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Ansa Complexes

Strained Metallocenophanes and Related Organometallic Rings Containing π-Hydrocarbon Ligands and Transition-Metal Centers

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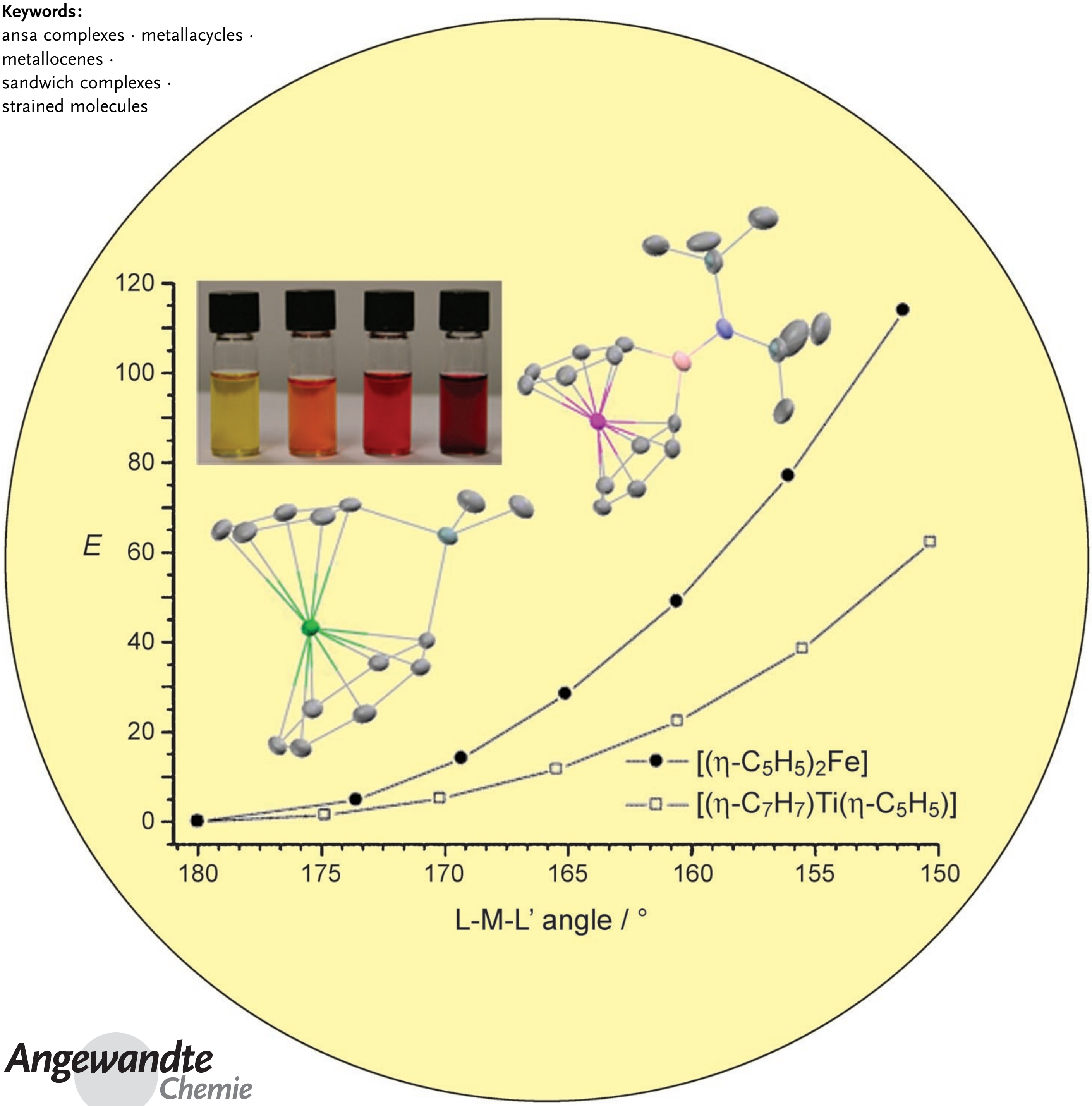
Keywords:
ansa complexes · metallacycles · metallocenes · sandwich complexes · strained molecules



The structures, bonding, and ring-opening reactions of strained cyclic carbon-based molecules form a key component of standard textbooks. In contrast, the study of strained organometallic molecules containing transition metals is a much more recent development. A wealth of recent research has revealed fascinating nuances in terms of structure, bonding, and reactivity. Building on initial work on strained ferrocenophanes, a broad range of strained organometallic rings composed of a variety of different metals, π-hydrocarbon ligands, and bridging elements has now been developed. Such strained species can potentially undergo ring-opening reactions to functionalize surfaces and ring-opening polymerization to form easily processed metallopolymers with properties determined by the presence of the metal and spacer. This Review summarizes the current state of knowledge on the preparation, structural characterization, electronic structure, and reactivity of strained organometallic rings with π-hydrocarbon ligands and d-block metals.

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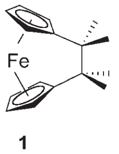
1. Introduction

Although strained cyclic organic compounds have been extensively studied and play an important role both in molecular synthesis and as monomers in ring-opening polymerization (ROP) reactions, their strained organometallic counterparts containing transition-metal centers are comparatively unexplored.[1] Over the past 40 years, metallocenophanes and related species have emerged as the first broad class of strained organometallic rings to be systematically developed and studied.[2] The first strained metallocenophane, a [2]ferrocenophane with a C_2Me_4 bridge (**1**), was reported by Rinehart Jr. et al. in 1960.[3] Despite suggestions that analogues with a single bridging atom would be too strained to exist,[4] the first [1]ferrocenophanes with a silicon bridge (for example, **2**) were successfully prepared by Osborne and co-workers in 1975.[5a] Analogous [1]ferrocenophanes with germanium and phosphorus in the bridge and stoichiometric ring-opening reactions of silicon-bridged species were reported shortly thereafter, and by 1980 the field of strained metallocenophanes had truly emerged.[6–8]



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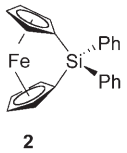

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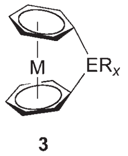

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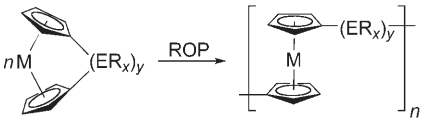
The unusual structures, reactivity, and potential utility of strained metallocenophanes and related species, such as metalloarenophanes (for example, **3**; E = main-group element), have led to extensive recent developments in the area. The discovery in the early 1990s that strained ferrocenophanes undergo ROP to yield high-molecular-weight polyferrocenes [Eq. (1)] has provided additional motivation to the development of this exciting field.[9] Significantly, the incorporation of different spacer groups, metal centers, and π-hydrocarbon ligands offers unique opportunities to vary and tune metallopolymer properties and applications. The expanding area of materials science and technology associated with the ring-opened polymers is covered by several reviews,[10a–c] including one in this issue by Rehahn and Bellas that complements this Review.[10d]



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In this article we review the current state of knowledge in the area of strained metallocenophanes and related species. Work on ferrocenophanes is discussed first, as this area is particularly well-developed and provides a framework with which to compare and contrast other related systems.

2. Organometallic Rings with Two Cyclopentadienyl Ligands: Strained Metallocenophanes

2.1. Geometric Parameters and Ring Strain

The introduction of short ansa [n] bridges ($n = 1, 2$) affects the normal metallocene geometry as shown in Figure 1. The degree of ring tilt is usually expressed in terms of the tilt angle α, which is the dihedral angle between the two cyclopenta-

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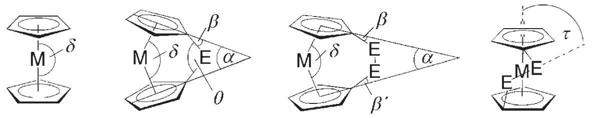


Figure 1. Definition of geometric parameters α, β, δ, θ, and τ in unbridged metallocenes as well as [1]- and [2]metallocenophanes (see text for details).

dienyl (Cp) ring units. In addition, β denotes the $Cp_{centroid}$-C_{ipso}-E angle, θ describes the C_{ipso}-E-C'_{ipso} angle, and δ denotes the $Cp_{centroid}$-M-$Cp'_{centroid}$ angle. In E_2-bridged metallocenophanes, an angle τ is defined as the projected dihedral angle between the axis $Cp_{centroid}$-M-$Cp'_{centroid}$ and the bond vector between the bridging atoms.

Bending back the two Cp rings to generate a ring-tilted structure opens up more coordination space, facilitating the introduction of additional ligands, as well as making the metal center more Lewis acidic or basic.[11] However, ring-tilted ansa metallocenes are not necessarily strained. Using DFT calculations, Green has showed that the d-electron configuration of the metal profoundly influences the geometrical preferences of the ansa [*n*]metallocenes.[12] The commonly found parallel ring structures in metallocenes are a consequence of the d electrons avoiding antibonding interactions and minimizing electron–electron repulsion. In the absence of these factors, there is no inherent weakening of the metal–ring bonding upon tilting, exemplified by a comparison of how the calculated total energy of both $[Cp_2Fe]$ (Fe^{II}, d^6) and the hypothetical triplet $[Cp_2Zr]$ (Zr^{II}, d^2) vary with the bending angle α (Figure 2). When all three HOMO orbitals are fully occupied, as in the case of a d^6 configuration for iron, the total energy of the molecule is raised significantly upon ring tilting. As a result, ferrocene shows a strong preference for a parallel ring arrangement. In contrast, $[Cp_2Zr]$ shows little resistance to angle variation.[12] These results suggest that metallocenophanes with two or fewer d electrons are unlikely to possess significant strain even when highly tilted structures are imposed.

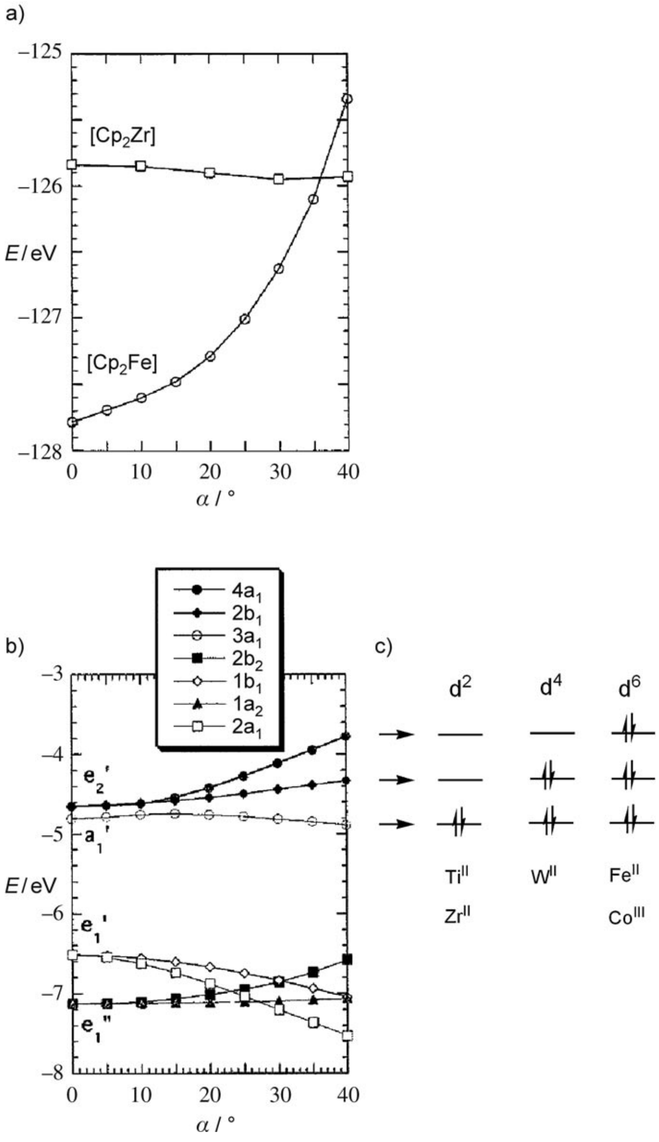


Figure 2. a) Variation of the total energy of $[Cp_2Fe]$ and triplet $[Cp_2Zr]$ as a function of the ring tilt angle α. b) Variation of electron energies of $[Cp_2Fe]$ as a function of the tilt angle α. c) d-Orbital occupation in representative transition metals (singlet states shown). (a) and (b) reproduced with permission from reference [12].

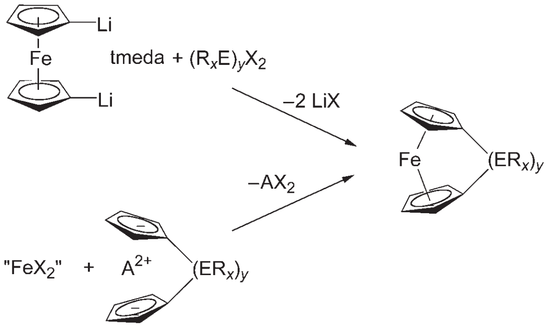
Ulrich F. J. Mayer was born in 1977 in Regensburg, Germany. He studied chemistry at the Friedrich-Schiller University in Jena and spent one year at the Universidad del Pais Vasco and at the University of Bristol in the group of Professor P. Pringle, with whom he carried out his Diploma thesis on the design and synthesis of chiral monodentate phosphines for asymmetric hydrogenation reactions. In 2005 he joined Ian Manners' group with his PhD work focusing on the development of strained organometallic compounds and their applications directed towards the area of new materials.

