acetate/hexane = 1/10–1/1) gave 105.6 mg (78%) of the *endo* isomer and 13.1 mg (10%) of the *exo* isomer.

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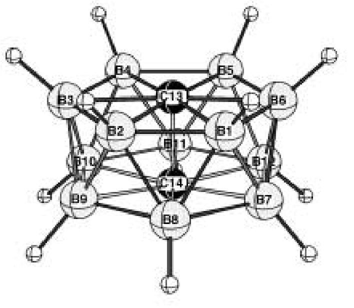
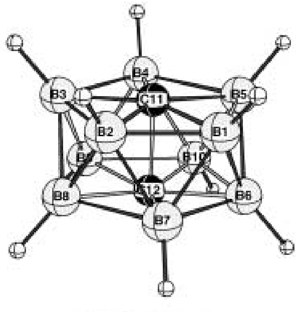
Planar Hypercoordinate Carbons Joined: Wheel-Shaped Molecules with C−C Axles[**]

Zhi-Xiang Wang and Paul von Ragué Schleyer[*]

After two centuries of organic chemistry and the characterization of over 14 million carbon compounds with conventional bonding, our recent computational predictions of molecules with planar hexacoordinate [1] and pentacoordinate carbon atoms[2] has demonstrated that the bonding capabilities of this central element have not been exhausted. We now show computationally [3] that the coordination of carbon can be raised to seven (or six) by the perpendicular extension of two planar hexacoordinate (or pentacoordinate) carbon atoms to form wheel-shaped (**W**) molecules (e.g. **1W** and **2W**, respectively).



1W ($C_2B_{12}H_{12}$)



2W ($C_2B_{10}H_{10}$)

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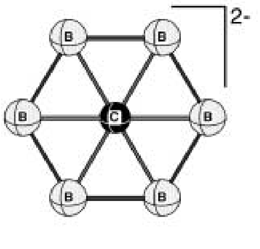
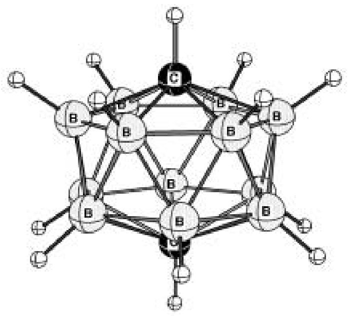
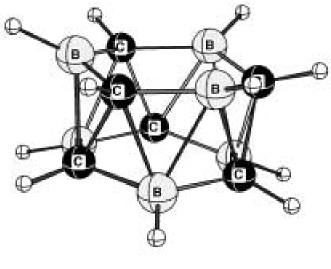
There is an experimental precedent for our findings, but not involving carbon. The highly unusual geometry of the "nanowheel" $[Al_{14}\{(NSiMe_3)_2\}_6I_6Li(OEt_2)_2]^-[Li(OEt_2)_4]^+\cdot$toluene reported by Schnöckel et al.[4] resembles **1W** structurally in having a "collapsed" polyhedron with "approximately Al-centered Al_6 rings". This molecule and **1W** contain structural features found in species we have reported previously: the computed planar hexacoordinate carbon prototype, CB_6^{2-}(**3**, D_{6h}),[1] the predicted but experimentally unknown *closo*-$C_2B_{12}H_{14}$ (**4**, D_{6d}),[5] and the drum-shaped hexacarba-*arachno*-dodecarborane, $C_6B_6H_{12}$ (**5**, D_{3d}).[6]



3 (CB_6^{2-})



4 ($C_2B_{12}H_{14}$)



5 ($C_6B_6H_{12}$)

