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Non-iron [*n*]Metalloarenophanes

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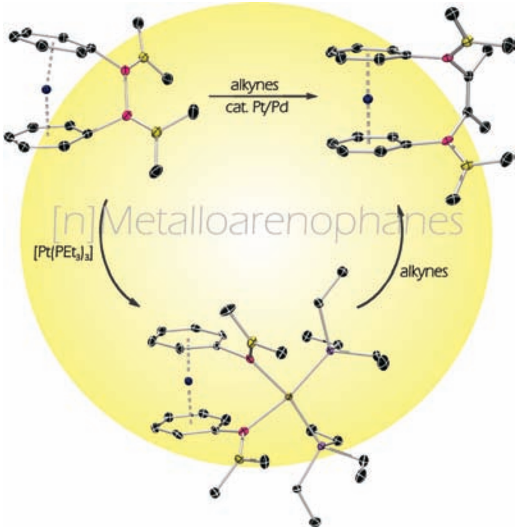
CONSPECTUS



The past 15 years have witnessed the creation of a wealth of fascinating applications for strained [*n*]ferrocenophanes, in which the aromatic sandwich rings of ferrocene are covalently tethered (*n* denotes the number of bridging elements). By contrast, the related [*n*]metalloarenophanes, that is, *ansa*-complexes not derived from ferrocene, have been neglected for a long time. In this Account, we present the tremendous progress that has been achieved in this field, mostly over the last five years. We focus on systems that have been developed in our laboratories, namely, those based on [M(η^6-C$_6$H$_6$)$_2$] (where M is V, Cr, or Mo), [Mn(η^5-C$_5$H$_5$)(η^6-C$_6$H$_6$)], and [M(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)] (where M is V or Cr).

We begin by examining the synthetic precursors to [*n*]metalloarenophanes, the selectively 1,1′-dilithiated sandwich complexes. These species can be isolated and characterized both in the solid state and in solution, and an appreciation of their structural properties is essential for the controlled synthesis of strained [*n*]metalloarenophanes. About 25 different [*n*]metalloarenophanes ($n = 1, 2$) have been obtained from 1,1′-dilithiated sandwich complexes by their stoichiometric reaction with appropriate element dihalides, and most have been fully characterized. X-ray diffraction data confirm the presence of tilted structures, with the extent of the tilt depending on the number of bridging elements, their covalent radii, and the nature of the metal center. The tilt angle, α, between the planes of the two carbocyclic ligands represents a good measure of the amount of ring strain present in these species, ranging from 31.23° for a highly strained [1]boravanadoarenophane to 2.60° for the almost unstrained [2]silatrochrocenophane.

The strained character of [*n*]metalloarenophanes is reflected in their rich and unusual reactivity. The thermodynamic driving force for most of the observed transformations is a significant reduction of molecular ring strain, as evidenced by smaller tilt angles in the products. For example, the [1]sila derivatives undergo facile oxidative addition of the strained Si-$^{\text{arene}}$C bond to low-valent transition metal complexes. Catalytic reaction with Karstedt's catalyst results in the transition-metal-catalyzed ring-opening polymerization (ROP) of a [1]silatrochrocenophane, yielding a polymeric species ($M_W = 6.4 \times 10^3$ g mol^{-1}). The transition-metal-catalyzed ROP of a paramagnetic [1]silavandoarenophane provides a rare example of a well-characterized macromolecule ($M_W \geq 2.8 \times 10^4$ g mol^{-1}) containing spin-active metal centers in the main chain.

The B—B bond of the [2]borametalloarenophanes was found to be particularly susceptible to further functionalizations. Facile oxidative addition was observed, and the resulting [3]diboraplatina derivatives could be successfully employed in the diboration of alkynes to form *ansa*-bis(boryl)alkenes. This transformation was also accomplished directly from the [2]borametalloarenophanes, that is, a diboration of alkynes under both homogeneous and heterogeneous catalysis conditions. Similarly, the stoichiometric diboration of the N═N double bond of azobenzene by a [3]diboraplatinachromoarenophane is possible. The Si—Si bond in [2]silachromoarenophanes can also be used in further derivatizations, although higher temperatures are required. The bis-silylation of propyne proceeded via palladium mediation under homogeneous conditions to yield *ansa*-bis(silyl)alkenes.

Finally, we discuss the electronic properties of [*n*]metalloarenophanes developed in our laboratories, revealing correlations between selected NMR, EPR, and UV—visible parameters and molecular distortion.

10.1021/ar900234z

Introduction

The discoveries of ferrocene, [Fe(η^5-C_5H_5)$_2$], by Kealy and Pauson,[1] and Miller, Tebboth, and Tremaine[2] in 1951 and bis(benzene)chromium, [Cr(η^6-C_6H_6)$_2$], four years later by Fischer and Hafner[3] have facilitated access to a hitherto unknown class of organometallic molecules, whose impact continuously increased during the last few decades. The initial findings prompted huge research efforts and resulted in the preparation of numerous ring-substituted derivatives. Nowadays, the ubiquitous presence of ferrocene in all areas of chemistry including bio(in)organic chemistry, catalysis, and materials science is easily highlighted by a simple SciFinder query, which yields more than 30 000 publications for "ferrocen(e)". *Ansa*-complexes derived from ferrocene or [*n*]ferrocenophanes (n = number of bridging atoms) deserve closer attention due to their unique structure, bonding, and reactivity patterns and have already been isolated in the late 1950s. However, it was not until 1975 that the first strained [1]silaferrocenophane appeared in the literature.[4] Since then, it has been impressively demonstrated that the molecular ring strain present in [*n*]metallocenophanes can be exploited in a variety of useful ways. In particular, the discovery of the ring-opening polymerization (ROP) of strained [*n*]ferrocenophanes to yield high-molecular-weight polyferrocenes represented a landmark moment in both organometallic chemistry and materials science.[5] As a consequence of this advance, the last 15 years has seen tremendous interest in the syntheses of compounds containing this structural motif.[6−10]

By contrast, non-ferrocene systems attracted much less attention, and their chemistry has only been sporadically investigated thus far. The reason for the predominance of ferrocene is closely connected to its high stability, cheap availability, and well-established dimetalation, which enables a straightforward access to ring-substituted and *ansa*-type derivatives. The first examples of *ansa*-complexes not derived from bis(cyclopentadienyl)metal complexes or [*n*]metalloarenophanes had not been published until 1990 by C. Elschenbroich.[11] However, most progress has been made during the last five years, primarily by our group and the groups of M. Tamm (**VI, VII**) at the TU Braunschweig/Germany and J. Müller (**II**−**IV**) at the University of Saskatchewan/Canada (Figure 1). Our research interests include a wide range of different non-metallocene sandwich precursors, namely [M(η^6-C_6H_6)$_2$] [M = V (**II**), Cr (**III**), Mo (**IV**)], [Mn(η^5-C_5H_5)(η^6-C_6H_6)] (**V**), and [M(η^5-C_5H_5)(η^7-C_7H_7)] [M = V (**VII**), Cr(**VIII**)] (Figure 1). It should also be noted that Ragogna and co-workers have recently been able to incorporate the cyclobutadienyl moiety into a strained [2]cobaltoarenophane for the first time.[12]

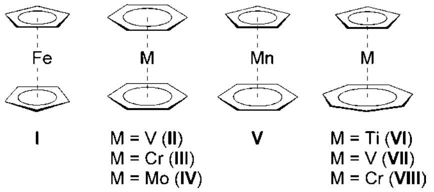
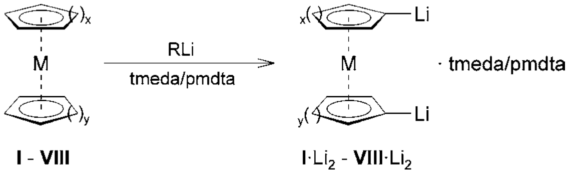


FIGURE 1. Sandwich complexes employed as starting materials.