David E. Herbert was born in North York, Canada in 1982. He graduated from the University of King's College in 2004 with a BSc honors degree, gaining experience in phosphorus coordination chemistry with Professor Neil Burford at Dalhousie University. After completing an MSc at the University of Toronto in 2005, he began doctoral studies with Ian Manners in Bristol, exploring synthetic routes to inorganic and organometallic polymers. He is currently in his second year and is a recipient of a Postgraduate Scholarship from the Natural Sciences and Engineering Research Council of Canada.

2.2. Strained [n]Ferrocenophanes

2.2.1. Synthetic Approaches

Various synthetic routes have been employed to prepare strained [*n*]ferrocenophanes. The main routes involve a salt metathesis reaction of dilithioferrocene(tmeda)[5b] (tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine) and an organoelement dihalide, or a "fly-trap" approach involving an appropriate bridged $(C_5H_4)_2$ dianionic linker (A = alkali or alkaline-earth metal) and iron(II) halides [Eq. (2)]. Other approaches include the direct reaction of ligands with iron vapor, and various ring-closing transformations on preformed ferrocene derivatives. The earliest reported ferrocenophane was the [2]ferrocenophane **1** prepared in 1960 by the "fly-trap" method.[3] On the other hand, the first [1]ferrocenophane, the silicon-bridged species **2**, was prepared in 1975 by using the reaction of dilithioferrocene(tmeda) and Ph_2SiCl_2.[5a]



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The high-yield dilithiation of ferrocene[5b] has been vital to the preparation of most [1]ferrocenophanes, including compounds bridged by main-group elements from Group 13 (B, Al, Ga), Group 14 (Si, Ge, Sn), Group 15 (P, As), Group 16 (S, Se), transition metals from Group 4 (Ti, Zr, Hf), and even actinides (U; Table 1). The dilithiation is accomplished using *n*BuLi and tmeda in an organic solvent,[5b,8] though the product does not usually contain a predictable ratio of dilithiated salt to tmeda. The actual ratio can be determined and ranges from $^2/_3$ to 2 for different dilithioferrocenes.[13]

Table 1: Structural and spectroscopic data for representative [1]ferrocenophanes [fcER$_x$] (fc = Fe(η^5-C_5H_4)$_2$) arranged by period of bridging element E.

ER$_x$	α [°]	β [°]	δ [°]	θ [°]	λ_{max}[b] [nm]	δ(C$_{ipso}$) [ppm]	Ref.
BN(SiMe$_3$)$_2$	32.4(2)	33.9(2)	155.2(2)	100.1	479	45.0	[15]
Al(pytsi)[c]	14.9(3)	43.1	167.9	94.7(2)	–[a]	53	[20]
SiMe$_2$	20.8(5)	37.0(6)	164.74(8)	95.7(4)	478	33.5	[21,22]
PPh	26.9	32.3	159.8	90.7(2)	497	18.7	[7,23]
S	31.0(1)	29.0(2)	156.9(1)	89.03(9)	504	14.3	[24]
Ga(Me$_2$Ntsi)[c]	15.8(2)	38.4	166.8	92.8	–[a]	47.3	[25b]
GeMe$_2$	19.0(9)	36.8(7)	165.3(5)	91.7(3)	486	31.0	[26]
AsPh[d]	22.9	32.8	162.5	87.90(7)	494	18.3	[7,23]
Se	26.4(2)	30.0(2)	160.0(1)	86.0(1)	500	5.6	[24]
Sn(*t*Bu)$_2$	14.1(2)	36.2(2)	168.6(2)	86.5(2)	485	34.9	[27]
Zr(*t*BuCp)$_2$	6.0	40.1	177.3	86.3	352	159.0	[28]
U(fc)$_3$Li$_2$(py)$_3$[c]	0	–[a]	–[a]	82(1)	–[a]	–[a]	[29]

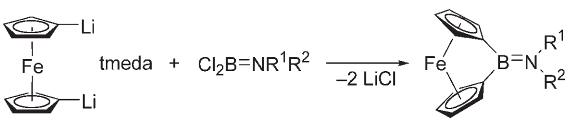
[a] Not reported. [b] UV/Vis data are reported in hexanes except for ER$_x$ = GeMe$_2$ and Sn*t*Bu$_2$ (in THF). [c] pytsi = C(SiMe$_3$)$_2$SiMe$_2$(2-C$_5$H$_4$N), Me$_2$Ntsi = C(SiMe$_3$)$_2$SiMe$_2$NMe$_2$, py = pyridyl. [d] One Cp ligand contains a (dimethylamino)ethyl substituent in the 2-position.

Ian Manners, born in London in 1961, received his PhD from the University of Bristol in 1985 in transition-metal chemistry (with N. G. Connelly) and conducted post-doctoral work on main-group chemistry with P. Paetzold (RWTH Aachen, Germany), and on polymeric materials with H. R. Allcock (Penn State, USA). He joined the University of Toronto in 1990 and after 15 years returned to his alma mater to take up a Chair in Inorganic, Macromolecular, and Materials Chemistry. His research focuses on the development of synthetic inorganic chemistry for applications in molecular synthesis, polymer/materials science, supramolecular chemistry, and nanoscience.

2.2.2. Group 13 Elements as Bridges

Boron[14]

The first reported boron-bridged ferrocenophanes **4**[15] prepared by Braunschweig and Manners [Eq. (3)] currently remain the only well-characterized examples of strained [1]ferrocenophanes incorporating an element of the second period in the bridge. In each case, the bridging boron center is incorporated as part of an aminoborane fragment with sterically bulky substituents on nitrogen (**4**: $R^1 = R^2 = SiMe_3$; $R^1 = SiMe_3$, $R^2 = t$Bu; $R^1 = R^2 = i$Pr). This is thought to be a decisive factor in stabilizing isolable, monomeric products, as the use of less sterically protected aminodichloroboranes leads only to insoluble products. For successfully isolated bora[1]ferrocenophanes, X-ray crystallographic analysis reveals boron–nitrogen bond lengths typical of double bonds for each of the three boron-bridged ferrocenophanes ($R^1 = R^2 = SiMe_3$: 1.399(2) Å; $R^1 = SiMe_3$, $R^2 = t$Bu: 1.371(6); $R^1 = R^2 = i$Pr: 1.384(6) Å; compare: 1.41 Å[16]). The extremely high tilt angles (up to $\alpha = 32°$, Table 1) suggest a large amount of strain, as supported by computational results, which indicate that constraining the Cp rings in ferrocene from an α value of 0° to 30° would lead to a strain energy of over 100 kJ mol^{-1} (ca. 1.2 eV in Figure 2a).[17] Indeed, thermal ROP at 180–200 °C to afford an insoluble polyferrocenylborane has been reported.[15b,18]



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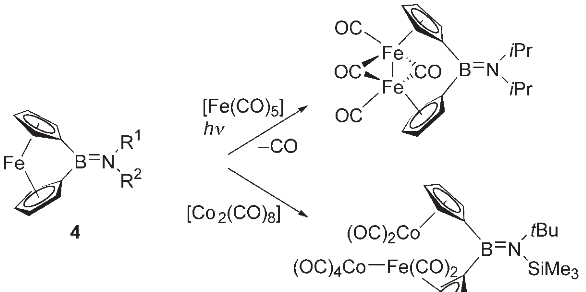
Differential scanning calorimetry (DSC) revealed a ROP exotherm at 190 °C that corresponds to a ΔH value of $-95\,\mathrm{kJ\,mol^{-1}}$ in the case of **4** ($R^1 = R^2 = SiMe_3$). These highly strained species exhibit different reactivity compared to less strained [1]ferrocenophanes, which tend to undergo reactions at the Cp-bridging element bond. For example, weakened Fe–Cp bonding allows insertion of metal carbonyl fragments [Eq. (4)]. A dibora[2]ferrocenophane was reported by Herberhold et al. with structural characterization mentioned but not published.[19]



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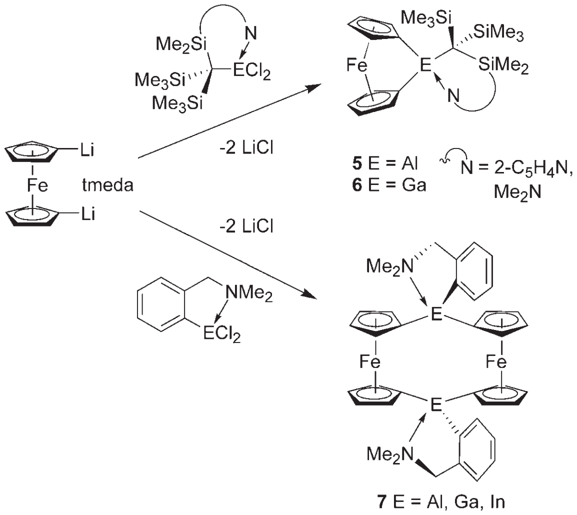
Aluminum and Gallium

While sterically demanding π-donor ligands have been used to stabilize bora[1]ferrocenophanes, the Al- and Ga-bridged [1]ferrocenophanes **5** and **6** employ bulky trisyl-derived ligands (trisyl = tris(trimethylsilyl)methyl; pytsi = $C(SiMe_3)_2SiMe_2(2\text{-}C_5H_4N)$; $Me_2Ntsi = C(SiMe_3)_2SiMe_2NMe_2$) to provide steric shielding from the trimethylsilyl groups and intramolecular stabilization through a pendant N donor.[20,25] Notably, use of a smaller intramolecularly stabilizing ligand leads to [1.1]ferrocenophanes (**7**) bridged by two base-stabilized Group 13 metal centers, presumably a result of diminished steric protection.[30,31] The syntheses of the monomeric compounds by Müller and co-workers follow a common route for metallocenophane formation: reaction of a doubly deprotonated metallocene with, in these cases, intramolecularly stabilized Group 13 dihalide complexes [Eq. (5)], and form the desired [1]ferrocenophanes in moderate to high yields (**5**: with pytsi 31 %, with Me_2Ntsi 97 %; **6**: with pytsi 59 %, with Me_2Ntsi 68 %).[20,25] As elements with larger covalent radii are used in the bridge, the tilt angles are, as expected, smaller (Al: $\alpha \approx 15°$ (Figure 3); Ga: $\alpha \approx 16°$) than for boron-bridged [1]ferrocenophanes ($\alpha \approx 32°$).



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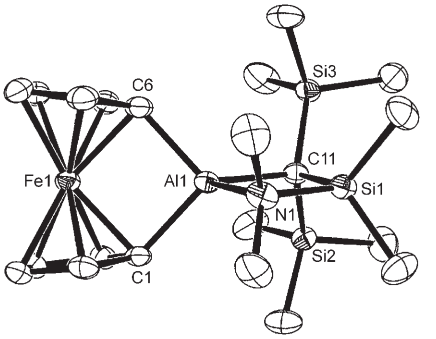
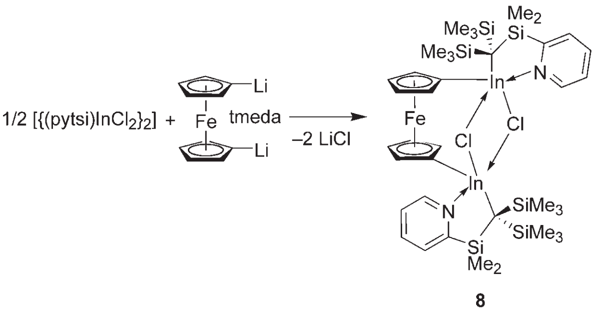


Figure 3. ORTEP representation of an aluminum-bridged [1]ferrocenophane. Reproduced with permission from reference [20].

Spectroscopic characterization is consistent with the formation of tilted [1]ferrocenophanes. For example, ^{13}C NMR spectroscopic studies of **6** reveal an upfield shift of the *ipso* carbon resonances relative to an unstrained analogue ($\delta = 47.2$ ppm [**6**(pytsi)], 47.3 ppm [**6**(Me_2Ntsi)];[25] 1,1′-di(methylgallyl)ferrocene: $\delta = 76.2$ ppm[32]). This upfield shift is characteristic of strained [*n*]metallocenophanes (for example, **4**, C_{ipso}: $\delta = 44$–45 ppm;[15] 1,2-bis(dimethylamino)-1,2-dibora[2]ferrocenophane, C_{ipso}: $\delta = 76.2$ ppm[19]).

Indium

In attempting the synthesis of an indium-bridged [1]ferrocenophane, the potential precursor (pytsi)$InCl_2$ was found to form dimers in the solid state.[25a] Despite fluxional solution behavior perhaps indicative of a fast monomer–dimer equilibrium, an indium-bridged [1]ferrocenophane could not be isolated from the reaction with dilithioferrocene(tmeda) and the diindane-bridged ferrocenophane **8** is isolated as the major product regardless of reactant stoichiometry [Eq. (6)].



