom within the cage of a superphane proves to be an interesting target. Inclusion of a chromium atom into 1 and its propano-bridged homologue has been achieved,[49] but it is futile to attempt to squeeze an atom into the center of the multibridged structure 2, as the cavity is completely shielded by the ethano bridges. Superferrocenophanes, of course, inherently contain the metal atom, and only those superphanes that contain fewer bridges will serve as suitable precursors for multidentate ligand bonding. The Ag complex of 13 and the Ni complex of 14 are good examples of trigonal and square planar geometry defined by the respective symmetry of the superphane ligand.[17a,50] Unfortunately Ag$^+$ and Cu$^+$ complexes of 38, 42, and 44 only form polymeric structures (62) and do not incorporate the cation, even though the cavity between the π-systems could easily accommodate a metal atom[51] Similar observations have been reported for the reaction of 5 with Ag salts.[9b]

Whereas the reactions described so far have involved attaching a new metal fragment to the superphane, 4 is ideally suited for removal of this stabilizing moiety. Oxidation of 4 with Ce^{IV} probably generates an antiaromatic superphane (63) that immediately rearranges
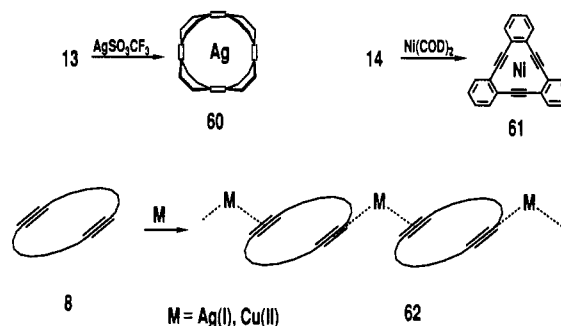
to 64 in an intramolecular Diels–Alder reaction.[52] On irradiation the obtained tricyclic structure affords the 2 + 2 cyclization product (65), which can be viewed either as a cyclotetramerization product of pentyne or as a representative of a class of compounds known as propella[n_m]prismanes. Decomplexation of the higher homologues (9 and 47) does not lead to the tricyclic cage compound, as the longer bridges hinder internal dimerization. The unsymmetrical analogue (52), on the other hand, again leads to the corresponding tricyclooctadiene derivative. The complexed cyclobutadiene of 16 also lends itself to removal of the CpCo unit. Oxidation does not give a clean reaction, but light-induced decomplexation and rearrangement yields two interesting compounds (58 and 59) in a 1:1 ratio.[37]
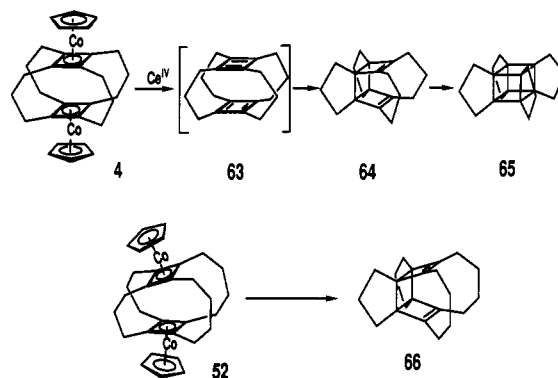
Conclusion and Outlook

Although it may seem strange to classify multibridged acetylenes and ethylenes (5 and 6) as *superphanes*, this Account has collected structural, spectroscopic, and chemical evidence that justifies the extension of the given terminology to include not only cyclic conjugated systems (2–4) but also simple π-systems. This classification allows reactions of a seemingly diverse nature to be related within a general concept.

The following compounds serve to illustrate some intriguing possibilities that arise from this mode of connectivity. Structures 68–70 would complete the series of stacked π-systems (2–6) up to a ring size of eight. The above synthetic and experimental details make 68 an especially interesting synthetic target. The angles of the substituents at the three-membered π-moiety are ideally bent to ease the strain usually implemented in multibridged structures. A doubly bridged cyclophane (67) has been synthesized recently,[37,53] and formation of the final bridge should present

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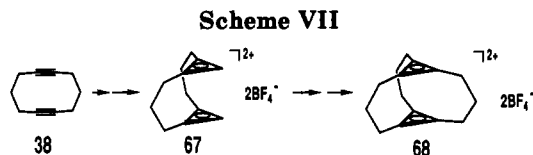
Scheme VII

no serious problems (Scheme VII). Cyclobutadieno-superphane **71** and cyclopentadienylsuperphane **72** demonstrate the idea of "inverting" the metal-stabilized structures of **4** and **3**.

Instead of extending ethylenophane **5** lengthwise to yield **13**, an extension can be imagined perpendicularly to the double bond thus resulting in laterally fused cyclohexadiene moieties. This leads to a class of compounds known as beltenes that have been discussed on a theoretical basis;[54] their synthesis will probably be accomplished in the near future.[55] The relation of these polycyclics to the well-documented area of supramolecular chemistry and host–guest interactions need only to be mentioned, and an extension of these toroidal belts is easily imagined by including a base to furnish large cavities; all that remains to be done is to cap the structure with a lid and a spheroid results, very much resembling C_{60}, which is, of course, a prime example of
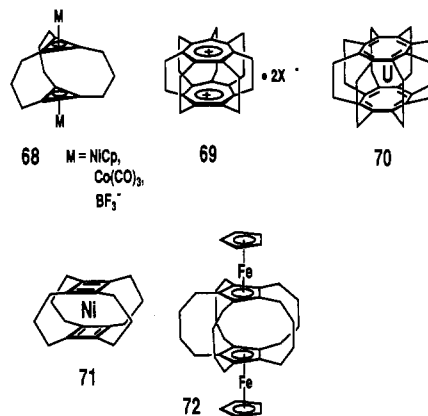
a "super" phane. Finally, the chemist will remain inspired by beauty and symmetry in his research, and it remains to be seen what the area of "super" phanes will have to offer in the future.

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