SCHEME 1. General Outline for the Selective Dimetalation of Sandwich Complexes **I**−**VIII**



In this Account, we examine the generation, isolation, and structural properties of the highly reactive, dilithiated sandwich precursors, as well as their conversion into strained [*n*]metalloarenophanes. We will mainly focus on our own results, but relevant research from other groups will be mentioned where appropriate. In addition, we will show that the molecular ring strain present in these species entails interesting reactivity patterns. We also discuss our findings regarding the electronic structure of these species and try to find a correlation between their electronic and structural properties.

Selective Dimetalation

In general, the preparation of *ansa*-complexes is accomplished by stoichiometric salt-elimination reactions of dimetalated sandwich complexes with element dihalides and, hence, requires the availability of selectively 1,1′-dimetalated and well-defined metallocene precursors. In this context, the double deprotonation of ferrocene has been an early and important achievement.[13] Subsequently, selective dilithiation of several homoleptic (**II**−**IV**)[14−16] sandwich complexes has become accessible by employing alkyl lithium bases in the presence of chelating amines. However, the resulting highly reactive species have not been isolated nor characterized, and the solid state structures remained elusive for a long time. Recently, we developed methods for the selective dimetalation of the sandwich complexes **V**[17] and **VIII**,[18] and optimized the procedures for the dilithiation of **II**−**IV**[19−21] and **VII**.[22] Selective 1,1′-deprotonation was achieved with ^{n}BuLi and ^{t}BuLi in the presence of tmeda (*N*,*N*,*N*′,*N*′-tetramethyletylenediamine) or pmdta (*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine; Scheme 1). The optimized conditions are summarized in Table 1, whereby the dimetalation of **I** and **VI** is included for complete-

TABLE 1. Optimized Conditions for the Selective 1,1′-Dimetalation

	sandwich precursor	*x*	*y*	RLi	amine	equiv[a]	*T* [°C]	yields [%]	ref
I·Li_2	$[Fe(\eta^5\text{-}C_5H_5)_2]$	1	1	^{n}BuLi	tmeda	2.2	rt	85	13
II·Li_2	$[V(\eta^6\text{-}C_6H_6)_2]$	2	2	^{n}BuLi	tmeda	2.5	80	85	19
III·Li_2	$[Cr(\eta^6\text{-}C_6H_6)_2]$	2	2	^{n}BuLi	tmeda	5	80	90	20
IV·Li_2	$[Mo(\eta^6\text{-}C_6H_6)_2]$	2	2	^{n}BuLi	tmeda	6	60	85	21
V·Li_2	$[Mn(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$	1	2	^{n}BuLi	pmdta	2.7	rt	85	17
VI·Li_2	$[Ti(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)]$	1	3	^{n}BuLi	tmeda	2.5	rt	*b*	23[c]
VII·Li_2	$[V(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)]$	1	3	^{n}BuLi	tmeda	2.6	60	71	22
VIII·Li_2	$[Cr(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)]$	1	3	^{t}BuLi	tmeda	2.2	rt	70	18

[a] Equivalents of RLi and amine (1:1) with respect to the sandwich precursor. [b] Not isolated. [c] Very recently, M. Tamm reported the selective metalation of troticene along with structural characterization of **VI**·Li_2: Mohapatra, S. K.; Büschel, S.; Daniliuc, C.; Jones, P. G.; Tamm, M. *J. Am. Chem. Soc.* **2009**, *131*, 17014−17023.

ness. **I**·Li_2−**VIII**·Li_2 can be isolated in high yields by simple gravity filtration on a Schlenk frit as pyrophoric powders, which are surprisingly stable in the absence of air and moisture. Storage is possible under an inert atmosphere over a period of several months without any signs of decomposition.

The diamagnetic species **III**·Li_2−**V**·Li_2 and **VIII**·Li_2 were fully characterized in solution by NMR spectroscopy. Dissolving in thf-d_8 causes the replacement of the tmeda ligands by coordinating thf molecules, as authenticated by NMR spectroscopy. By contrast, the coordination of pmdta in **V**·Li_2 seems to be much stronger, and no exchange was observed in thf solution. These findings were validated by the solid state structures, which were determined by X-ray diffraction for **II**·Li_2−**V**·Li_2[17,19−21] and **VIII**·Li_2.[24] Only the tridentate pmdta ligand in **V**·Li_2 remains coordinated after recrystallization from thf or thf/alkane mixtures. Three different structural motifs can be distinguished, and examples of each are depicted in Figure 2 (**III**·Li_2 is isostructural to **II**·Li_2; **V**·Li_2 and **VIII**·Li_2 exhibit the same Li core). A common feature of the solid state structures is given by the dimeric nature of the dilithio derivatives. In each case, two distinct sandwich fragments deprotonated in the 1,1′-positions are connected by a variable number of bridging and semibridging lithium atoms. While the symmetrical dimers **V**·Li_2 and **VIII**·Li_2 are linked by two unsaturated lithium bridges, unsymmetrical **II**·Li_2 and **III**·Li_2, and symmetrical **IV**·Li_2 contain three and four bridging lithium atoms, respectively. The presence of a semibridging lithium atom in the crystal structures of **II**·Li_2 and **III**·Li_2 is noteworthy. These interactions serve to complete the tetrahedral coordination sphere of the unsaturated terminal lithium atoms, and most likely consist of an η^1-bonding mode to the respective deprotonated *ipso*-carbons.[19,20]

Synthesis of [*n*]Metalloarenophanes (*n* = 1, 2)

These highly reactive sandwich precursors were successfully employed in the synthesis of numerous strained [*n*]metalloarenophanes (*n* = 1, 2) by reacting with suitable element dihalides (Scheme 2). In the following section, we will present the results for each sandwich molecule studied in our lab.

$[V(\eta^6\text{-}C_6H_6)_2]$ (II). Reaction of **II**·Li_2 with a variety of element dihalides yielded the [1]bora- (**1**, **2**), [2]bora- (**3**), [1]sila- (**4**), and [2]silavanadoarenophanes (**5**) in moderate to good yields (Figure 3).[19,25] These paramagnetic species were fully characterized both in solution and in the solid state. X-ray diffraction proved that the introduction of an *ansa*-bridge is accompanied by a substantial deviation from the coplanar arrangement of the ring ligands observed in the unstrained precursor $[V(\eta^6\text{-}C_6H_6)_2]$; a common observation for all "strained" *ansa*-complexes. In general, the degree of ring tilting provides direct information on the molecular ring strain and strongly depends on the number, and the covalent radii of the bridging element(s) and the nature of the metal center. In this context, the tilt angle, α, between the planes of the carbocyclic ligands represents an excellent measure for the ring strain present in these systems that is easily derived from the solid state structure. Table 2 summarizes the tilt angles, α, of all [*n*]metalloarenophanes prepared in our group. Due to the small covalent radius of the boron atom, **1** ($\alpha = 29.44°$) and **2** ($\alpha = 31.12°$, Figure 4) are the most strained derivatives, consequently showing a much stronger ring tilting than the [1]sila congener (**4**, $\alpha_{calcd} = 20.9°$), and the [2]vanadoarenophanes (**3**, $\alpha = 14.40°$; **5**, $\alpha = 4.38°$). Other structurally characterized examples in the literature include [1]vanadoarenophanes with Al ($\alpha = 14.7°$),[26] Ga ($\alpha = 15.6°$),[26] Si ($\alpha = 19.9°$),[11] and Zr ($\alpha = 3.7°$)[27] in the bridging positions. The ring strain of the [1]bora and the [1]sila derivatives has been quantified by differential scanning calorimetry (DSC). The DSC thermograms show distinct exothermic processes at temperatures of 169 °C for **2** ($\Delta H = 92$ kJ mol^{-1}) and 204 °C for **4** ($\Delta H = 18$ kJ mol^{-1}).[25]