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2.2.3. *Group 14 Elements as Bridges*

Carbon

[1]Ferrocenophanes bridged by a single carbon atom are currently unknown, presumably a reflection of the unstable, high-energy conformations the cyclopentadienyl ligands would have to adopt (either exceedingly unstable tilting relative to the parallel orientation in ferrocene or an unfavorable puckered conformation) and the resulting bond angle distortion at the bridging element. Mononuclear [*n*]ferrocenophanes with $n > 2$[33] and multinuclear [*m.m*]metallocenophanes[34] are essentially unstrained although some containing olefinic bridges are appropriate candidates for ring-opening metathesis polymerization (ROMP).[35–39] Propane-bridged [3]ferrocenophanes can be synthesized with tilt angles up to 12.6° (Table 2),[33,40–43] although photoelectron spectroscopy reveals more similarity between the electronic structure of these compounds and nonbridged analogues than with more highly strained ferrocenophanes.[44] Carbon-bridged [2]ferrocenophanes with saturated (e.g. **1**) or unsaturated bridges[37,47] are isolable and these strained compounds will undergo ROP.[46] The most highly strained carbaferrocenophane, stable only under inert gas at −50 °C, is a doubly strapped [2_2]ferrocenophane with $\alpha = 28.8°$. This species is tilted 7.2° more than the singly bridged analogue (Figure 4).[45]

Table 2: Selected parameters of representative carba[*n*]ferrocenophanes $[\mathrm{fc(CR}_x)_y]$ and [n_2]ferrocenophanes $[\mathrm{fc(CR}_x)_y(\mathrm{C'R'}_{x'})_{y'}]$.

$(\mathrm{CR}_x)_y$	α [°]	β [°]	τ [°]	Ref.
$1,1',3,3'$-$[(\mathrm{CH_2})_3]_2$	9.9	7.0, 8.7	–	[33b]
$\mathrm{R^1R^2CCH{=}CR^3}$	12.6	1.8, 1.2	–	[43]
$\mathrm{CH_2CH_2}$	21.6(5)	20.1(3), 12.7(3)[a]	18.4(1)	[46]
$\mathrm{HC{=}CH}$	22.6	15.8	5.0	[37,47]
$1,1',2,2'$-$[(\mathrm{CH_2})_2]_2$	28.8	11.3, 11.5	8.2(10), 6.9(10)	[45]

[a] The C_2 bridge is disordered over two sites with occupancies of 0.60 and 0.40.

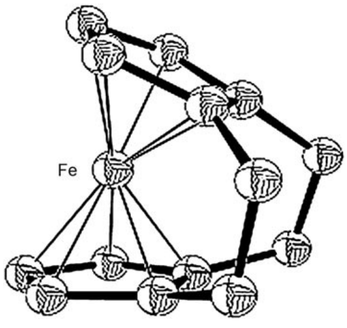


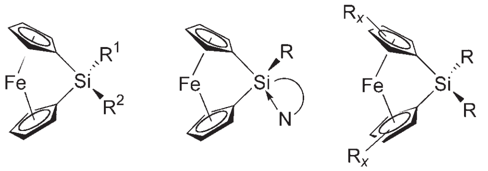
Figure 4. Solid-state depiction of a doubly strapped ethane-bridged [2_2]ferrocenophane. Reproduced with permission from reference [45].

Ethane-bridged [2]ferrocenophanes can be polymerized thermally to produce high-molecular-weight poly(ferrocenylethylenes), however methylation of the cyclopentadienyl ligands is crucial for polymer solubility in organic solvents.[46] Though the hydrocarbon bridge is relatively inert despite substantial ring strain, specific activation of the Fe–Cp bond is achieved by photolysis of the unsubstituted ethane-bridged [2]ferrocenophane and haptotropic shifts of the cyclopentadienyl ligands are observed in the presence of chelating phosphines.[48] Photolytic ROP is initiated by monodentate phosphines in the presence of light to give insoluble polymeric material.[48]

Additional reactivity studies were inspired by the presumption that the cyclopentadienyl ligands in ferrocene tilt upon protonation of the metal center.[49] As a corollary, tilting the cyclopentadienyl rings might affect the Lewis basicity of the metal center by exposing occupied d orbitals to incoming Lewis acids.[50] Small hypsochromic shifts are observed in the UV/Vis spectra of strongly acidic solutions of tilted carbon-bridged [2]- and [3]ferrocenophanes.[50,51] An increase in molar absorptivity is also detected for the reaction mixtures, consistent with the Laporte-forbidden transition becoming more allowed given the further decrease in symmetry of tilted ferrocenophanes upon protonation.

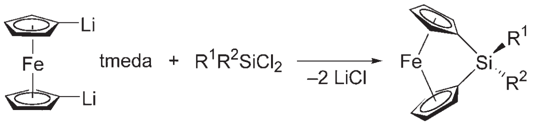
Silicon

Silicon-bridged [1]ferrocenophanes were first prepared in the mid-1970s[5a] and subsequently explored as agents for derivatizing surfaces through stoichiometric ring-opening reactions.[21] More recently, interest in using strained sila[1]ferrocenophanes as precursors to polyferrocenylsilanes by means of ROP [Eq. (1)] and the use of these materials have spurred research into their diversification to modify the properties of the ring-opened polymers.[52] A vast range of sila[1]ferrocenophanes has now been prepared by a variety of research groups (representative types are depicted in Scheme 1) and in this Review we provide a non-exhaustive overview.



Scheme 1. Representative sila[1]ferrocenophane derivatives.

Numerous diorganodichlorosilanes can be treated with dilithioferrocene to prepare symmetrically and unsymmetrically substituted sila[1]ferrocenophanes **9** in high yield [Eq. (7)].[53–59] Additionally, halogen replacement at the bridging silicon atom in dichlorosila[1]ferrocenophanes using alcohols, phenols, or amines in the presence of a base presents a facile route to alkoxy-, aryloxy-, and amino-substituted silyl-bridged [1]ferrocenophanes.[55,56] Reaction of chloro-substituted derivatives with lithium reagents at low temperature (−78 °C) is a general synthetic route to a variety of sila[1]ferrocenophanes that avoids polymer formation despite the tendency for strained [1]ferrocenophanes to ring-open with alkyl anions (Scheme 2). The substituted, strained metallocenophane forms a kinetic product at low



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$R^1 = R^2$ = Me, Ph, Cl, ferrocenyl, O*t*Bu, O*i*Pr, OCH_2Ph
R^1 = Me, R^2 = Et, Ph, Cl, H, allyl, vinyl, *n*-$C_{18}H_{37}$, norbornyl
R^1 = Me, R^2 = $(CH_2)_nX$ (*n* = 1, 2, 3; X = Cl)
R^1 = Ph, R^2 = Cl
R^1 = CH_2Cl, R^2 = Cl

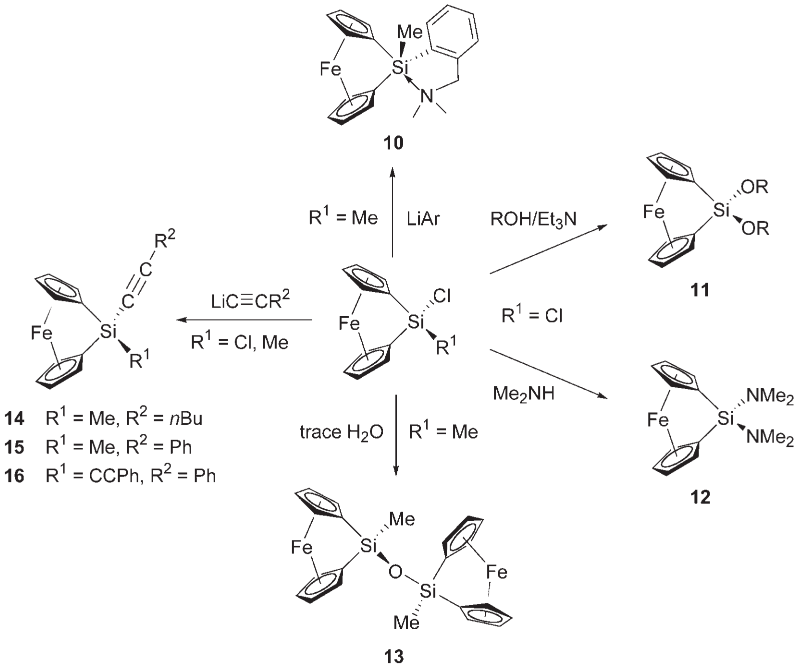
temperatures, driven by the more favorable leaving-group ability of a chloride ion compared with a ferrocenyl substituent.[70]

The nature of the substituents at silicon does not result in large structural variations between the sila[1]ferrocenophanes (Table 3), which generally possess tilt angles between 19 and 22° and corresponding strain energies of 70–80 kJ mol^{-1}.[60] Accordingly, ROP is a viable route for obtaining high-molecular-weight ($M_n \approx 10^4$–10^5) polymers from many of these compounds.[9,57–59] ROP can be achieved by a variety of methods such as thermal, transition-metal-catalyzed, anionic, and photolytic means.[52,61] Anionic and photolytic routes are "living" polymerizations that provide control over molecular weights and yield narrow molecular-weight distributions.[61–63]

Table 3: Structural data for selected sila[1]ferrocenophanes **9** [fcSiR^{1}R^2].

R^1	R^2	α [°]	β [°]	θ [°]	δ [°]	$\delta(C_{ipso})$ [ppm]	Ref.
Me	Me	20.8(5)	37.0(6)	95.7(4)	164.74(8)	33.5[c]	[21a,22]
Ph	Ph	19.1(10)	40.0(9)	99.2(5)	167.3(6)	31.0[a]	[5a,59,64]
O*t*Bu	O*t*Bu	20.7	38.4	97.5	165.1	32.4/43.8[b,d]	[54]
Cl	Cl	19.2(4)	40.7(5)	100.9(2)	166.5(2)	36.1[c]	[8,65]
Me	Cl	19.4(3)	39.3	98.0(2)	166.0	33.8[c]	[65,66]
Me	Ph	21.0(2)	37.5	96.2(2)	164.7	32.2[c]	[58,67]
Me	*N*[e]	21.0(2)	37.0	95.0(1)	164.4	38.0[c]	[68]
Fc	Fc	20–22[f]	–	94.6(3)	–	34.8[a]	[69]

[a] $CDCl_3$. [b] CD_2Cl_2. [c] C_6D_6. [d] Of the two peaks, the authors assigned the higher-field resonance to *t*Bu and the other to the *ipso* carbon atom. [e] $N = \{N(CH_2)_3SiMe_2(CH_2)_2SiMe_2\}$. [f] Disordered structure with two distinct molecules in the unit cell; Fe and Si atoms were refined properly.



Scheme 2. Selected substitution reactions of chloro-substituted sila[1]ferrocenophanes (**10**[70] (Ar = C_6H_4-2-CH_2NMe_2); **11**–**12**;[55] **13**;[71,72] **14**–**16**[73]).

Hypercoordinated sila[1]ferrocenophanes [**10** and **17**; Figure 5; Eq. (8)] and their ring-opened polymers have been reported by the Manners and Hatanaka groups.[70,74,75] The significant structural changes upon hypercoordination of the silicon center include a longer Fe–Si separation, a change to a trigonal bipyramidal geometry at the silicon atom accompanied by narrower θ angles and elongated C_{ipso}–Si bonds.[74,75] In **17**, the weaker C_{ipso}–Si bond is easily cleaved in the presence of a cationic catalyst to initiate ROP, unlike the analogous tetracoordinate sila[1]ferrocenophane, which is inert under similar conditions.[74] Higher-coordinate [1]ferrocenophanes are useful models for the nucleophilic ring-opening polymerization[77] of tin-bridged [1]ferrocenophanes. Interestingly, ROP of sila[1]ferrocenophanes leads to water-soluble organometallic polymers after introduction and quaternization of pendent amino substituents.[78]

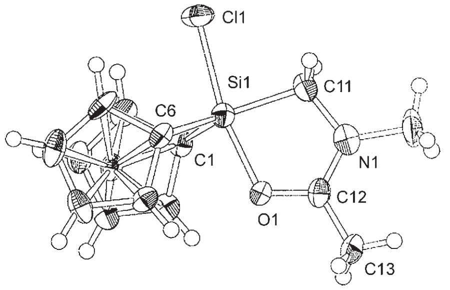
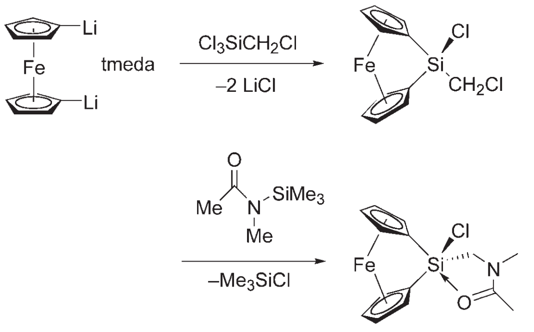


Figure 5. ORTEP depiction of a hypercoordinated sila[1]ferrocenophane **17**. Reproduced with permission from reference [74].