If the two hydrogen atoms linked to the apical carbons in **4** are removed, the two electrons remaining can form an extra axial bond inside the cages. This results in the "collapse" of the spherical structure of **4** and leads to **1W**. While lacking the C–C "axle" of **1W**, **5** has the same staggered skeletal structure. The 14-vertex $C_2B_{12}H_{12}$ (**1W**) can be viewed as a hydrogenated dimer of **3**; a C–C single bond joins two $C(BH)_6$ moieties each of which possesses nearly planar hexacoordinate carbons. Within the $C(BH)_6$ moieties of **1W**, the out-of-plane deviation angle, α (the C13-B1-B2-B3 dihedral angle, Table 1) is only 2.2°, and the C–B bond lengths are 1.817 Å. The internal axial bond in **1W** is characterized by a short C–C separation (1.597 Å), which corresponds to a Wiberg C–C bond index (WBI)[7] of 0.98 (compared to 1.04 for ethane), and by the nature of the HOMO (Figure 1). Similarly, removal of the two apical hydrogen atoms from *closo*-1,12-$C_2B_{10}H_{12}$ results in $C_2B_{10}H_{10}$ (**2W**), which possesses D_{5d} symmetry. In this structure, two nearly planar pentacoordinate carbons are joined. The angle, α, is 3.9°; the C–B and C–C separations are 1.634 Å and 1.661 Å, respectively, and the C–C WBI is 0.94 (Table 1). Excluding the electron pair required for axial C–C bonding, **1W** and **2W** have the same skeletal electron pair count as the regular fourteen and twelve vertex *closo* boranes and carboranes. Hence, Wade's "*closo*" rule[8] is still followed.

If, after removal of the two hydrogen atoms in **4**, the two electrons remain located on the carbon atoms (at least formally), the cages retain the regular polyhedral (**P**) shapes in the singlet biradical (**PS**) or in the triplet (**PT**) states. Both **1PS** and **2PS** are minima with long C–C separations, small WBIs (Table 1), and have nonbonding HOMOs (Figure 1). They do not follow Wade's *closo* rule if the two diradical electrons are added to the skeletal electron pair count.

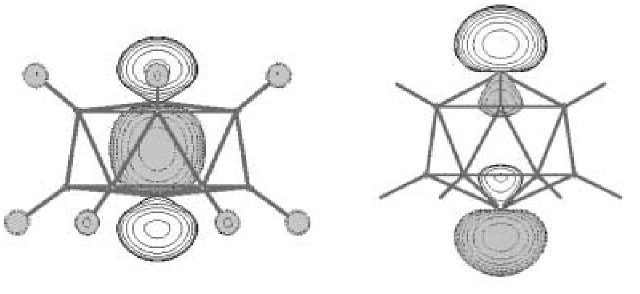
The less favorable electronic structures of **1PS** and **2PS**, when compared with **1W** and **2W**, are also characterized by smaller HOMO–LUMO gaps (in eV): 3.7 for **1PS** and 4.0 for **2PS** versus 6.2 for **1W** and 7.1 for **2W**. The triplets are discussed below.

The C–C axial bonding in **1W** and **2W** favors the wheel-shaped forms, but also leads to an increase in strain because of cage expansion and planarization of the carbon arrangements. The competition between the stabilizing axial bonding and destabilizing strain effects determines whether a **W** or a **P** isomer is favored. While **1W** is 18.2 kcal mol^{-1} more stable than **1PS**, **2W** is 61.0 kcal mol^{-1} less stable than **2PS**. Electronegative substituents can increase the relative stability of **W** over **P** isomers decisively. Highly σ-electron-withdrawing fluorine atoms weaken the cage bonding of the perfluorinated **W** forms and thus decrease the cage deformation strain. Indeed, the 14-vertex $C_2B_{12}F_{12}$ only has a wheel-shaped minimum, **8W**. In complete contrast to $C_2B_{10}H_{10}$ (**2W** and **2P**), the 12-vertex $C_2B_{10}F_{10}$ (**9W**) is ac-

Table 1. Interatomic distances R [Å] between apical atoms and their deviation angles (see text for definition) out of the face planes α [°], number of imaginary (NIMG) frequencies, energy differences between wheel-shaped (**W**), polyhedral singlet (**PS**), and triplet (**PT**) isomers ΔE [kcal mol^{-1}], and Wiberg bond indexes (WBIs) between apical atoms.