$[Cr(\eta^6\text{-}C_6H_6)_2]$ (III). Si- ($\alpha = 14.4°$)[11,28] and Ge-bridged ($\alpha = 14.4°$)[29] bis(benzene)chromium species have already been reported during the 1990s. Accordingly, the synthesis of [*n*]chromoarenophanes with monatomic boron (**6**−**8**),[30] as well as dibora (**9**)[30] and disila (**10**)[20] bridges, is straightforward using the well-defined precursor **III**·Li_2. As expected, the [1]bora congener **8** shows the largest tilt angle $\alpha = 26.6°$, thus representing the most strained of all [*n*]chromoarenophanes known so far. Due to the diatomic bridge, the geometries of **9** ($\alpha = 10.1°$) and **10** ($\alpha = 2.78°$, Figure 4) deviate less from the coplanar precursor $[Cr(\eta^6\text{-}C_6H_6)_2]$. The Al- ($\alpha = 11.8°$) and Ga-bridged ($\alpha = 13.2°$) species published by J. Müller exhibit moderate ring strain, which is of similar magnitude as that in **9**.[26]

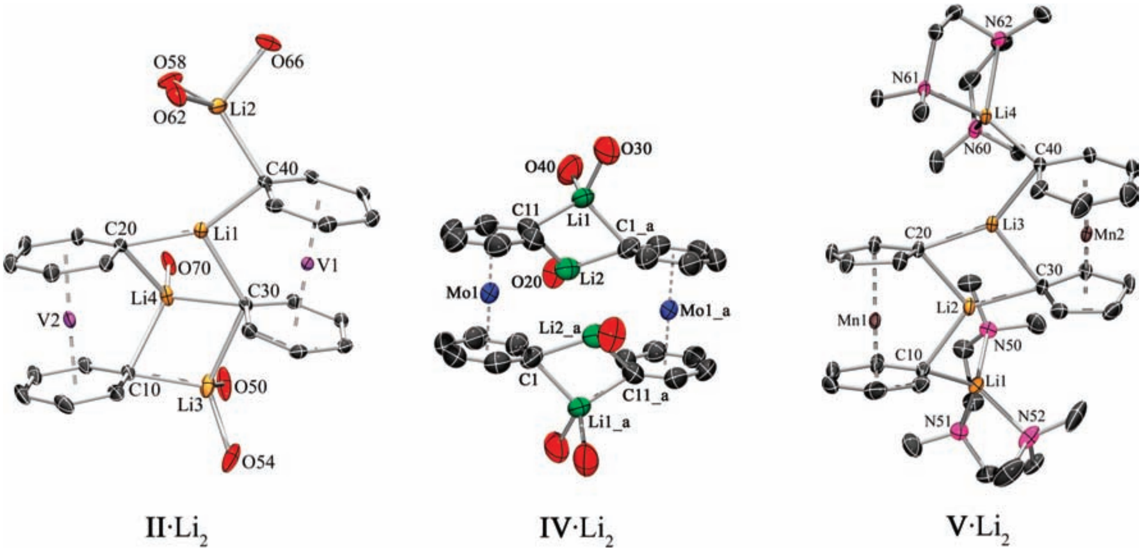
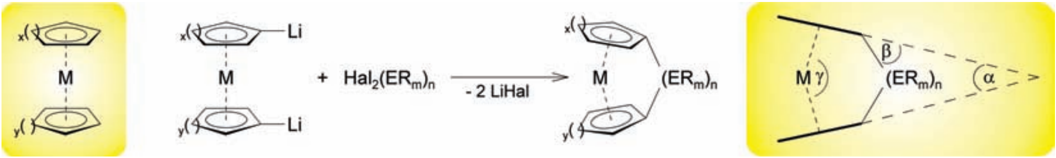
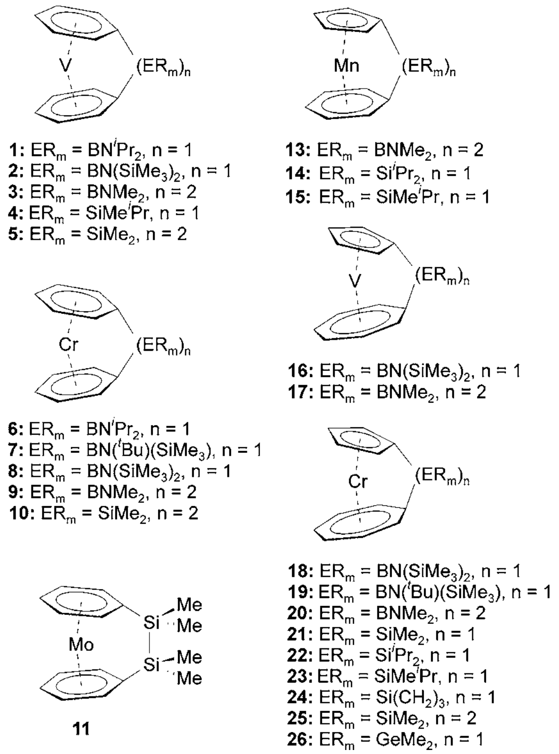


FIGURE 2. Solid state structures of **II**·Li_2, **IV**·Li_2, and **V**·Li_2. For clarity, only the oxygen atoms of the coordinated thf molecules are shown.

SCHEME 2. General Outline for the Synthesis of [*n*]Metalloarenophanes via the Salt-Elimination Approach



[Mo(η^6-C_6H_6)$_2$] (IV). All our efforts to prepare a [1]molybdoarenophane by reaction of **IV**·Li_2 with element dihalides such as $X_2BN(SiMe_3)_2$ (X = Cl, Br) or X_2SiR_2 (R = Me, ^{i}Pr, Ph; X = Cl, Br, OTf) have been unsuccessful, and only resulted in the formation of 1,1′-disubstituted derivatives regardless of the reaction stoichiometry.[21] First evidence for the formation of an *ansa*-complex was obtained with the synthesis of the thermally labile [2]silamolybdoarenophane **11**, which was unambiguously identified by NMR spectroscopy. However, we have never been able to isolate **11** analytically pure but always contaminated with two additional, highly symmetrical compounds in a ratio of 8:1:1 (Figure 5). One component was found to be the parent [Mo(η^6-C_6H_6)$_2$], while the identity of the second remained unclear until its structure was determined by X-ray diffraction as the molybdenum-containing paracyclophane **12** (Scheme 3). The ancillary formation of one equivalent of bis(benzene)molybdenum strongly suggested that this species was generated by deprotonation of the *ansa*-bridged complex **11** in the *para* positions by the dilithiated precursor **IV**·Li_2 and subsequent reaction with a second equivalent of $Me_2(Cl)Si{-}Si(Cl)Me_2$ (Scheme 3).[21] To date, we have not been able to structurally characterize the [2]sila derivative **11**. It was not until 2007 that J. Müller reported on the isolation of the first aluminum- (α = 18.3°), gallium- (α = 21.2°), and silicon-bridged (α = 20.2°) [1]molybdoarenophanes along with X-ray diffraction data.[31]