Acetylenic substituents have been used to bind multiple metal fragments to sila[1]ferrocenophanes.[79,80] After polymerization and subsequent introduction of the metal fragments, clusterized bimetallic polymers with high metal content are obtained, which are suited for applications as resists for electron-beam and UV photolithography.[81]

The first spirocyclic [1]ferrocenophane **18** was reported in 1975 by Osborne and Whiteley[5a] in 7% yield from the reaction of dilithioferrocene with $SiCl_4$. Preparation of **18** in higher yield (which allowed for



17

(8)

crystallographic characterization; see Figure 6) and the new spirocyclic species **19** was achieved in the 1990s.[76] These species display typical ring-tilt (α angles) and bond-angle distortions (β, θ, and δ values) for silicon-bridged [1]ferrocenophanes. The silacyclobutane moeity in **19** constrains the C-Si-C bond angle opposite θ to 81.10(8)°,[76] unlike in other sila[1]ferrocenophanes (as for the case of **9** with $R^1 = R^2 =$ Me; C_{Me}-Si-C_{Me} 114.8(6)° [22]), in which a scissoring effect is observed, resulting in wider angles opposite θ. The lack of steric protection of the bridging silicon atom arising from narrow angles is thought to contribute to the considerable moisture sensitivity of **19**.[76] In contrast, a larger angle θ in **18** (98.5(1)°) compared to **9** ($R^1 = R^2 =$ Me; 95.7(4)°) points to less distortion of the geometry about the silicon atom from an ideal tetrahedron.[76] The unusual air and moisture stability of **18** has been attributed to the combined effect of this and the steric protection of the four surrounding Cp rings.[76]

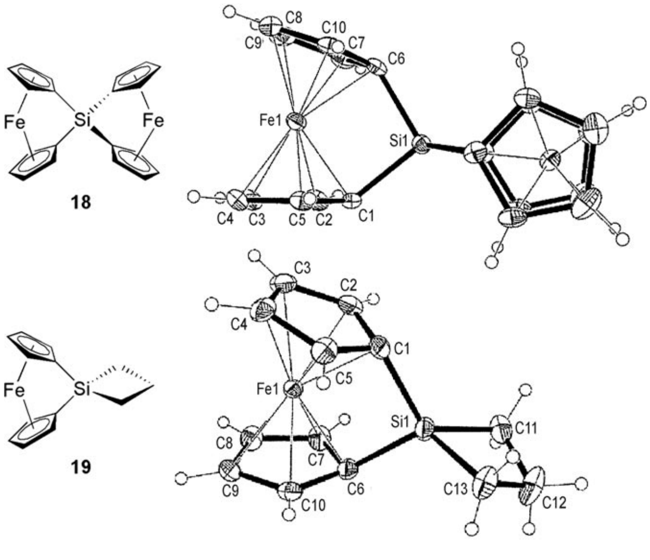
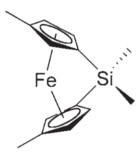


Figure 6. ORTEP depictions of spirocyclic sila[1]ferrocenophanes. Reproduced with permission from reference [76].

When polymerized, spirocyclic ferrocenophanes yield network structures as both strained rings undergo ROP. In the case of **19**, copolymerization with dimethylsila[1]ferrocenophane in certain solvents can lead to cross-linked polymer microspheres.[82,83] Redox-active gels have been prepared using cross-linked polyferrocenylsilanes[84] as well as shaped magnetic ceramics following pyrolysis.[85]

The two basic synthetic strategies to ferrocenophanes [see Eq. (2)] can be modified to accommodate substituted cyclopentadienyl rings in preparing derivatives **20**–**26**.[13,86–88]



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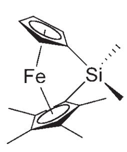

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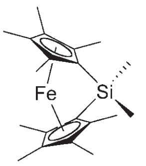

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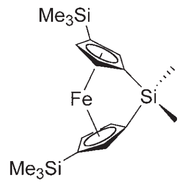

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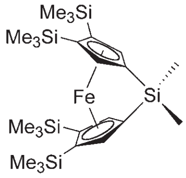

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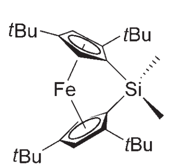

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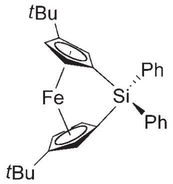


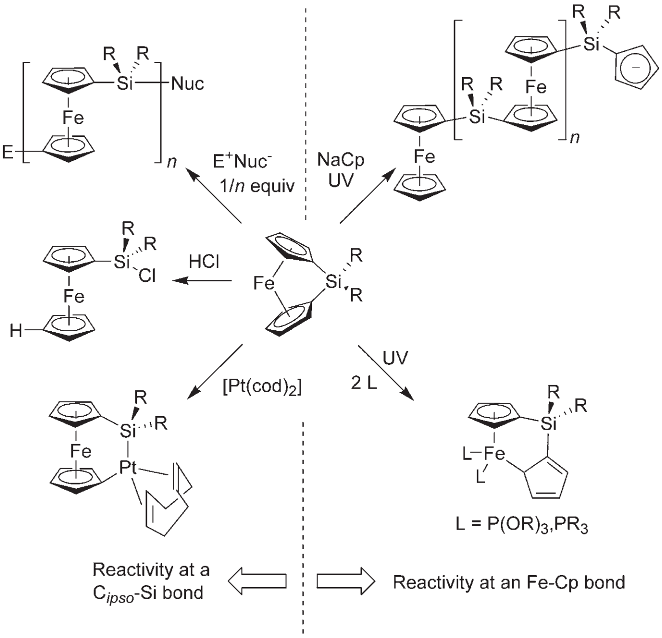
26

Trends such as decreasing ring tilt and Fe–Cp distances are associated with strengthened Fe–Cp bonding as the Cp ligands become increasingly electron-rich on substitution of Cp hydrogen atoms for electron-donating groups.[17] Other effects, such as increased stability towards air and moisture, are observed when sterically bulky substituents are introduced, such as the *t*Bu groups in **25** and **26**.[13,88] Interestingly, in **24** the trimethylsilyl substituents are forced to stack on top of each other and the steric repulsions between these large groups presumably contribute to the large tilt angle (26.3°, compare $\alpha = 20.8°$ for **9** ($R^1 = R^2 =$ Me).[88] The *t*Bu substituents in **25** and **26** do not induce significant structural changes and the ferrocenophanes adopt less sterically demanding configurations, with the ring substituents lying between each other.[13,88] A number of bis(indenyl) and mixed cyclopentadienyl–indenyl sila[*n*]ferrocenophanes have also been reported ($n = 1$: reference [89–90]; $n = 2$: reference [91]).

Characteristic reactivity of sila[1]ferrocenophanes occurs at a bond between the bridging silicon atom and an *ipso* Cp carbon atom, and includes the insertion of Pt^0 fragments and protic cleavage to produce ring-opened products (Scheme 3).[92–94] Notably, the Fe–Cp bond in sila[1]ferrocenophanes has been shown to be susceptible to a reduction of hapticity and ultimately cleavage with photoirradiation in the presence of weak bases such as $[C_5H_4R]^-$ (R = H, Me).[48,61,63]

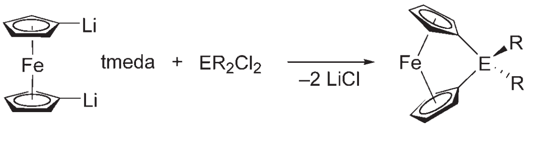
Germanium and Tin

Heavier Group 14 element bridged [1]- and [2]ferrocenophanes include germyl and stannyl derivatives, although only the [1]ferrocenophanes contain appreciable ring strain. In addition to spirocyclic Ge-bridged bis[1]ferrocenophanes[76] and an unusual germacyclopentadienyl-bridged compound,[26c] a range of germa[1]ferrocenophanes (**27**) have been prepared by the traditional salt metathesis routes



Scheme 3. Characteristic reactivity of sila[1]ferrocenophanes; cod = 1,5-cyclooctadiene.

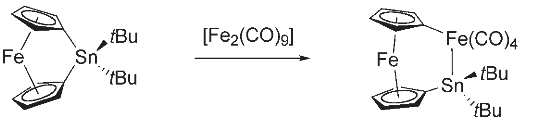
[Eq. (9)].[6,26a–b,95] These complexes exhibit ring-tilted structures with α values ($\approx 18°$) that are intermediate between those of stanna- and sila[1]ferrocenophanes. Thermal ROP, driven by ring-strain release, can yield high-molecular-weight polyferrocenylgermanes.[26] Though Ge-Pt-Ge bridged [3]ferrocenophanes can be prepared[97] and the transition-metal-catalyzed ROP of 1,1,2,2-tetramethyldigerma[2]ferrocenophane has been reported,[96] it is unlikely that the chemistry of germanium-bridged [2]ferrocenophanes is driven by the relief of ring strain.



(9)

27 E = Ge; R = Me, *n*Bu, Ph, Cl, ferrocenyl
28 E = Sn; R = *t*Bu, 2,4,6-triisopropylphenyl, 2,4,6-trimethylphenyl

Stanna[1]ferrocenophanes **28** were first isolated in 1996[98] [Eq. (9)] and several examples have been described since. In all cases to date, the stability of stanna[1]ferrocenophanes is owed to sterically imposing substituents on the tin atom (e.g. *t*Bu,[27] 2,4,6-trimethylphenyl,[27] 2,4,6-triisopropylphenyl[99]). For example, the reaction of dilithioferrocene(tmeda) and diorganodichlorostannanes R_2SnCl_2 produces only oligomeric products ($M_n < 4600$; for R = Me, Et, *n*Bu, Ph) and/or cyclic dimers (for R = Et, *n*Bu). This result is presumably due to highly reactive and exposed tin centers[100] and is compounded by the high reactivity of Sn–C_{ipso} bonds upon formation of the [1]ferrocenophane. Thermal as well as nucleophile-assisted and cationic ROP can lead to polyferrocenylstannanes, emphasizing the reactivity of the C_{ipso}–Sn bond.[27,77] Unlike the more highly tilted boron-bridged [1]ferrocenophanes ($\alpha > 30°$), which react with metal carbonyl reagents with cleavage of Fe–Cp bonds, reactions with stanna[1]ferrocenophanes lead to metal insertion into a C_{ipso}–Sn bond [for example, as illustrated in the reaction with $[Fe_2(CO)_9]$, Eq. (10)] and other ring-opened products.[101]

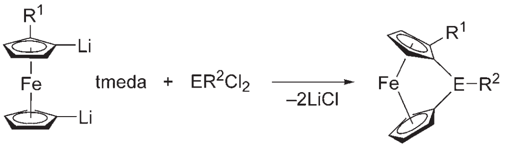


(10)

2.2.4. Group 15 Elements as Bridges

Phosphorus and Arsenic

P- and As-bridged [1]ferrocenophanes have been well-characterized, whereas N, Sb, and Bi species are currently unknown. The synthesis of phosphorus-bridged [1]ferrocenophanes **29** [Eq. (11); Men = menthyl] was first reported in 1980 by Osborne et al.[6] and by Seyferth and Withers, Jr.[7] Most known derivatives to date bridged by phosphorus and arsenic have been prepared by the versatile reaction of dilithioferrocene(tmeda) with Group 15 organodihalides.[102] In some cases, the use of enantiomerically resolved dichlororganophosphines has allowed access to chiral phosphorus-bridged [1]ferrocenophanes.[103]

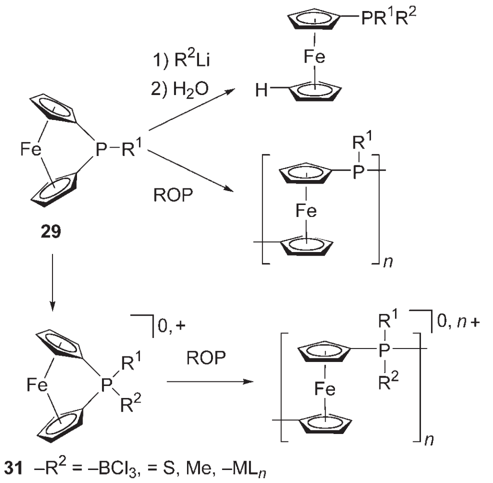


(11)

29 E = P, R^1 = H, R^2 = N*i*Pr_2, Ph, (–)-Men, *t*Bu, Cl, *p*-*t*BuC_6H_4
R^1 = CH(Me)NMe_2, R^2 = Ph
30 E = As, R^1 = H, CH(Me)NMe_2 R^2 = Ph

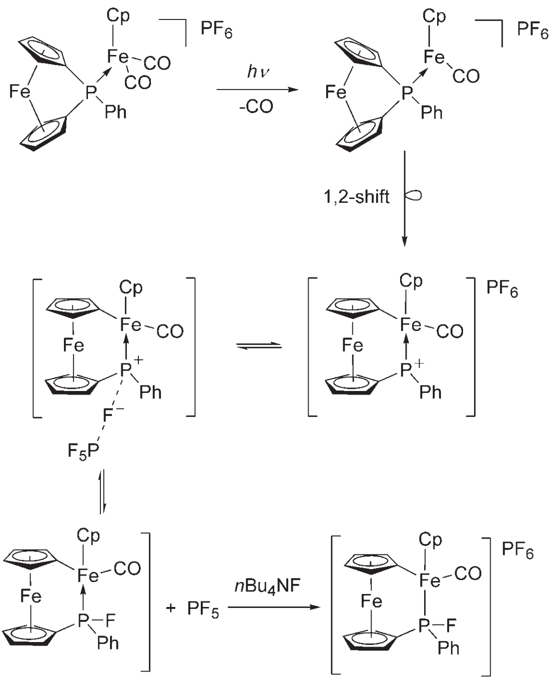
The similarities between phosphorus-bridged [1]ferrocenophanes are manifested in the narrow range of α angles (26.9–27.9°).[6,7,23,103–107] The single example of a structurally characterized arsa[1]ferrocenophane **30** (R^1 = CH(Me)NMe_2) contains more tilted cyclopentadienyl rings ($\alpha = 22.9°$) than expected given the larger covalent radius of arsenic.[23] The similarities between As- and P-bridged [1]ferrocenophanes are much more pronounced than between As- and Ge-bridged derivatives despite their nearly identical covalent radii (P 1.10 Å; As 1.21 Å; Ge 1.22 Å).[108] This suggests that strain is absorbed by different parts of the molecular structure. For example, the large β angles (35–38°) present in the germanium-bridged species **27** might indicate that significant ring strain arises from the deformed bond angles about the C_{ipso} atoms,[6] whereas As- and P-bridged [1]ferrocenophanes have smaller, and nearly identical β angles (**29**: 31–33°, **30**: 32.8°) and reduced θ values of about 88–90° compared to Ge-bridged analogues (92–94°).