		R[a]	α	NIMG[b]	ΔE[c]	WBI
$C_2B_{12}H_{12}$	**1W**[d]	1.597	2.2	0(119)	0.0	0.98
	1PS	2.709	21.7	0(95)	18.2	0.01
	1PT	2.670	21.2	0(112)	17.1	
$C_2B_{10}H_{10}$	**2W**	1.661	3.9	0(352)	0.0	0.94
	2PS	2.916	29.5	0(398)	−61.0	0.17
	2PT	2.859	28.7	0(431)	−50.9	
$C_2Al_{12}H_{12}$	**6W**	1.421	−9.7	8(231i)		1.47
$C_2Al_{10}H_{10}$	**7W**	1.568	−9.2	0(44)	0.0	1.09
	7PT	3.464	16.6	2(61i)	93.5	
$C_2B_{12}F_{12}$	**8W**	1.576	2.5	0(28)	0.0	0.96
	8PT	2.603	28.3	0(46)	46.3	
$C_2B_{10}F_{10}$	**9W**	1.667	5.0	0(118)	0.0	0.87
	9PS	2.833	27.9	0(138)	3.6	0.02
	9PT	2.829	27.8	0(118)	25.0	
$B_{14}H_{12}^{2-}$	**10W**	1.902	7.3	0(326)	0.0	0.81
	10PS	3.055	26.8	0(302)	−12.9	0.03
	10PT	3.008	26.1	0(315)	−12.8	
$Al_{14}H_{12}^{2-}$	**11W**	2.708	5.0	0(114)	0.0	0.75
	11PS	4.929	29.1	0(90)	10.2	0.17
	11PT	4.376	24.1	0(108)	12.7	
$Si_2Al_{12}H_{12}$	**12W**	2.420	2.2	0(85)	0.0	0.95
	12PT	3.798	18.3	2(67i)	34.4	
$Ge_2Al_{12}H_{12}$	**13W**	2.559	4.1	0(76)	0.0	0.94
	13PT	3.962	20.4	2(42)	25.1	
$B_{14}F_{12}^{2-}$	**14W**	1.990	9.1	0(123)	0.0	0.65
	14PT	2.893	25.4	0(129)	18.1	
$Al_{14}F_{12}^{2-}$	**15W**	2.801	6.0	0(68)	0.0	0.65
	15PT	4.227	21.9	0(40)	20.8	

[a] At R(U)B3LYP/6-311 + G**. [b] At R(U)B3LYP/6-31G*; the magnitudes of the of smallest frequencies are in parentheses. [c] At R(U)B3LYP/6-311 + G** + ZPE (R(U)B3LYP/6-31G*). [d] All 14-vertex molecules have D_{6d} symmetry and 12-vertex systems have D_{5d} symmetry except for **5PT** (D_{2d}).



1W-HOMO 1PS-HOMO

Figure 1. Comparison of the HOMOs of **1W** and **1PS**. Note the C–C bonding character of **1W**-HOMO and the biradical character of the **1PS**-HOMO.

tually 3.6 kcal mol^{-1} more stable than **9P**. The competition between central-atom bonding and cage strain is reflected in their isoelectronic analogues. While carbon atoms are "too small" to fit into an Al_6 ring (the 14-vertex **6W** has eight imaginary frequencies), the 12-vertex **7W** is a minimum containing concave hypercoordinate carbon atoms. Optimization starting with a polyhedral geometry of $C_2Al_{10}H_{10}$ collapsed into **7W**.

In the planar hexa- and pentacoordinate carbon molecules (for example, **3**), the carbon p_π orbital interacts with the ring π orbitals.[1,2] The corresponding p_π orbitals of the central atoms of the wheel dimers interact with their counterparts on opposite faces. The central carbon atoms in **1W**, **2W**, **8W**, and **9W** have nearly planar hexa- or pentacoordination in addition to the additional axial bond perpendicular to the plane. This bond, together with the cage binding, stabilizes the unusual structures. The isolated ring fragments lacking such cage interactions, for example, $C(BH)_6^{0,+2,-2}$ (D_{6h}), $C(BF)_6^{0,+2,-2}$ (D_{6h}), $C(BH)_5^{0,+2,-2}$ (D_{5h}), and $C(BF)_5^{0,+2,-2}$ (D_{5h}) are higher order saddle points.