1: $ER_m = BN^iPr_2$, n = 1
2: $ER_m = BN(SiMe_3)_2$, n = 1
3: $ER_m = BNMe_2$, n = 2
4: $ER_m = SiMe^iPr$, n = 1
5: $ER_m = SiMe_2$, n = 2

6: $ER_m = BN^iPr_2$, n = 1
7: $ER_m = BN(^tBu)(SiMe_3)$, n = 1
8: $ER_m = BN(SiMe_3)_2$, n = 1
9: $ER_m = BNMe_2$, n = 2
10: $ER_m = SiMe_2$, n = 2

13: $ER_m = BNMe_2$, n = 2
14: $ER_m = Si^iPr_2$, n = 1
15: $ER_m = SiMe^iPr$, n = 1

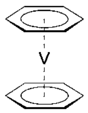
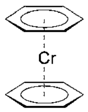
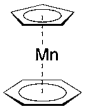
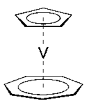
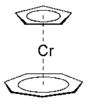
16: $ER_m = BN(SiMe_3)_2$, n = 1
17: $ER_m = BNMe_2$, n = 2

18: $ER_m = BN(SiMe_3)_2$, n = 1
19: $ER_m = BN(^tBu)(SiMe_3)$, n = 1
20: $ER_m = BNMe_2$, n = 2
21: $ER_m = SiMe_2$, n = 1
22: $ER_m = Si^iPr_2$, n = 1
23: $ER_m = SiMe^iPr$, n = 1
24: $ER_m = Si(CH_2)_3$, n = 1
25: $ER_m = SiMe_2$, n = 2
26: $ER_m = GeMe_2$, n = 1

FIGURE 3. [*n*]Metalloarenophanes prepared via salt-elimination reactions.

[Mn(η^5-C_5H_5)(η^6-C_6H_6)] (V). The heteroleptic sandwich complex [Mn(η^5-C_5H_5)(η^6-C_6H_6)] has almost been neglected in

TABLE 2. Summary of Isolated [*n*]Metalloarenophanes

precursor	compound	bridge[a]	α [deg]	δ [deg]
	**1**	–B–	29.44	156.9
	2	–B–	31.23	155.6
	3	–BB–	14.40	169.5
	4	–Si–	20.9[b]	*n.d.*[c]
	5	–SiSi–	4.38	176.8
	32	–BPtB–	6.15	175.2
	36	–BCCB–	3.40	177.7
	**8**	–B–	26.6	159.9
	9	–BB–	10.1	172.1
	10	–SiSi–	2.78	177.8
	33	–BPtB–	4.20	176.6
	38	–BCCB–	2.03	178.1
	39	–BNNB–	1.98	178.4
	**13**	–BB–	11.26	171.3
	14	–Si–	16.97	167.4
	15	–Si–	17.21[d]	168.1
	27	–SiPt–	8.98[d]	172.4
	**16**	–B–	28.23	157.8
	17	–BB–	11.40	171.1
	34	–BPtB–	4.98	176.0
	**18**	–B–	23.87	162.0
	20	–BB–	8.90	173.1
	21	–Si–	15.60	167.5
	22	–Si–	15.83	168.4
	24	–Si–	16.33	168.0
	25	–SiSi–	2.60	177.7
	26	–Ge–	15.07	168.3
	35	–BPtB–	3.48	176.9
	28	–SiPt–	7.51	174.9
	29	–SiPt–	7.77[d]	173.9
	30	–SiCCPt–	3.35[d]	178.4
	41a	–SiCCSi–	4.27	176.6

[a] only atoms directly involved in *ansa*-bridge are shown. [b] calculated value; [c] *n.d.* = not determined; [d] unpublished.

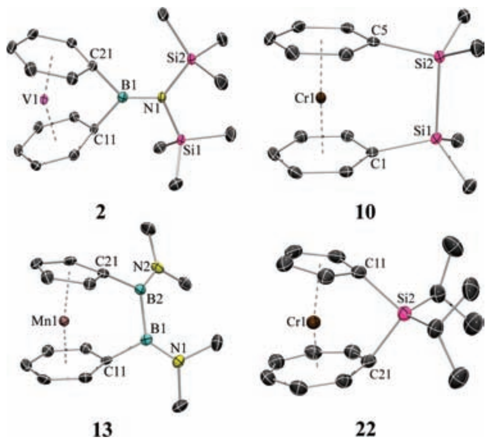


FIGURE 4. Solid state structures of selected [*n*]metalloarenophanes.

the literature regarding the synthesis of *ansa*-complexes, which is most likely attributable to its low-yield synthesis (2–4%). Solely the group of M. Herberhold published some ring-substituted derivatives providing no structural details, though.[32] In our hands, the isolation of the selectively dilithiated precursor **V**·Li_2 enabled us to follow the salt-elimination route under well-defined conditions.[17] All efforts to introduce a monatomic boron bridge were unsuccessful and only resulted in the isolation of 1,1′-disubstituted species, [Mn{η^5-$C_5H_4B(X)NRR'$}{η^6-$C_6H_5B(X)NRR'$}].[33] However, the synthesis of the [2]bora (**13**; Figure 4) and the [1]sila (**14**, **15**) congeners was accomplished without difficulty in yields of 50–70%. X-ray diffraction confirmed the presence of sub-

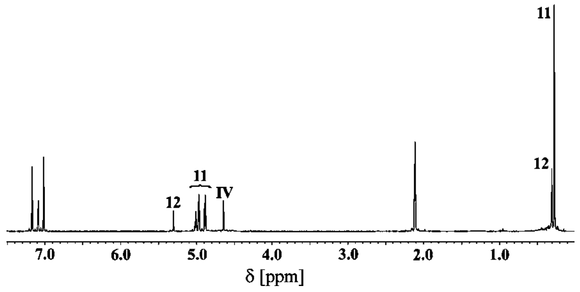
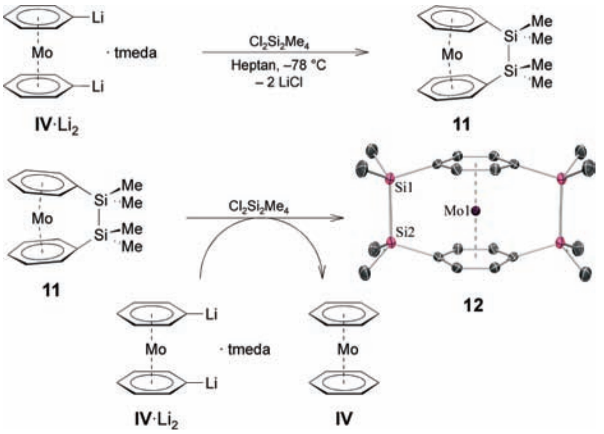


FIGURE 5. ^1H NMR spectrum of the isolated solid containing **11**, **12**, and **IV**.