The development of phosphorus-bridged [1]ferrocenophanes has attracted much attention, spurred by the potential use of ring-opened polymers as ligands or supports for transition-metal catalysts. Synthetic procedures have been used to access asymmetric monomers and oligomeric ferrocenylphosphines[109] and have been optimized at the macromolecular level to yield high-molecular-weight polyferrocenylphosphines by living anionic ROP (Scheme 4).[110,111]



Scheme 4. Representative reactions of phosphorus-bridged [1]ferrocenophanes; R^1: see Equation (11).

High-molecular-weight material can also be obtained by thermal ROP and, as shown by Miyoshi and co-workers, by photoirradiation in THF.[105,112] Strained phospha[1]ferrocenophanes **29** can also coordinate through the lone pair on phosphorus to metal fragments (Scheme 4),[113–117] which alternatively may insert into a P–C bond (Scheme 5).[118,119]



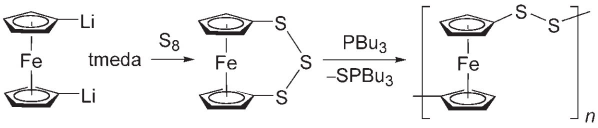
Scheme 5. Insertion of a metal fragment into a phosphorus–carbon bond in a phosphorus-bridged [1]ferrocenophane.

Stable phosphonium-bridged [1]ferrocenophanes, sulfurized P^V derivatives, and borane adducts of (phenyl)phospha[1]-ferrocenophanes (**31**) have been prepared and in some cases and subjected successfully to thermal transition-metal-catalyzed ROP.[120,121] Notably, the enthalpies of thermal ROP recorded for (phenyl)phospha[1]ferrocenophane (**29**, R = Ph, -68 ± 5 kJ mol^{-1})[120] and (methylphenyl)phosphonium[1]ferrocenophane (**31**, R^1 = Ph, R^2 = Me, -61 ± 5 kJ mol^{-1}) suggest slightly smaller strain energies than the typical values for dialkylsila[1]ferrocenophanes despite larger average tilt angles, though this is probably a consequence of the presence of the bulky phenyl substituent.

2.2.5. *Group 16 Elements as Bridges*

Sulfur and Selenium

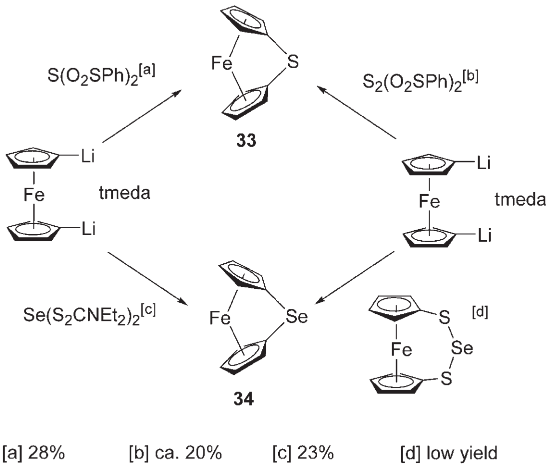
The first example of a chalcogen-bridged ansa ferrocene, the trithia-bridged ferrocenophane **32**, was synthesized by treating dilithioferrocene(tmeda) with elemental sulfur [Eq. (12)].[122] This methodology produced triselena-, tritellura-, and mixed chalcogena-bridged [3]ferrocenophanes, though these species do not appear to be substantially strained, with tilt angles of less than 4.5°.



32

(12)

Nevertheless, Rauchfuss and co-workers have demonstrated that ROP can be induced by chalcogen abstraction with tributylphosphine [Eq. (12)].[123] Potentially strained dithio-bridged [2]ferrocenophanes have been proposed as possible intermediates, though none have so far been identified or isolated. Interestingly, attempts to prepare two-atom-bridged ferrocenophanes produced the [1]ferrocenophane **33** in low yield [20%; Eq. (13)].[124] Sulfur- and selenium-bridged [1]ferrocenophanes **33** and **34** can be made by typical salt metathesis methods by using dilithiofer-

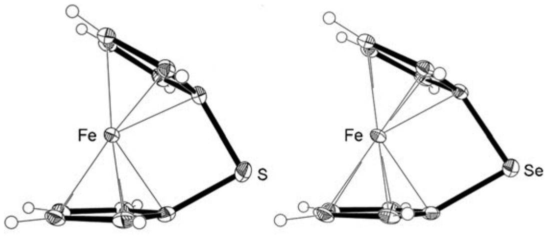


(13)

[a] 28% [b] ca. 20% [c] 23% [d] low yield

rocene, given careful workup at low temperatures.[24,124] These tilted, strained species should exhibit interesting reactivity but, to date, this area has not been explored in detail.

The solid-state structure of trithia[3_2]ferrocenophane reveals no appreciable strain.[125] In contrast, the sulfur-bridged [1]ferrocenophane **33** exhibits remarkable tilting of the cyclopentadienyl ligands ($\alpha = 31°$, Figure 7) as a consequence of the small atom in the bridge.

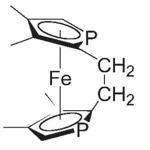


33 **34**

Figure 7. ORTEP depictions of chalcogena[1]ferrocenophanes **33** (left) and **34** (right). Reproduced with permission from reference [24].

2.2.6. *Bridged Diheteroleferrocenes*

In addition to bridged dicyclopentadienyl complexes of iron, two examples of diheterole-sandwich compounds bridged by two or fewer atoms have been reported. An ethane-bridged diphosphole ligand was used to form the ethane-bridged 3,3′,4,4′-tetramethyl-1,1′-diphospha[2]ferrocenophane **35** as a single isomer. This structure is expectedly tilted and its UV/Vis spectrum is consistent with a bathochromic shift typically introduced by strain ($\lambda_{max} = 511$ nm; compare: 438 nm for 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene).[126]



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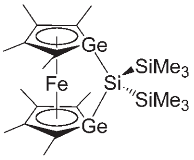
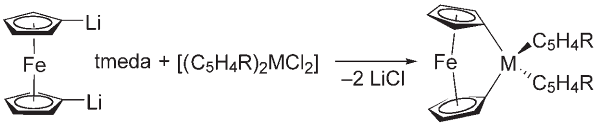


36

A silicon-bridged digerma[1]ferrocenophane (**36**) was serendipitously prepared from the reaction of bis{1,1′-di-[tris(trimethylsilyl)silyl]germa}ferrocene with methyllithium.[127] Despite superficial similarities to other strained sila[1]metallocenophanes, this species does not respond to thermal or anionic ROP conditions. This behavior can be explained with reference to the solid-state structure, which reveals that the Ge atoms lie 0.42 Å above the C_4 least-squares planes with a sum of bond angles about Ge of 296.1°.[127] This puckering presumably relieves any ring strain.

2.2.7. *Transition-Metal- and Actinide-Bridged [1]Ferrocenophanes*

A number of [1]ferrocenophanes have been prepared in which the bridging element is an early transition metal [**37**, Eq. (14)].[28] Iron-[128] and uranium-bridged[29] ferrocenophanes have also been isolated, though as moieties within larger, albeit homoleptic, clusters. Though all examples are devoid of appreciable ring strain, the pentanuclear Fe^{II} cluster $[(C_5H_4)_6Fe_5)]^{2-}$ is air- and moisture-sensitive and oligo(ferrocenylene) formation is proposed as a decomposition pathway on the basis of MALDI-TOF MS experiments.[128]

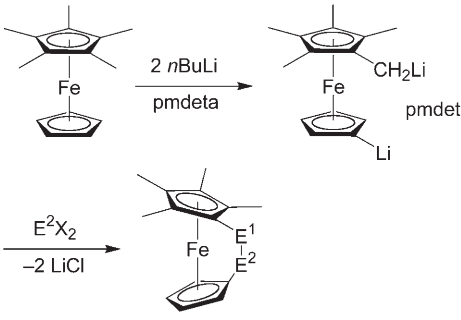


(14)

37 M = Ti, Zr, Hf
R = H, *t*Bu

2.2.8. *Mixed-Heteroatom-Bridged [2]Ferrocenophanes*

A number of [2]ferrocenophanes have been prepared containing unsymmetric diatomic bridges by applying developed dilithiation techniques to mixed sandwich ferrocenes [Eq. (15)]. These species provide a range of tilt angles (Table 4) and allow for systematic investigation of the effects of the degree of ring tilting and strain on the behavior of [2]metallocenophanes. For example, while [2]ferrocenophanes **38** ($E^2 = SiR_2$, PR, or S) with tilt angles of 14.8° or greater polymerize thermally with increasingly negative values of ΔH_{ROP} (ca. −10 to −20 kJ mol^{-1} and up), those with smaller values of α are resistant to thermal ROP.[129]



(15)

38 (E^1=CH_2)

pmdeta = *N,N,N′,N′,N″*-pentamethyldiethylenetriamine

Although the (dichloro)silaethane derivative **38** ($E^2 = SiCl_2$) was not characterized by X-ray diffraction, data from mass spectroscopic analysis, UV/Vis spectroscopy, NMR characterization, and analysis of the products from the reaction with ethanol in hexane suggest the formation of a reactive, but only slightly strained [2]ferrocenophane.[131]

Table 4: Structural data for mixed bridged [2]ferrocenophanes **38**.

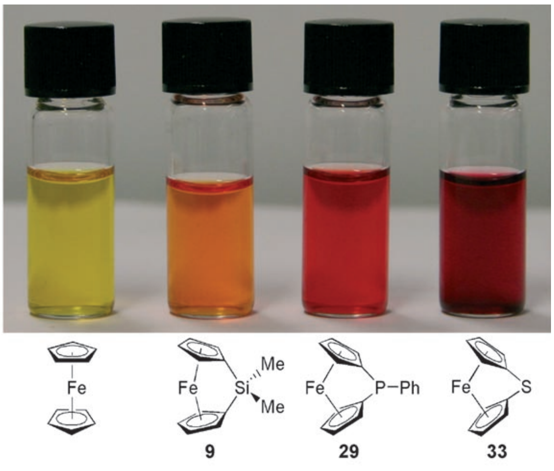
E^1–E^2	α [°]	β [°]	δ [°]	τ [°]	E^1–E^2 [Å]	λ [nm] (ε [$M^{-1}cm^{-1}$])[a]	ref
$NHSO_2$[d]	23	14 (S); 8 (N)	157	21	1.671(7)	–	[130]
CH_2SiCl_2	–	–	–	–	–	430 (120)[b]	[131]
CH_2SiMe_2	11.8	17.9 (Si); 7.3 (C)	170.9	0.5	1.914(3)	458 (120)	[129, 132]
CH_2GeMe_2	11.0	17.4 (Ge); 6.1 (C)	171.4	4.4	1.983(3)	461 (203)	[133]
CH_2SnMe_2	7.5	19.1 (Sn); 3.3 (C)	173.6	4.9	2.184(3)	453 (221)	[133]
CH_2PPh	14.8	18.0, 14.7 (P);	169.7	21.7	1.904(4); 1.892(5)	472 (280)	[129]
	15.0	9.8, 11.1 (C)	169.6	30.0			
CH_2PMePh^+	11.4	18.6 (P); 10.5 (C)	172.2	8.9	1.830(4)	465 (120)[c]	[129]
CH_2S	18.5	10.6 (S); 9.3 (C)	167.2	17.9	1.844(2)	475 (240)	[129, 132]
CH_2ZrCp_2	−5.5	31.6 (Zr); 1.9 (C)	175.2	1.5	2.390	366 (299)[c]	[134]

[a] In hexanes unless otherwise indicated. [b] In isooctane. [c] In THF. [d] Both Cp ligands are C_5H_4.

2.2.9. *Electronic Structure and Strain Energies of Ring-Tilted [n]Ferrocenophanes*

UV/Vis spectroscopy, photoelectron spectroscopy (PES), extended Hückel MO (EHMO) calculations, and density functional theory (DFT) treatments have been used separately and in concert to probe the electronic structure of highly strained [1]ferrocenophanes. These investigations elucidated trends in the perturbation of molecular-orbital energies upon tilting cyclopentadienyl rings in ferrocenophanes relative to their parallel arrangement in ferrocene.