The removal of two hydrogen atoms from carboranes (for example, from **4**) leading to the **W** or **P** forms (which may be considered to be "bond-stretch isomers") is similar to the 1,4-dehydrogenation of benzene that may lead to either butalene (corresponding to our **W** forms) or to *p*-benzyne (corresponding to our **P** forms). The through-bond coupling[9] interaction in *p*-benzyne also is present in **P** isomers. *p*-Benzyne and its derivatives, which are intermediates in the Bergman cyclization,[10] are well known anti-tumor agents.[11] Hydrogen abstraction by *p*-benzyne derivatives, generated from ene–diyne cyclizations, leads to the cleavage of DNA strands and to the death of tumor cells. The less stable polyhedral $C_2B_{12}H_{12}$ isomer (**1PS**, and its derivatives) of the more stable **1W** form, should behave similarly. The abstraction of a hydrogen atom from H_2 (as a computational model) by *p*-benzyne is exothermic by 4.0 kcal mol^{-1}. Hydrogen atom abstraction from H_2 by $C_2B_{12}H_{12}$ (**1PS**) is exothermic by 2.3 kcal mol^{-1}.[12] Furthermore, the eventual hydrogen abstraction product ($C_2B_{12}H_{14}$) also has potential as a boron neutron capture therapy (BNCT) agent, of which polyhedral carborane or borane-based compounds are examples.[13] Thus, derivatives might afford a two-pronged attack on malignant cells.

The same principles can be used to achieve planar hypercoordination for the B^-, Al^-, Si, and Ge analogues of carbon. Considering the optimum central atom-ring "fit", we located favorable congeners of **1** and **2** involving group 13 and heavier group 14 elements; Table 1 includes some examples, **10–15W** and **10–15PS**. Similar to the **PS** and **W** isomers of **1** and **2**, the two rings in both the **PS** and **W** isomers of **10–15** are more favorably bonded in staggered antiprismatic conformations. The electronic structures of **10–15W** also are similar and feature axial bonding between apical atoms, a short distance between the apical atoms, and WBIs in the 0.75–0.95 range (Table 1). As for **1** and **2**, the relative stability of **W** versus **PS** forms depends on the sizes of the apical atoms (that is, their covalent radii) in relation to the wheel radii. While **10W** is 12.9 kcal mol^{-1} less stable than **10PS**, **11W** is 10.2 kcal mol^{-1} more stable than **11PS**. On optimization, singlet **PS** starting geometries of $Si_2Al_{12}H_{12}$ and $Ge_2Al_{12}H_{12}$ collapsed into the wheel-shaped minima, **12W** and **13W**. As with **8W** and **9W**, electron-withdrawing substituents enhance the stability of the **W** forms over the **PS** forms. The **PS** starting geometries of $B_{14}F_{12}^{2-}$ and $Al_{14}F_{12}^{2-}$ collapsed into **W** isomers (**14W** and **15W**, respectively). Because B and Al atoms are too large to be incorporated into $(BH)_5$ and $(AlH)_5$ five-membered rings, respectively, the 12-vertex $B_{12}H_{10}^{2-}$ and $Al_{12}H_{10}^{2-}$ (both D_{5d}) only have **P** minima (not included in Table 1). Schnöckel's $[Al_{14}\{(NSiMe_3)_2\}_6I_6Li(OEt_2)_2]^-[Li(OEt_2)_4]^+\cdot$toluene nanowheel[4] is a derivative of **11W**, $Al_{14}H_{14}^{2-}$.

As mentioned above, the removal of two apical hydrogen atoms may result in a polyhedral biradical triplet (**PT**). For the species that have no **PS** minima (that is, **7** and **11–15**), **PT** triplets can be optimized in polyhedral geometries but are higher in energy than the corresponding **W** singlets (Table 1). For $C_2B_{12}H_{12}$ (**1**) and $Al_{14}H_{12}^{2-}$ (**11**), the **PT** triplets and the **PS** singlets have nearly the same energies; all are less stable than the **W** forms (Table 1). The $C_2B_{10}F_{10}$ triplet, **9PT**, is 25.0 kcal mol^{-1} higher in energy than **9PS**. The triplets of $B_{14}H_{12}^{2-}$ (**10PT**) and $C_2B_{10}H_{10}$ (**2PT**) are less stable than the **P** singlets but are more favorable than the singlet **W** forms.

We conclude that a family of "collapsed" polyhedral molecules is possible. These can contain hypercoordinated carbon atoms and other main group elements in unusual environments. Because cage substituents can help determine whether wheel-shaped or "bond-stretched" polyhedral isomers are more stable, it should be possible to control the properties of these species, for example, to adjust their "Bergman *p*-benzyne-like" capabilities.