SCHEME 3. Proposed Mechanism for the Formation of the Paracyclophane **12**



stantial molecular ring strain, as evidenced by tilt angles $\alpha = 11.26°$, $\alpha = 16.97°$, and $\alpha = 17.21°$.[17] These values are smaller than those of the corresponding [*n*]vanadoarenophanes[19,25] but significantly larger than those found for the bis(benzene)chromium derivatives.[28,30] These findings correlate very well with the interannular ring–ring distances observed in the parent sandwich complexes (**II**, 332 pm; **III**, 322 pm; **V**, 328 pm). Compounds **13**–**15** are stable in the solid state under ambient conditions but readily decompose on heating. Moreover, solutions in benzene or more polar solvents such as thf are prone to decomposition at room temperature over a period of days ($t_{1/2} \approx 18$ h), as judged by the appearance of new signals in the aromatic region of the ^{1}H NMR spectra.[33] We suggest that the Mn–benzene bond is most likely the weakest point of this system therefore preventing the isolation of highly strained derivatives.

[V(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)] (VII). The derivatization of trovacene to form *ansa*-complexes was first reported by C. Elschenbroich in 2004[34] and by M. Tamm in 2005[35] with the isolation of [1]sila- ($\alpha = 17.3°$) and [2]sila-bridged ($\alpha = 3.8°$) species. We prepared the corresponding [1]bora (**16**) and [2]bora derivatives (**17**) by addition of $Cl_2B{=}N(SiMe_3)_2$ and (NMe$_2$)(Cl)B–B(Cl)(NMe$_2$) to a suspension of **VII**·Li$_2$ in alkanes.[22] As deduced from the large interannular distance in trovacene (338 pm), **16** and **17** show significant deviations from a coplanar arrangement of the carbocyclic ligands, reflected by tilt angles $\alpha = 28.23°$ and $\alpha = 11.40°$, respectively. However, the values are not as large as expected, and are even smaller than those found in the bis(benzene)vanadium congeners (**2**, $\alpha = 31.12°$; **3**, $\alpha = 14.40°$).[19,25] This is surprising given the smaller ring–ring distance in [V(η^6-C$_6$H$_6$)$_2$] (332 pm). The reason for this behavior can be ascribed to the flexibility of the seven-membered ring that is capable of compensating ring strain, which is well documented by a noticeable distortion from planarity.

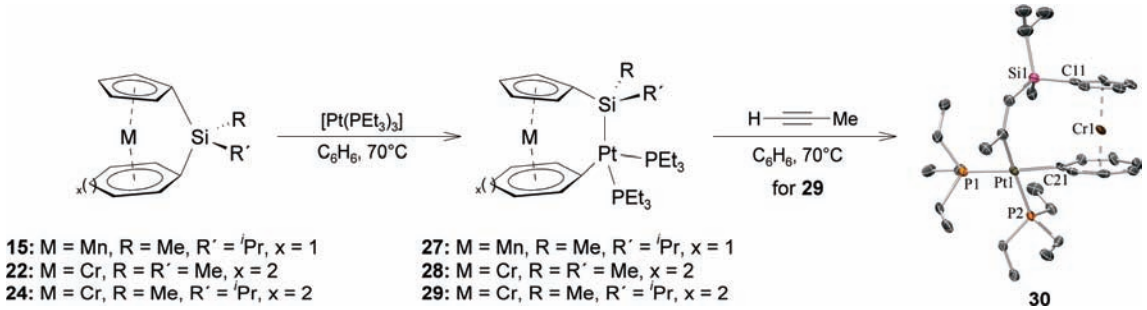
[Cr(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)] (VIII). Trochrocene was first prepared by E. O. Fischer and S. Breitschaft in the 1960s.[36] Experiments regarding the functionalization of the aromatic ligands have been scarce. So far, the derivatization of [Cr(η^5-C$_5$H$_5$)(η^7-C$_7$H$_7$)] to form *ansa*-complexes has been exclusively studied in our laboratories. Since the publication of its selective dimetalation in 2005,[18] we have been able to isolate a series of strained [*n*]trochrocenophanes with different bridging atoms, that is, [1]bora (**18**, **19**),[24] [2]bora (**20**),[18] [1]sila (**21**–**24**; **22**, see Figure 4),[37] [2]sila (**25**),[37] and [1]germa (**26**)[24] derivatives. Most of these species were structurally characterized in the solid state by X-ray diffraction. The degree of molecular distortion covers a wide range with tilt angles between $\alpha = 23.87$ for the highly strained **18** and $\alpha = 2.60°$ for the almost unstrained **25**. Again, the flexibility of the seven-membered ring allows for the reduction of the ring strain in **18** as evidenced by the small value for the tilt angle α, in comparison to the bis(benzene)chromium analog **8** ($\alpha = 26.6°$),[30] even though the interannular distance in trochrocene (326 pm) is larger than that in [Cr(η^6-C$_6$H$_6$)$_2$] (322 pm). The [1]sila (**21**–**24**, $\alpha \approx 16°$), [1]germa (**26**, $\alpha = 15.07°$), and [2]bora (**20**, $\alpha = 8.90°$) congeners are found in the expected ranges between these two extremes.

Reactivity of [*n*]Metalloarenophanes

Due to the intrinsic molecular ring strain, [*n*]metallocenophanes show rich and unusual reactivity patterns. The strained character of [*n*]metallocenophanes is reflected by enhanced reactivity of either the bond between the carbocyclic ligands and the bridging element(s), that between the bridging elements, or that between the metal and one of the carbocyclic ligands.[5–10] In the following section, we will demonstrate that this reactivity is not restricted to the *ansa*-ferrocenes and provide examples for each of the aforementioned reaction types.

Ring-Opening Polymerization. It has been shown that strained [1]silaferrocenophanes undergo transition metal catalyzed ROP, if suitable catalyst systems such as Karstedt's catalyst are applied.[7–10] I. Manners and co-workers recently extended this methodology to the polymerization of [1]silachromoarenophanes.[28] Platinum catalysts were shown to follow a heterogeneous catalytic mechanism, and the first step is believed to be the insertion of the platinum fragment into the strained Si–^{Cp}C bond. In order to verify the suitability of our [1]sila systems to undergo transition metal catalyzed ROP, we performed reactions of [1]silametalloarenophanes **15**, **21**,

SCHEME 4. Regioselective Silicon−Carbon Bond Activation by [Pt(PEt$_3$)$_3$] and Regioselective Insertion of Propyne into the Si−Pt Bond in **29**

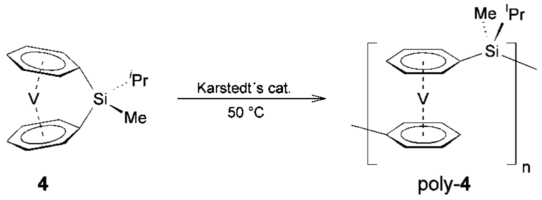


and **23** with stoichiometric amounts of [Pt(PEt$_3$)$_3$]. The reactions proceeded smoothly and quantitatively with **15**,[33] **21**,[37] and **23**[33] over a period of 24 h to afford the [2]platinasila derivatives **27**−**29** (Scheme 4).[17,33] Carbon−silicon bond cleavage occurred regioselectively at the Si−$^{\text{arene}}$C (**15**)[33] or Si−$^{\text{Cht}}$C (**21**,[37] **23**[33]) linkage (Cht = cycloheptarienyl), as evidenced by NMR spectroscopy and X-ray diffraction. The regioselectivity of this transformation is clearly linked to the larger distortion of the six- and seven-membered rings with respect to the Cp ring. As expected, the molecular ring strain is significantly reduced with respect to the starting materials (**27**, α = 8.98°; **28**, α = 7.51°; **29**, α = 7.77°). Similar results have already been obtained by the group of M. Tamm for related [1]silatroticenophanes and [1]silatrovacenophanes.[35,38]