A steady gradient in the color from amber (ferrocene) to increasingly intense red (for Si- and P-bridged [1]ferrocenophanes) to deep purple for a sulfur-bridged [1]ferrocenophane arises from a bathochromic shift of the lowest energy absorbance of [1]ferrocenophanes when bridged by increasingly smaller elements from the third period (Figure 8). This red shift is accompanied by an increase in the intensity of the band and is understood in terms of a decreasing HOMO–LUMO gap with progressively tilted cyclopentadienyl ligands.[24] Figure 9 depicts an EHMO comparison of the frontier orbitals of ferrocene with two [1]ferrocenophanes with moderately tilted ([fcSiH_2], $\alpha = 19.1°$) and highly tilted ([fcS], $\alpha = 31.05°$) cyclopentadienyl ligands and the hypothetical highly tilted, but unbridged, ferrocene ($\alpha = 31.05°$). The two weakest absorptions (440 and 325 nm in ferrocene) have been attributed to transitions between filled e′ and a_1' molecular orbitals and the e″ LUMO. These transitions are predominantly d–d in nature and Laporte-forbidden, whereas the highest-energy UV/Vis absorption in ferrocene (270 nm) has been previously assigned to a ligand-to-metal charge transfer (LMCT). Tilting affects the lowest-energy transition in two ways.[24] As the tilt angle increases, the a_1' HOMO is raised in energy while the LUMO energy is lowered, which leads to the red shift to lower energy (see Figure 8). Additionally, as tilting reduces the symmetry of the complex (ferrocene is of D_{5d} (staggered) or D_{5h} (eclipsed) symmetry while an ansa metallocene can at most have C_{2v} symmetry) and ligand contributions to the LUMO appear to increase,[15b] the Laporte selection rule is relaxed resulting in a more intense absorption.



λ_{max} [nm]	440	478	498	504
α [°]	ca. 0	20.8	26.7	31.1

Figure 8. Colors of solutions of increasingly tilted [1]ferrocenophanes (in hexanes).

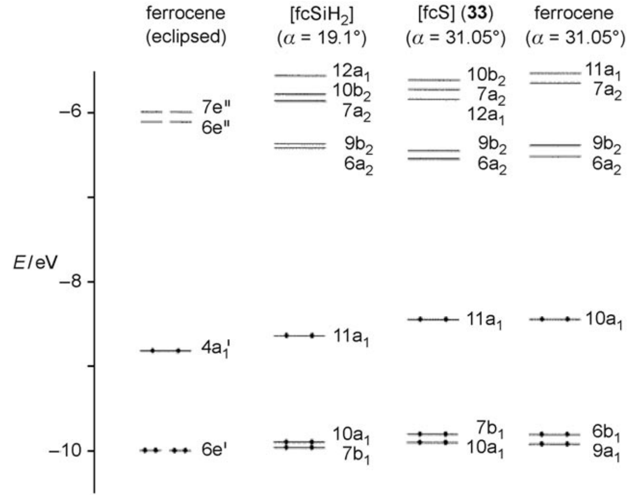


Figure 9. EHMO comparison of frontier orbitals of (eclipsed) ferrocene, [fcSiH_2] ($\alpha = 19.1°$), **33** ($\alpha = 31.05°$), and ferrocene ($\alpha = 31.05°$) with energies given in eV (fc = Fe(η^5-C_5H_4)$_2$). Reproduced with permission from reference [24].

Green has emphasized the importance of the predominantly d–d character of the HOMO–LUMO transition in comparing the energy penalties associated with bending sandwich compounds of metals from across the d block (see Section 2.1).[12] As three d orbitals are fully occupied in ferrocene (d^6), calculations show that the energy of the molecule is raised substantially in energy on bending. This increase in energy has been verified experimentally by measuring the enthalpy associated with ring-opening selected [1]ferrocenophanes by using differential scanning calorimetry

(DSC). Values of -130 ± 20 kJ mol^{-1} (theory: ca. -100 kJ mol^{-1})[17] are observed for the highly tilted sulfur-bridged [1]ferrocenophane **33** ($\alpha = 31.05°$), whereas values of -70 to -80 kJ mol^{-1} are typical for moderately tilted sila[1]ferrocenophanes (**9**, $\alpha = 19$–$22°$). Less tilted [2]ferrocenophanes (**38**, $\alpha = 14.8$–$18.5°$) polymerize thermally with small negative values of ΔH_{ROP} (-10 to -20 kJ mol^{-1}).[129] DFT calculations closely predict the geometries found from single-crystal X-ray diffraction experiments.[17]

2.3. Strained Metallocenophanes of Metals Other than Iron

Although less explored, strained metallocenophanes without a ferrocene moiety have been reported and are of growing interest. According to theoretical studies on metallocenophanes (see Section 2.1) species with less than two d electrons are expected to be essentially unstrained. Classic examples are the d^0 ansa metallocenes utilized as olefin polymerization catalysts such as the Group 4 species **39**[135] and Group 5 species **40**[136] (Figure 10).

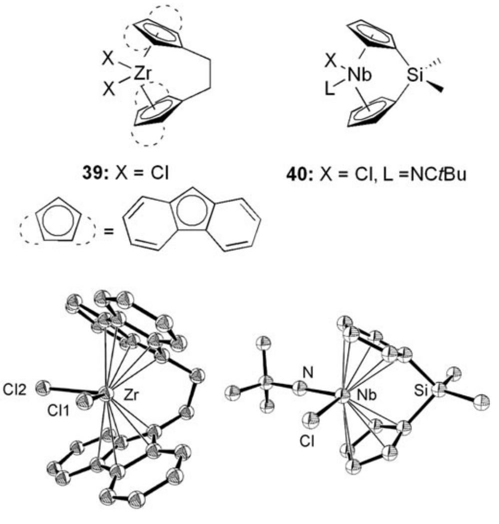
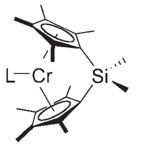


Figure 10. ORTEP depictions of ethane-bridged [2]zirconocenophane **39** and sila[1]niobocenophane **40**. Reproduced with permission from references [135],[136].

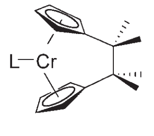
Although such species display fascinating reactivity, which can differ significantly from analogues without an ansa bridge,[137–143] there is no evidence to date to suggest such species possess significant strain energy, and attempted ROP reactions have been unsuccessful.[144] These and related compounds will not be discussed in this Review.

2.3.1. Metallocenophanes of Chromium, Molybdenum, Tungsten, and Rhenium

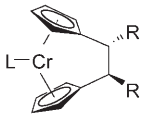
Reactions of lithium or magnesium salts of bridged Cp$_2$ anionic ligands with CrCl$_2$ in the absence of additional ligands give insoluble, presumably oligomeric materials.[145,146] Performing the reactions in the presence of an additional ligand such as CO has given a range of chromium(II) d^4 18-electron species (**42**–**46**, **48**, and **49**), mostly courtesy of the research groups of Shapiro and Brintzinger. The CO molecule can be substituted by an isocyanide unit, generally considered a better σ-donor and weaker π-acceptor ligand. Species without additional ligands such as **41** and **47** have also been reported but are very rare.[146,147] For unsubstituted **41** the α angle is about 5° less than that found in the substituted analogue **42**, whereas a similar comparison of **47**–**49** reveals nearly invariant α angles due to intramolecular substitution. However, no examples of ring-opening reactions have been reported for these d^4 species, and the presence of strain is an intriguing and still open question.



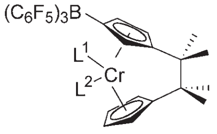
41 L= no ligand
42 L= CO



43 L = CO
44 L = CN*t*Bu

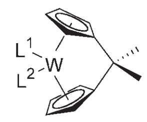


45 L = CN*t*Bu, R = Ph
46 L = CO, R = Ph

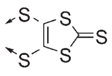


47 L^1= L^2= no ligand
48 L^1= no ligand, L^2= CN-*o*-Xy
49 L^1= NC, L^2= CN-*o*-Xy

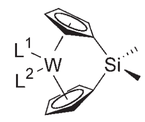
A wide range of 18-electron molybdenum(IV) and tungsten(IV) d^2 metallocenophanes is also known. Representative examples are species **50**–**62**. Typical tilt angles (α) lie in the range 55–65°, accompanied by β angles of 15–25°. Generally, the introduction of an ansa bridge results in higher thermal stability and increased stability towards ligand dissociation, reductive elimination, and bond insertion. Again, evidence for ring strain in these species is not generally apparent. However, interestingly, the W species **56** is reported to undergo polymerization to uncharacterized insoluble



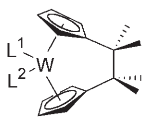
50 L^1,L^2=



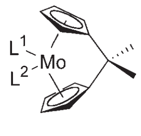
51 L^1=Cl, L^2= CN-*o*-Xy, [PF$_6$]$^-$
52 L^1=L^2= Me
53 L^1=L^2= Cl
54 L^1=L^2= SPh
55 L^1=L^2= H



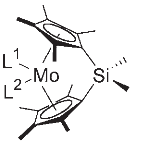
56 L^1=L^2= Cl



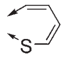
57 L^1=L^2= Me



58 L^1=L^2= Cl
59 L^1=L^2= Et



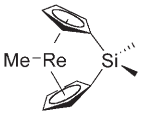
60 L^1,L^2=



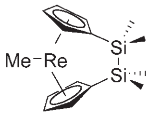
61 L^1=L^2= H
62 L^1=L^2= Cl
63 L^1= no ligand, L^2= CO

materials with identical elemental composition on standing at room temperature.[148]

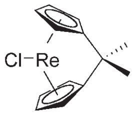
In 1999 Heinekey and Radzewich reported the synthesis and the structure of the rhenium(III) d^4 ansa complexes $[Re\{(C_5H_4)_2SiMe_2\}Me]$ (**64**, $\alpha = 40.0°$, $\beta = 26.8°$) and $[Re\{(C_5H_4)_2(SiMe_2)_2\}Me]$ (**65**).[149] A year later, Green and coworkers reported the synthesis and structure of $[Re\{(C_5H_4)_2CMe_2\}Cl]$[150a] (**66**, $\alpha = 53.1°$, $\beta = 21.9°$). The tilt angles are slightly smaller (**64**) and significantly greater (**66**) than in the case of the analogous complex without the ansa bridge $[Cp_2ReCl]$ ($\alpha = 41.1°$, $\beta = 0°$).[150b] Such species would also be of interest with respect to ring-opening reactions.



64



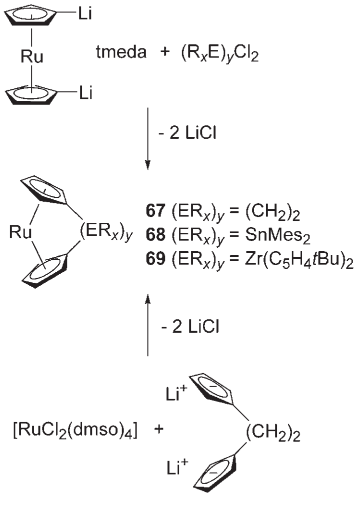
65



66

2.3.2. Metallocenophanes of Ruthenium

Incorporating the larger Group 8 ruthenium atom into an [*n*]metallocenophane framework produces more tilted structures relative to ferrocenophane analogues. This effect is consistent with the greater separation between the cyclopentadienyl rings in ruthenocene (3.68 Å) compared to ferrocene (3.32 Å). The preparation of these compounds mirrors iron analogues. The ethane-bridged [2]ruthenocenophane **67** was synthesized by using the appropriate deprotonated dicyclopentadienyl salt and a ruthenium dihalide precursor. In this case, a ligand-stabilized ruthenium(II) source, $[RuCl_2(dmso)_4]$, was required [Eq. (16)].



67 $(ER_x)_y = (CH_2)_2$
68 $(ER_x)_y = SnMes_2$
69 $(ER_x)_y = Zr(C_5H_4tBu)_2$

(16)

The first well-characterized [1]ruthenocenophanes containing Sn (**68**; Mes = 2,4,6-trimethylphenyl) and Zr (**69**) in the bridge were reported in 2004 and were prepared by using the reaction of dilithioruthenocene(tmeda) and Mes_2SnCl_2 and $[(C_5H_4tBu)_2ZrCl_2]$, respectively.[155] As expected, the deformation parameters for [*n*]ruthenocenophanes are larger than those for analogous [*n*]ferrocenophanes (Table 5). For example, the stanna[1]ruthenocenophane **68** has a tilt angle (20.6°) about 5.5° higher than the Fe analogue. A substantial upfield shift of the ^{13}C NMR resonance attributed to the *ipso* carbon atoms was also observed. The downfield shift of the signal assigned to the *ipso* carbon atom on the ruthenocene fragment of the zirconium-bridged [1]ruthenocenophane **69** is unusual for tilted ansa metallocenes, but consistent with the analogous [1]ferrocenophane (C_{ipso}: $\delta = 159.0$ ppm).[28] Thermal ROP has been reported for ethane-bridged [2]ruthenocenophanes[153] and stanna[1]ruthenocenophanes[155] to yield high-molecular-weight polyruthenocenes.