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Rational Synthesis of Tetranuclear Ruthenium Polyhydride Clusters and Their Mixed-Ligand Analogues**

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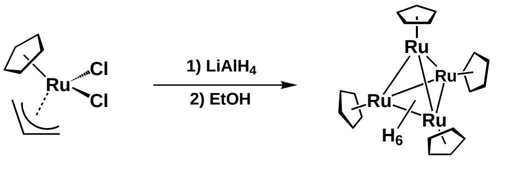
Hiroharu Suzuki*

The reactivity of transition-metal cluster complexes has recently been attracted considerable attention because of their potential applicability to organic synthesis.[1] There have been a number of examples of unique reaction modes, such as successive cleavage of the carbon–hydrogen bond of alkanes,[2] the cleavage of the carbon–carbon double bond of 1,1′-disubstituted alkenes,[3] and the catalytic hydrogenation of aromatic compounds in aqueous media,[4] originating from the cooperative action of the metal centers. The advantageous properties of a multimetallic system over a monometallic one in the substrate activation step are its ability to *multiply coordinate* the substrate and the *multielectron transfer* between the substrate and the cluster. Such unique reactivity of the cluster likely comes from these two remarkable properties. The reactivity is most probably affected by the nuclearity of the cluster because the reactivity strongly depends on the number of transferable electrons: the more nuclei in the cluster, the more effectively electrons are transferred.[5] It is well established for mononuclear transition-metal complexes that the auxiliary ligand allows control over the reactivity of the complex through electronic and steric perturbation of the reaction site. Thus, the development of a rational method for the synthesis of clusters with higher nuclearity and a variety of auxiliary ligands seems to be essential for the application of such clusters to organic synthesis.

Recently, we have established the high and unique reactivity of the di- and trinuclear ruthenium polyhydride complexes $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}H)_4]$ (**1**) and $[\{(\eta^5\text{-}C_5Me_5)Ru\}_3(\mu\text{-}H)_3(\mu_3\text{-}H)_2]$ (**2**).[6] As an extension of the chemistry of "*trimetallic activation*", we tackled the development of a rational method for the synthesis of a tetranuclear ruthenium polyhydride cluster. We report herein, to the best of our knowledge, the first example of a rational synthesis of a series of tetranuclear polyhydride complexes having several combinations of the auxiliary cyclopentadienyl ligands.

Treatment of $[CpRuCl_2(\eta^3\text{-}C_3H_5)]$ (**3a**)[7] ($Cp = \eta^5\text{-}C_5H_5$) with $LiAlH_4$ in tetrahydrofuran followed by workup with ethanol [Eq. (1)] gave a new complex which was identified as the tetranuclear ruthenium hexahydride $[(CpRu)_4H_6]$ (**4a**) by ^1H and ^{13}C NMR spectroscopy and an X-ray diffraction study. In a similar manner, tetranuclear clusters $[\{(\eta^5\text{-}C_5H_4Me)Ru\}_4H_6]$ (**4b**) and $[\{(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)Ru\}_4H_6]$ (**4c**) were derived from the corresponding Ru^{IV} precursors, $[(\eta^5\text{-}C_5H_4Me)RuCl_2(\eta^3\text{-}C_3H_5)]$ (**3b**) and $[(\eta^5\text{-}1,3\text{-}Me_2\text{-}C_5H_3)RuCl_2(\eta^3\text{-}C_3H_5)]$ (**3c**),[8] respectively. Although the yields of **4a** and **4c** were not high (ca. 40%), the ^1H NMR spectra of the crude products obtained after removal of the aluminum salt showed that the tetranuclear hydride complexes **4a** and **4c** were formed exclusively. In the reaction of **3b** with $LiAlH_4$, however, the formation of **4b** was accompanied by a significant amount (ca. 40%) of the corresponding pentanuclear hydride complex, which was readily separated by column chromatography on alumina.



3a **4a** (1)

The ^1H NMR spectrum of the cluster **4a** exhibited two resonance signals assignable to Cp and hydride ligands at $\delta = 4.45$ ppm (20H) and $\delta = -8.59$ ppm (6H), respectively. The

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