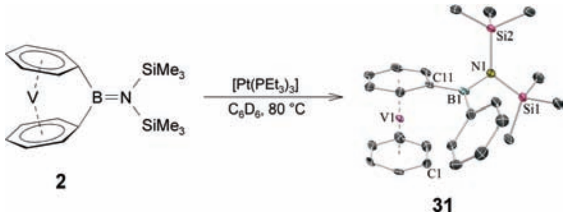
The reactivity of **27**−**29** toward alkynes was studied exemplarily for the trochrocene derivative **29**. In analogy to the reactivity of the related ferrocene species,[39] alkynes can easily be inserted into the Si−Pt bond at slightly elevated temperatures, and the insertion is highly regioselective. Insertion of propyne yielded exclusively **30**, the product in which the methyl group of the alkyne is oriented toward platinum.[33]

After the [1]silatrochrocenophanes have proven their ability for silicon−carbon bond activation, **22** was treated with Karstedt's catalyst in order to induce ROP. The polymerization was carried out applying 5 mol % Karstedt's catalyst in benzene at 50 °C. After 4 days, the product poly-**22** was isolated as a light green, highly air- and moisture-sensitive powder. The NMR spectra only showed broad peaks in agreement with the presence of a polymeric material. Characterization of poly-**22** by gel permeation chromatography (GPC) revealed a moderate molecular weight of $M_W = 6.4 \times 10^3$ g mol^{-1} and $M_n = 4.0 \times 10^3$ g mol^{-1} (PDI = 1.6).[37] Transition metal catalyzed ROP of [1]silavanadoarenophane **4** proceeded without difficulty. Treatment of a toluene solution of **4** at 50 °C with 5 mol % Karstedt's catalyst over a period of 18 h produced a dark orange solution and a yellow-orange solid after precipitation into hexanes (Scheme 5). The EPR spectrum of the isolated material (poly-**4**) contained only one broad signal (*g* = 1.987 G) at 110 K, which may be ascribed to spin communication of the vanadium centers in a polymeric species. Small angle X-ray scattering (SAXS) analysis of poly-**4** gave a radius of gyration of ≥5.8 ± 0.4 nm, which corresponds to a M_W value of at least 28 000 g mol^{-1}. Poly-**4** thus represents a rare example of a well-characterized macromolecule containing spin-active metal centers in the main chain.[25]

SCHEME 5. Transition Metal Mediated ROP of **4**

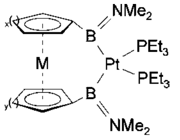


SCHEME 6. Stoichiometric Ring-Opening Reaction of **2**



Another type of ring-opening reaction was observed with the highly strained [1]boravanadoarenophane **2**. Heating a solution of **2** in C$_6$D$_6$ to 85 °C in the presence of catalytic amounts of [Pt(PEt$_3$)$_3$] led to the cleavage of the V−$^{\text{arene}}$C bond to yield unstrained, monometallic **31** (Scheme 6). No reaction occurred in the presence of aliphatic solvents and in the absence of [Pt(PEt$_3$)$_3$]. This transformation is driven by the reduction of molecular ring strain (**31**, α = 5.62°; **2**, α = 31.12°).[25] We are currently attempting to develop this reactivity into a controlled ROP process for [1]borametalloarenophanes.

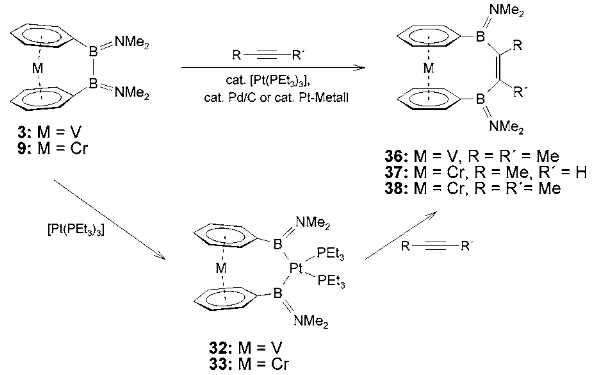
Diboration Reactions. B−B bonds are also known to undergo facile oxidative addition reactions with low-valent transition metal complexes with concomitant formation of bis(boryl) metal species. As a consequence, diboranes(4) have been widely applied to the diboration of unsaturated organic substrates under



32: M = V, x = y = 2
33: M = Cr, x = y = 2
34: M = V, x = 1, y = 3
35: M = Cr, x = 1, y = 3

FIGURE 6. Products obtained by B−B bond activation.

SCHEME 7. Synthesis of *ansa*-Bis(boryl)alkenes **36**−**38** by Transition Metal Mediated Diboration of Propyne and 2-Butyne



homogeneous catalysis conditions. Oxidative addition of the strained B−B bond of [2]borametalloarenophanes **3**, **9**, **17**, and **20** is readily accomplished by reaction with stoichiometric quantities of $[Pt(PEt_3)_3]$ in benzene at elevated temperatures (60−85 °C).[18,19,22,40] The reactions proceed quantitatively without the formation of detectable side products, and the [3]diboraplatina derivatives **32**−**35** can be isolated in yields of 50−75% (Figure 6). The insertion of the platinum fragment is facilitated by the reduction of molecular ring strain and by the formation of two stable Pt−B bonds.

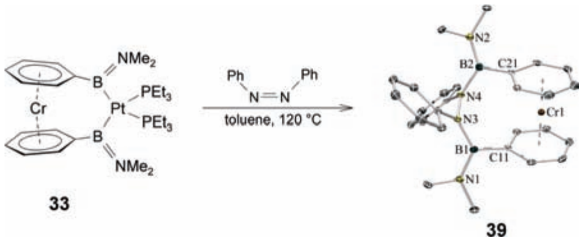
To confirm the anticipated propensity of the [2]borametalloarenophanes to undergo platinum-mediated insertion of alkynes into the strained B−B bond, **32** and **33** were reacted with a 10-fold excess of propyne or 2-butyne at slightly elevated temperatures, which afforded the *ansa*-bis(boryl)alkenes **36**−**38** quantitatively (Scheme 7). As expected for this transformation, the tilt angles (**36**, $\alpha = 3.40°$; **38**, $\alpha = 2.03°$) are further reduced with respect to the precursors **32** ($\alpha = 6.15°$) and **33** ($\alpha = 4.20°$). Subsequent experiments proved that the synthesis of *ansa*-bis(boryl)alkenes **36**−**38** can be attained under homogeneous and, for the first time, under heterogeneous catalysis conditions. In a typical experiment, a resealable tube was charged with the [2]borametalloarenophane (**3** or **9**), a 10-fold excess of the alkyne, and either 5 mol % $[Pt(PEt_3)_3]$, 6 mol % Pd/C, or 6 mol % Pt sponge and heated to 80−100 °C in benzene (Scheme 7). Reactions took place quantitatively; no soluble side or degradation products were detected. Reaction times strongly depended on the catalysis conditions (homogeneous vs heterogeneous) and on the substrate (Table 3). The pure products were isolated in high yields, up to 93%. Control experiments were carried out, which proved that [2]borametalloarenophanes **3** and **9** underwent no reaction with alkynes in the absence of any transition metal catalyst. It should be noted that we obtained similar results with the related [2]boraferrocenophane.[19,40]