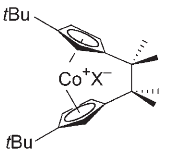
Table 5: Structural parameters for [*n*]ruthenocenophanes $[rc(ER_x)_y]$ ($rc = Ru(\eta^5\text{-}C_5H_4)_2$).

$(ER_x)_y$	α [°]	β [°]	δ [°]	λ_{max} [nm]	$\delta(C_{ipso})$ [ppm]	Ref.
$(CH_2)_3$	14.8	4.5	168.9	325[a]	–	[151,152]
$(CH_2)_2$	29.6	13.4	159.3	–	93.6[b]	[153]
$(SiMe_2)_2$	7.8	12.4	174.2	318[c]	71.0[b]	[154]
1,1′,2,2′-$[(SiMe_2)_2]_2$	12.9	13.3	170.8	345[c]	71.0[b]	[154]
$Zr(C_5H_4tBu)_2$	10.4	41	175	310[d]	162.5[e]	[155]
$SnMes_2$	20.6	35.4	164.6	363[d]	31.8[e]	[155]

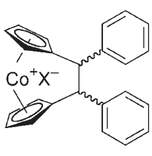
[a] In absolute EtOH. [b] In $CDCl_3$. [c] In THF. [d] In CH_2Cl_2. [e] In C_6D_6.

2.3.3. Metallocenophanes of Cobalt

Only two ansa cobaltocenophanes have been reported in the literature: a cationic cobalt(III) d^6 [2]cobaltocenophane with a C_2Me_4 bridge (**70**)[156] and a species with a $C_2H_2Ph_2$ bridge (**71**).[157] Species **70** was prepared from $[(MgCl)_2][(C_5H_4)_2C_2Me_4]\cdot x\,THF$ by the reductive dimerization of a *t*Bu-substituted 6,6-dimethylfulvene using Mg, whereas **71** was prepared from $[Ca(C_5H_4)_2C_2H_2Ph_2]\cdot x\,THF$ by the Ca-mediated reductive dimerization of 6-phenylfulvene. The unsymmetrical steric demand in the fulvene used in this synthesis determines the *cis* and *trans* distribution (30:70) of the product.[158]



70 X = PF_6

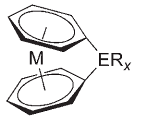


71 X = PF_6

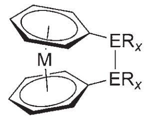
Both of the crystallographically characterized species **70** and *trans*-**71** show evidence of appreciable strain ($\alpha = 24.8°$ and 22.9°, $\beta = 9.2°$ and 12.2° (av.)). Ring-opening reactions of these and related cationic [2]cobaltocenophanes would be expected as these d^6 species are isoelectronic with ferrocenophanes. [1]Cobaltocenophanes are currently unknown. Future studies in the virtually undeveloped area of strained cobaltocenophanes (and extensions to other Group 9 elements) are of considerable interest, especially as studies by O'Hare and co-workers of model linear dimers with $SiMe_2$ bridges suggest that the interaction between Co centers would be greater than between iron centers in polymetallocenes.[159]

3. Organometallic Rings with Two Arene Ligands: Strained ansa Bis(arene) Complexes or Metalloarenophanes

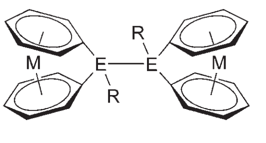
Since the first example (**94**) reported by Elschenbroich et al. in 1988,[160] metal-atom ligand-vapor co-condensation techniques or the use of dilithiated bis(arene) metal complexes has allowed the preparation of a broad range of ansa bis(arene)complexes or metalloarenophanes (**72**–**103**),[25b,161–167] including spirocyclic species. These complexes are based on the metals Cr and V with bridges such as Si, Ge, and most recently B and Zr. Various parameters are considered to be indicators for ring strain in these d^5 V species and d^6 Cr analogues, of which the latter are formally isoelectronic with ferrocenophanes. In addition to the structural parameters apparent from X-ray crystal structure analyses (see Table 6), in many cases upfield shifts of ^1H NMR signals for the *ortho*-, *meta*-, and *para*-hydrogen atoms in the phenyl rings, upfield-shifted ^{13}C NMR signals for the C_{ipso} atoms, and bathochromic shifts in the UV/Vis spectra relative to unstrained analogues have been identified.



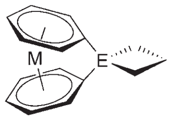
72 M = V, E = Si, R_x = Me,Me
73 M = V, E = Si, R_x = Ph, Ph
74 M = V, E = Si, R_x = Ph, Cl
75 M = V, E = Si, R_x = 4-nPrC_6H_4, Cl
76 M = V, E = Al, R_x = (Me_2Ntsi)
77 M = V, E = Ga, R_x = (Me_2Ntsi)
78 M = V, E = Ge, R_x = Me, Me
79 M = V, E = Ge, R_x = Ph, Ph
80 M = V, E = Zr, R_x = tBuC_5H_3, tBuC_5H_3
81 M = Cr, E = B, R_x = N$i$$Pr_2$
82 M = Cr, E = B, R_x = N$(SiMe_3)_2$
83 M = Cr, E= B, R_x = N$(SiMe_3)$$t$Bu
84 M = Cr, E = Al, R_x = (Me_2Ntsi)
85 M = Cr, E = Ga, R_x = (Me_2Ntsi)
86 M = Cr, E = Si, R_x = Me, Me
87 M = Cr, E = Si, R_x = Ph, Ph
88 M = Cr, E = Si, R_x = Ph, R = Cl
89 M = Cr, E = Ge, R_x = Me, Me
90 M = Cr, E = Ge, R_x = Ph, Ph
91 M = Cr, E = Zr, R_x = C_5H_5, C_5H_5
92 M = Cr, E = Zr, R_x = tBuC_5H_4, tBuC_5H_4



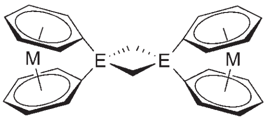
93 M = Cr, E = B, R = NMe_2
94 M = Cr, E = Si, R = Me
95 M = Cr, E = Ge, R = Me
96 M = Cr, E = Ge, R = Me



97 M = V, E = Si, R = Ph
98 M = V, E = Si, R = 4-nPrC_6H_4
99 M = Cr, E = Si, R = Ph



100 M = V, E = Si
101 M = Cr, E = Si



102 M = V, E = Si
103 M = Cr, E = Si

Table 6: Structural data for mono- and binuclear [*n*]metalloarenophanes.

	α [°]	β [°]	δ [°]	θ [°]	δ(C_{ipso}) [ppm][a]	M–E [Å]	Ref.
76	14.7	39.0/38.9	168.5	93.8	–	2.981	[25b]
77	15.7	38.0/38.3	167.3	92.4	–	3.021	[25b]
80	8.0	36.2/36.2	176.4	47.9	–	3.254	[166]
83	26.6	34.1/35.2	159.5	98.1	–[b]	2.742	[162a]
84	11.8	39.3/39.6	170.6	91.9	62.1	2.974	[25b]
85	13.2	37.9/38.0	169.4	89.8	56.6	3.026	[25b]
86	16.7	37.2/37.4	167.6	93.0	39.5[c]	2.906	[163]
87	14.5	39.8/40.2	169.4	96.0	–[d]	2.843	[161]
90	14.4	38.0/38.5	169.1	91.8	36.4	2.959	[164]
93	10.1	20.4/20.8	172.1	–	–[b]	–	[162a]
100	19.9	36.8/36.2	164.4	94.6	–	2.901	[165]

[a] All recorded in C_6D_6 unless otherwise stated. [b] No signal for the C_{ipso} atom with significant up- or downfield shift due to hybridization distortion has been reported. [c] Recorded in $CDCl_3$. [d] No NMR data reported.

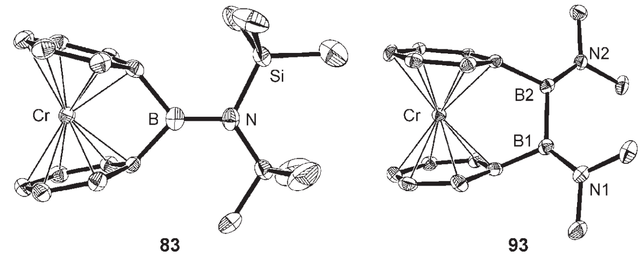
Radicals based on spirocyclic species have attracted attention with respect to the metal–metal interactions present. For example, EPR measurements on the paramagnetic vanadium species **73** showed that tilting is accompanied by an increase in metal-to-ligand spin delocalization.[161]

Ring-opening reactions have been characterized for several examples. The black, crystalline sila[1]chromarenophane **87** ($\alpha = 14.5°$, $\beta = 40°$ (av.)) undergoes proton-induced cleavage of the Si–C_{ipso} bond.[161] The polymerization behavior of the $SiMe_2$-bridged analogue has also been explored. Attempted thermal ROP of **86** yielded films of Cr metal as the Cr–arene bonds were cleaved. This behavior was attributed to the lower bond strength compared to Fe–Cp bonds, which remain intact during the thermal ROP of sila[1]ferrocenophanes under similar conditions. However, thermal and anionic copolymerization of **86** with the polymerizable [1]ferrocenophane $[Fe(C_5H_4)_2SiMe_2]$ successfully yielded bimetallic air-sensitive oligomeric/polymeric materials.[163] Metal-catalyzed ROP of **86** and related species, which proceeds at room temperature, has led to the first bis(arene) chromium homopolymers, however these materials were both rather air- and moisture-sensitive and of limited solubility.[167]

Braunschweig and co-workers have reported the introduction of boron bridges to form the first bora[1]chromarenophanes **81**–**83** and dibora[2]chromarenophane **93** from the reaction of 1,1′-dilithiobis(benzene)chromium and the corresponding aminodihaloboranes [Eq. (17) and Figure 11].[162a] These strained species showed extreme air and moisture sensitivity and readily decomposed in polar solvents. Prelimi-

(17)

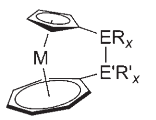
81 R = R′= iPr
82 R = R′= $SiMe_3$
83 R = $SiMe_3$, R′= tBu



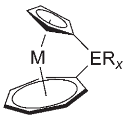
83 **93**

Figure 11. ORTEP depictions of bora[1]chromarenophane **83** and dibora[2]chromarenophane **93**. Reproduced with permission from reference [162a].

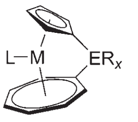
nary experiments using complex **82** indicated a propensity for anionic ROP although initial attempts to induce thermal ROP were unsuccessful.



104 M = V, E = E' = B, R = R' = NMe$_2$
105 M = V, E = E' = Si, R = R' = Me
106 M = V, E = Si, E' = Pt, R = Me, R' = PEt$_3$
107 M = Ti, E = Si, E' = Pt, R = Me, R' = PEt$_3$
108 M = Ti, E = Ge, E' = Pt, R = Me, R' = PEt$_3$
109 M = Cr, E = E' = B, R = R' = NMe$_2$
110 M = Cr, E = E' = Si, R = R' = Me
111 M = Cr, E = Si, E´ = Pt, R = Me, R´= PEt$_3$



112 M = V, E = B, R = N(SiMe$_3$)$_2$
113 M = V, E = Si, R = Me, Me
114 M = V, E = Si, R = Ph, Ph
115 M = Ti, E = Si, R = Me, Me
116 M = Ti, E = Ge, R = Me, Me
117 M = Cr, E = Si, R = Me, Me
118 M = Cr, E = Si, R = *i*Pr, *i*Pr
119 M = Cr, E = Si, R = Me, *i*Pr
120 M = Cr, E = Si, R = C$_3$H$_6$



121 M = Ti, E = Si, R = Me, L = CN-*o*-Xy
122 M = Ti, E = Si, R = Me, L = CN-*t*Bu
123 M = Ti, E = Si, R = Me, L = CO

4. Strained Organometallic Rings with Different π-Hydrocarbon Ligands

4.1. Ansa-Bridged Complexes of the Type [M^0(η^5-C$_5$H$_4$)ER$_x$(η^7-C$_7$H$_6$)]

In recent years several examples of fascinating bridged (η^5-cyclopentadienyl)M(η^7-tropylium) complexes have been reported which contain formally M^0 transition-metal centers from Group 4, Group 5, and Group 6. These [(η^5-C$_5$H$_5$)M(η^7-C$_7$H$_7$)] complexes are commonly referred to as troticenes (Ti), trovacenes (V), and trochrocenes (Cr). The corresponding ansa complexes are referred to as [*n*]troti-, [*n*]trova-, or [*n*]trochrocenophanes, which have d^4, d^5, and d^6 configurations, respectively.