TABLE 3. Reaction Conditions upon Formation of *ansa*-Bis(boryl)alkenes **36**−**38**

	stoichiometric[a]		catalytic[a]				
catalyst			$[Pt(PEt_3)_3]$		Pt	Pd	
ansa-compound	**32**	**33**	**3**	**9**	**9**	**3**	**9**
mol % catalyst[b]			5	5	6	6	6
T [°C][b]	75	70	95	80	100	95	100
t (CH_3CCH)		3 h		1 d	4 d		8 d
t (CH_3CCCH_3)	24 h	3 h	5 d	2 d	7 d	14 d	16 d
yield[c] [%] (CH_3CCH)		57		83	92		93
yield[c] [%] (CH_3CCCH_3)	63	51	90	80	87	93	93

[a] Reactions were conducted in the presence of a 10-fold excess of alkynes. [b] Conditions for both propyne and 2-butyne. [c] Yields of isolated product after workup.

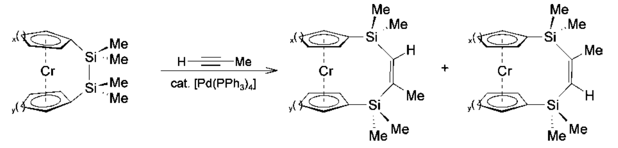
SCHEME 8. Diboration of Azobenzene To Afford *ansa*-Bis(boryl)hydrazine **39**



This reactivity was successfully extended to the diboration of the N=N double bond of azobenzene. Thus, reaction of the [3]diboraplatina species **33** with 4 equiv of azobenzene in toluene at 120 °C resulted in the formation of the *ansa*-bis(boryl)hydrazine **39** (Scheme 8). The reaction was almost quantitative (∼90−95% product), and **39** was isolated after recrystallization from hexanes in yields of 54%. The thermal lability of the [2]bora complex **9** prevented its utilization in a catalytic process, since the high reaction temperature entailed quantitative decomposition of **9** into chromium metal and the free ligand. However, it should be noted that the diboration of azobenzene mediated by $[Pt(PEt_3)_3]$ was achieved with the thermally more robust [2]boraferrocenophane. These results represent, to the best of our knowledge, the first instances of a metal-mediated diboration of a N=N double bond using nonreactive diborane(4) precursors.[41]

Bis-silylation of Propyne. The comparable strength of the Si−Si bond and the B−B bond suggested that the [2]silametalloarenophanes **10** and **25** might exhibit a reactivity similar

SCHEME 9. Palladium-Mediated Syntheses of *ansa*-Bis(silyl)alkenes **40** and **41a/b**



10: x = y = 2
25: x = 1, y = 3

40: x = y = 2
41a: x = 1, y = 3

41b: x = 1, y = 3

to that described above. Oxidative addition of the Si−Si bond to low-valent metal centers and catalytic bis-silylation of unsaturated organic substrates are well-documented. However, the Si−Si bond in **10** and **25** resisted cleavage by transition metal complexes such as $[Pt(PEt_3)_3]$, $[Pt(PCy_3)_2]$, $[Pd(PPh_3)_4]$, or $[Pd(^tBuNC)_2]$. However, if toluene solutions of **10** and **25** were treated with excess propyne in the presence of catalytic amounts of $[Pd(PPh_3)_4]$ at 125 °C, bis-silylation occurred yielding the *ansa*-bis(silyl)alkenes **40** and **41** (Scheme 9). The transformation proceeded smoothly and quantitatively within 48 h, and the products could be isolated in very high yields of 92% and 95%, respectively. Due to the presence of two different carbocyclic ligands, the bis-silylation of propyne by **25** produced two regioisomers **41a** and **41b** in a ratio of 3:1. Isomer **41a** could be separated by crystallization and was fully characterized including X-ray diffraction, which confirmed the anticipated unstrained character. No reaction was detected in the absence of the palladium catalyst.[20]

Electronic Structure of [*n*]Metalloarenophanes

Due to the availability of numerous derivatives, the electronic structure of [*n*]ferrocenophanes has been studied in great detail.[9] By contrast, only a few examples were available for each nonferrocene sandwich complex until recently. The large number of [*n*]metalloarenophanes prepared in our laboratories, particularly those derived from bis(benzene)vanadium and trochrocene, enabled us to examine the electronic properties in detail by NMR or EPR spectroscopy, UV−vis spectroscopy, and DFT (density functional theory) calculations. Some aspects are presented below.

NMR Spectroscopy. It was already recognized for [*n*]ferrocenophanes that the separation of the α- and *β*-proton signals of the Cp rings in the ^1H NMR spectra correlates with the degree of molecular distortion, that is, with the tilt angle α. A similar correlation was found for the ^{13}C NMR shift of the $^{Cht}C_{ipso}$ atoms. A closer inspection of the NMR spectra of [*n*]trochrocenophanes **18**−**26**, as well as of some unstrained, 1,1′-disubstituted derivatives, revealed two similar, highly characteristic features, namely, the chemical shifts of the α-Cht protons and the $^{Cht}C_{ipso}$ carbon atoms in the ^1H and ^{13}C NMR spectra, respectively (Figure 7). Both features strongly depend on the tilt angle α, and illustrate very well that the seven-membered ring is much more sensitive to structural and electronic changes upon introduction of an *ansa*-bridge. DFT calculations support these findings. Accordingly, the Cr−Cht bond is mainly covalent in nature showing large contributions of the chromium atomic orbitals (AOs), while the Cr−Cp bond is mainly ionic without significant chromium AO character. Hence, the highfield shift of the α-^{Cht}H atoms and $^{Cht}C_{ipso}$ carbon atoms is linked to the shorter and stronger Cr−$^{Cht}C_{ipso}$ carbon bond, which increases the electron density at the $^{Cht}C_{ipso}$ carbon and to a somewhat smaller extent at the adjacent α-^{Cht}C and α-^{Cht}H atoms.[18,24,37]

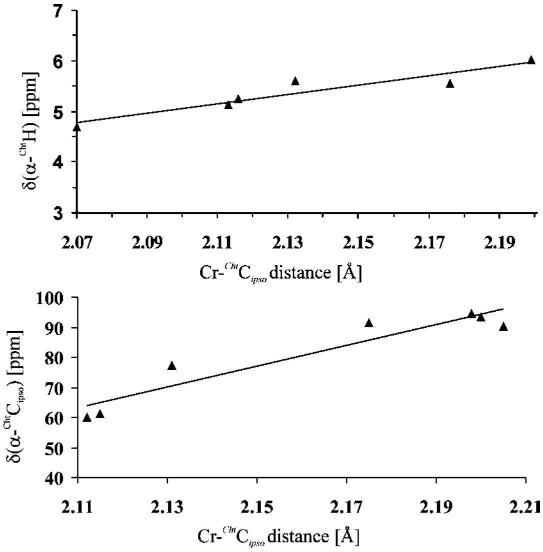


FIGURE 7. Chemical shift [ppm] of the ^1H NMR signals of the α-^{Cht}H atoms (top) and the ^{13}C NMR resonances of the $^{Cht}C_{ipso}$ atoms (bottom) as a function of the Cr−$^{Cht}C_{ipso}$ bond distances [Å].

EPR Spectroscopy. As already noted by C. Elschenbroich and co-workers, the metal hyperfine coupling constant $a_{iso}(^{51}V)$ in [*n*]vanadoarenophanes is highly dependent on the molecular distortion; that is, a larger tilt angle α, is associated with a smaller value for $a_{iso}(^{51}V)$. This was ascribed to enhanced metal-to-ligand spin delocalization from the singly occupied SOMO, which is primarily metal-centered (d_{z^2}), to the ligand orbitals.[11,29] We recorded EPR spectra of our bis(benzene)vanadium species **1**−**5**, **32**, and **36** in fluid and rigid solutions (toluene) at 240 and 110−140 K, respectively, and determined all relevant EPR parameters. The isotropic spectra are all very similar and feature a well-resolved coupling to one ^{51}V center ($I = ^7/_2$). The hyperfine coupling constants $a_{iso}(^{51}V)$ confirm the anticipated trend and show an excellent correlation with the tilt angles α (Figure 8).[19,25]

State-of-the art DFT calculations were able to reproduce the measured isotropic vanadium hyperfine couplings and the coupling anisotropies. The calculations confirmed the decrease of the absolute isotropic hyperfine couplings with increasing

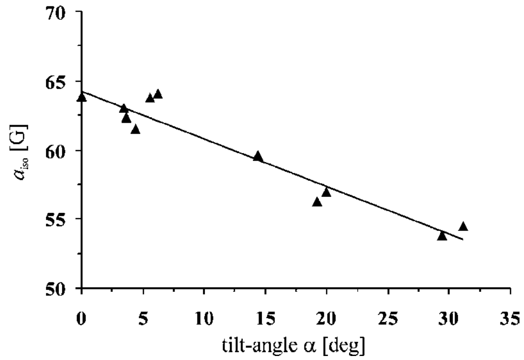


FIGURE 8. Hyperfine coupling constants a_{iso} [G] as a function of the tilt angle, α [deg].

tilt angle. Close analysis showed that this is mainly due to increased positive contributions to the spin density at the vanadium nucleus from the spin polarization of doubly occupied valence orbitals of vanadium−ligand σ-antibonding character. The latter are destabilized and thus made more polarizable in the bent structures.[19]

UV−Vis Spectroscopy. We also investigated the UV−vis absorptions of the [*n*]vanadoarenophanes and [*n*]trochrocenophanes in thf solution. In the latter series, we also included some unstrained 1,1′-disubstituted trochrocene species for comparison. In general, the lowest energy absorption is highly characteristic for each sandwich complex. In addition, this absorption is significantly shifted upon introduction of ring strain by means of an *ansa*-bridge, as described for the related ferrocene and troticene systems.[9,23] Whereas the UV−visible spectra of the [*n*]vanadoarenophanes did not reveal any distinct correlation,[19] the introduction of a nonboron *ansa*-bridge into [Cr(η^5-C_5H_5)(η^7-C_7H_7)] resulted in a significant red shift of the first spin-allowed electronic excitations in a range of λ_{max} = 559 nm in trochrocene (**VIII**) to λ_{max} = 593 nm in the highly strained [1]germatrochrocenophane **26**. However, the boron-containing complexes **18**, **20**, and [Cr{η^5-$C_5H_4B(Cl)N^iPr_2$}{η^7-$C_7H_6B(Cl)N^iPr_2$}] (**42**) showed a complementary correlation; that is, the most strained *ansa*-derivative (**18**) featured a noticeable blue shift (λ_{max} = 535 nm) with respect to trochrocene. According to quantum chemical calculations, this phenomenon can be attributed both to the strong electronic influence of the B−N π-system (Figure 9) and to the complexity of the electronic transitions in these systems.[24]

Conclusions

The field of strained [*n*]metallocenophanes and [*n*]metalloarenophanes has developed rapidly during the past decade. Whereas initial work focused on [*n*]ferrocenophanes, important advances have been achieved for several non-ferrocene systems. The availability of various dimetalated sandwich precursors enabled the synthesis of numerous *ansa*-type species that feature a wide range of molecular distortion. Since more and more examples appear in the literature, the electronic structure becomes better and better understood. The intrinsic ring strain in the [*n*]metalloarenophanes has been successfully exploited in a variety of useful ways. The ROP of [1]silametalloarenophanes yielded novel polymeric materials, among others, a well-defined polymer-containing spin-active metal center in the main chain. The latter is particularly noteworthy, since it facilitates access to novel materials with interesting magnetic properties. The transition metal mediated diboration and bis-silylation of alkynes allowed for the facile synthesis of *ansa*-bis(boryl)- and *ansa*-bis(silyl)alkenes, which are excellent candidates for the preparation of organometallic polymers via ROMP. Despite this tremendous progress, the newly discovered species always raise new questions, and much more needs to be done in the future.

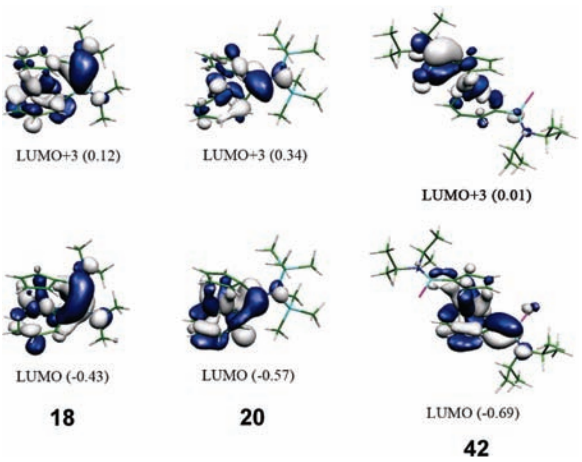


FIGURE 9. Contribution of the B−N π system to the LUMO and LUMO + 3 in **18**, **20**, and **42**.

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BIOGRAPHICAL INFORMATION

Holger Braunschweig, born in 1961 in Aachen, obtained his Ph.D. from the RWTH Aachen with P. Paetzold and then took a postdoctoral position with M. F. Lappert, FRS, at the University of Sussex, Brighton. After his habilitation at the RWTH Aachen, he spent two years at Imperial College, London. In 2002, he moved to a chair for inorganic chemistry at the Julius-Maximilians-University Würzburg. He was initiated a fellow of the Royal Society of Chemistry in 2002 and was recently elected a member of the Bayerische Akademie der Wissenschaften. In 2009, he was awarded the prestigious Gottfried Wilhelm Leibniz Prize. His research interests are in organometallic synthesis and catalysis in boron chemistry.

Thomas Kupfer was born in 1979 in Würzburg, Germany, and studied Chemistry at the Julius-Maximilians-University Würzburg. After obtaining his Ph.D. in 2007 at Würzburg under the supervision of Holger Braunschweig, he moved to MIT, Cambridge, MA, for postdoctoral studies in the research group of R. R. Schrock. In 2009, he returned to Würzburg and currently pursues independent research. He was awarded a Ph.D. fellowship from the Fonds der Chemischen Industrie (FCI) in 2005 and a postdoctoral fellowship from the German Academic Exchange Service (DAAD) in 2008. His interests include organometallic and actinide chemistry.

FOOTNOTES

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