In 2004 Elschenbroich and co-workers reported the synthesis and characterization of paramagnetic sila[1]trovacenophanes **113** and **114** and disila[2]trovacenophanes **105** by the dilithiation of the parent unbridged trovacene and the subsequent introduction of the corresponding bridging moiety. X-ray crystal structures showing ring-tilted conformations were reported for **105** ($\alpha = 3.8°$) and **114** ($\alpha = 17.3°$; see Figure 13). EPR spectra were interpreted to reflect this in the change of the $\langle g \rangle$ tensors from tetragonal ($g_x = g_y \neq g_z$) for **105** to rhombic ($g_x \neq g_y \neq g_z$) for **113** and **114**. Whereas cyclic voltammetry experiments displayed reversibility for oxidation and reduction in relatively undistorted **105**, irreversible behavior was observed in the case of **114**, which was attributed to a cleavage of the ansa bridge. However, at elevated temperatures (280 °C) no indication of thermal ROP was detected for **114**.[169] Bora[1]trovacenophane **112** and dibora[2]trovacenophane **104** were reported in 2006.[162b] Pt-mediated activation of the B–B moiety in **104** produced the corresponding diboraplatina[3]trovacene, and EPR measurements confirmed the previously observed trend,[169,173] that an increasing tilt angle α is accompanied by an increase of g_{iso} and a decrease of $a(^{51}\text{V})$.[162b]

After the synthesis of tmeda-stabilized dilithiated troticene in 1991[171] the successful introduction of a single monosila bridge was briefly mentioned in a review of cycloheptatrienyl (Cht) complexes of early transition metals.[172] Tamm and co-workers reported the synthesis and full characterization of sila[1]troticenophane **115**[168a] in 2004 and germa[1]troticenophane **116**[168b] in 2007. For both compounds experimental and theoretical investigations revealed strong structural distortion in particular at the {Si-C$_7$H$_6$} site, and unusually high values for β angles (see Table 7) were observed, suggesting highly strained molecules (Figure 12 and Figure 13). Indeed, **115** exothermically polymerizes at 140–160 °C and **116** at 130 °C. By DSC measurements the strain energies were estimated to be approximately 45 kJ mol^{-1}, which is considerably less than found for comparable [1]ferrocenophanes.[9a] Comparison of the energy content of troticenes to ferrocene as a function of

Table 7: Characterization of bridged [(η^5-C$_5$H$_4$)M(η^7-C$_7$H$_6$)] complexes presented in the literature.

	α [°]	β [°][c]	δ [°]	θ [°]	δ(C$_{ipso}$) [ppm][a,c]	M–E [Å]	Ref.
104	11.4	14.8/28.3	171.1	–	–	–	[162b]
105	3.8	5.56/18.12	176.76	–	–	–	[169]
110	2.60	4.68/18.34	177.74	–	92.4/91.4[b]	–	[170]
111	7.51	7.45/5.37	174.02	–	87.1/94.7	–	[170]
112	28.2	29.1/41.8	157.8	102.8	–	2.769	[162b]
114	17.3	32.2/46.1	167.0	98.2	–	2.880	[169]
115	24.1	28.7/41.1	160.5	95.6	83.6/61.6	3.008	[168a]
116	22.9	28.5/40.4	161.0	92.8	81.6/58.8	3.090	[168b]
117	15.55	30.44/45.15	168.44	93.92	60.10/51.66[b]	2.909	[170]
118	15.83	30.54/45.15	168.40	94.14	60.17/51.67[b]	2.915	[170]
120	16.33	30.90/45.22	167.98	94.67	60.2/49.9[b]	2.889	[170]
122	37.3	23.1/35.8	147.6	93.5	85.4/63.3	3.190	[168a]

[a] Recorded in C$_6$D$_6$ unless otherwise stated. [b] Not assigned to the C$_5$H$_4$ or C$_7$H$_6$ unit. [c] Values given in the order (C$_5$H$_4$/C$_7$H$_6$).

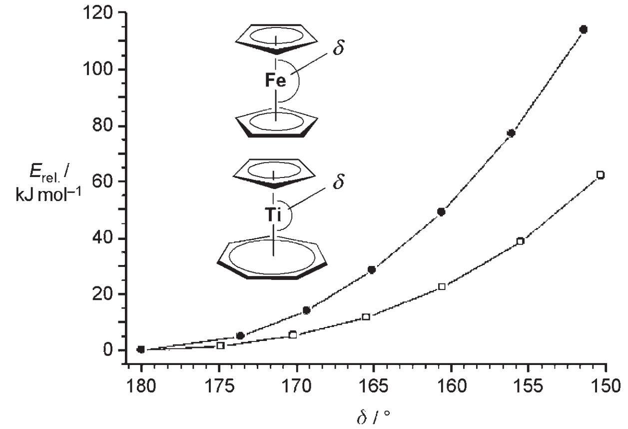


Figure 12. Relative potential energy for ferrocene (●) and troticene (□) as a function of the angle δ. Reproduced with permission from reference [168b].

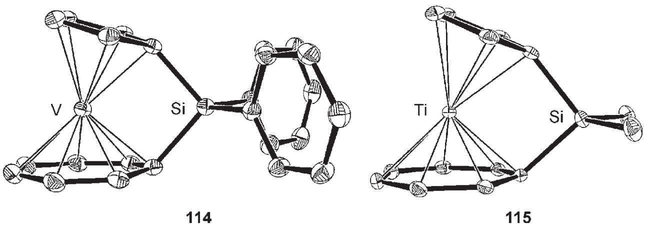


Figure 13. ORTEP depictions of sila[1]trovacenophane **114** and sila[1]-troticenophane **115**. Reproduced with permission from reference [168a] and from reference [169].

the bending angle δ, using DFT calculations showed a similar, yet less drastic dependency (Figure 12).[168b]

Further calculations indicated strong and appreciably covalent Ti–(η^7-C_7H_6) interactions leading to highly stabilized frontier orbitals and consequently to a diminishing of the ligand π-electron release ability. Hence attempts to create CO derivatives of **115** (such as **123**) at ambient temperature have so far been unsuccessful. However, an exchange to more σ-donating, less π-accepting isocyanide ligands produced adducts **121** and **122** as brown crystalline solids in nearly quantitative yields. Coordination of an additional ligand in **122** leads to pronounced elongation of the metal–carbon bonds, in particular to the seven-membered ring (from 1.496 Å to 1.649 Å). As a result, modified coordination is observed in the solid state, indicating a $\eta^7 \rightarrow \eta^5$ haptotropic shift in **122**.[168a]

The introduction of an ansa bridge leads to a slight increase of the HOMO–LUMO gap, which was assigned to be partly a d–d transition and partly ligand-to-metal charge transfer (LMCT). UV/Vis measurements were used to quantify these effects: owing to a lowering of the symmetry and as a consequence of relaxation of the Laporte selection rule, a blue shift of the lowest energy band in the visible spectrum with enhanced intensity was observed (from $\lambda = 696$ nm and $\varepsilon = 31\ \mathrm{L\,mol^{-1}\,cm^{-1}}$ in unbridged troticene to $\lambda = 663$ nm and $\varepsilon = 105\ \mathrm{L\,mol^{-1}\,cm^{-1}}$ in **115**).[168a] It is worth noting here that the introduction of a Si bridge in troticenes has an opposite effect on the splitting and energy of the molecular orbitals than observed for sila[1]ferrocenophanes and other [1]ferrocenophanes (see Section 2.2.9).

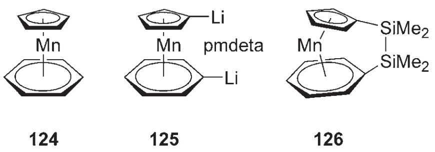
The Tamm research group also reported the oxidative addition and regioselective insertion of a {$Pt(PEt_3)_2$} moiety into the Si–C bond to the seven-membered ring of Lewis acidic [1]troticenophanes **115** and **116** and paramagnetic [1]trovacenophane **113** to form platinasila[2]trovacenophane **106**, platinasila[2]troticenophane **107**, and platinagerma[2]-troticenophane **108**. Complexes **106** and **107** can then be used as catalysts for the transition-metal-catalyzed ROP of the original strained molecules **113** and **115**.[173]

In 2005, the reaction of [(η^5-C_5H_4Li)Cr(η^7-C_7H_6Li)] with stoichiometric amounts of $Br(NMe_2)B$-$B(NMe_2)Br$ to form the dibora[2]trochrocenophane **109** was reported.[174] Pt^0-mediated oxidative cleavage of the B–B bond produced a B-Pt-B-bridged diboraplatina[3]trochrocenophane, which was structurally investigated. In accordance with the geometry of [(η^5-C_5H_5)Cr(η^7-C_7H_7)][175] and in contrast to the geometrical structure of the titanium and vanadium analogues, **109** does not show any marked difference in the M–Cht and M–Cp distances.

The synthesis of sila[*n*]trochrocenophanes **110** ($n = 2$) and **117**–**120** ($n = 1$) from the reaction of [(η^5-C_5H_4Li)Cr(η^7-C_7H_6Li)] with a variety of dialkyl(dihalo)silanes was presented along with their structures and ROP behavior. The $SiMe_2$-bridged sila[1]trochrocenophane **117** underwent facile Pt^0-mediated oxidative addition into the Si–C bond at the Cht site. Transition-metal-catalyzed ROP of **117** was also demonstrated.[170]

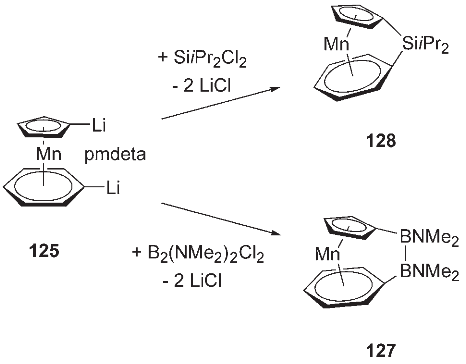
4.2. Ansa-Bridged Complexes of the Type [Mn(η^5-C_5H_4)ER_x(η^6-C_6H_5)] and [Mn(η^5-C_5H_4)E_2R_x(η^6-C_6H_5)]

Ansa derivatives of heteroleptic M^I sandwich complexes [M(η^5-C_5H_5)(η^6-C_6H_6)] (e.g. **124**) or "metallarenocenophanes" can be considered as the link between the field of metallarenophanes, containing predominantly M^0 transition-metal centers, and metallocenophanes, containing mostly M^{II} centers (Scheme 6).



Scheme 6. Heteroleptic sandwich complexes containing mixed π-hydrocarbon ligands.

The very low-yield synthesis of **124** was reported in 1966[176] following reports detailing the synthesis of the methylcyclopentadienyl derivative.[177] Three decades later, the dilithiation of **124** was reported and subsequent quenching with a diorganodihalosilane produced the first ansa-bridged heteroleptic sandwich complex **126**, which was isolated and characterized by NMR and MS techniques.[178] Deeper insight into the nature and the structural aspects of the dilithiated intermediate was provided in 2007, when the X-ray crystal structure of dilithiomanganarenocene(pmdeta) (**125**; pmdeta = pentamethyldiethylentriamine) was published.[179] Treatment with stoichiometric amounts of the corresponding main-group-element organodihalide afforded the dibora[2]-manganarenocenophane **127** and the sila[1]manganarenocenophane **128** [Eq. (18)].[179]



(18)

Since these d^6 species, for example, manganarenocenophane **128**, are isoelectronic with ferrocenophanes and chromarenophanes, they should offer a similar propensity towards ROP. However, detailed studies on the ROP behavior of these metallarenocenophanes have not been reported to date, and this area will be an interesting subject for future research.

5. Summary and Outlook

The field of strained organometallic rings is developing rapidly. Much of the initial work focused on ferrocenophane systems, but important recent advances have permitted expansion to other metals and also other π-hydrocarbon ligands based on arene (C_6) and tropylium (C_7) moieties. The scope of this area is likely to be expanded even further in the future. For example, ferrocenophane analogues with phospha- or germacyclopentadienyl rings have been briefly reported.[126,127] Moreover, strained organoiron rings containing a single cyclopentadienyl ligand as part of the cyclic structure have been isolated and even shown to undergo ROP.[180]

Strained organometallic molecules containing d-block elements are of interest in their own right as their study reveals interesting nuances in terms of structure, bonding, and reactivity, which complement the extensive results available from strained organic systems. A significant further impetus for the exploration of this area involves potential applications. In particular, stoichiometric ring-opening reactions of strained organometallic rings can be used to derivatize surfaces, and ROP potentially opens the door to easily processed polymers with functionality determined by the presence of the metal and spacer.

To date, thermal and anionic ROP of [1]ferrocenophanes has been especially well-developed and some polyferrocenylsilanes are now available commercially.[10,52] The generally robust nature of the ferrocene nucleus facilitates successful ROP reactions by limiting bond cleavage to a single site in the monomer even at high temperatures and in the presence of strongly basic anionic initiators such as alkyl lithium reagents. However, such robustness is not a characteristic of many other strained organometallic rings and uncontrolled decomposition owing to bond cleavage at multiple sites can occur under analogous conditions. New mild routes for polymerization that operate at room temperature such as transition-metal-catalyzed ROP are therefore of key importance and have already been successfully used for thermally sensitive sila[1]chromarenophanes and also sila[1]trochrocenophanes and some analogues.[167,170,173]

The recently reported photolytic living ROP method,[61] which involves cleavage of the metal–π-hydrocarbon bond, utilizes initiators of low basicity (e.g. NaCp) at ambient or subambient temperatures, and offers additional opportunities for molecular-weight control and access to block copolymers. The latter are of considerable current interest with respect to their self-assembly to form functional supramolecular materials such as thin films with phase-separated metal-rich nanoscale domains and nanoscopic micelles in solvents that are selective for one block.[10,181] Thus, future developments in the field of strained organometallic rings may have impact not only in terms of fundamental molecular chemistry but also in the areas of materials science and nanotechnology.

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